Advanced Statistical Physics
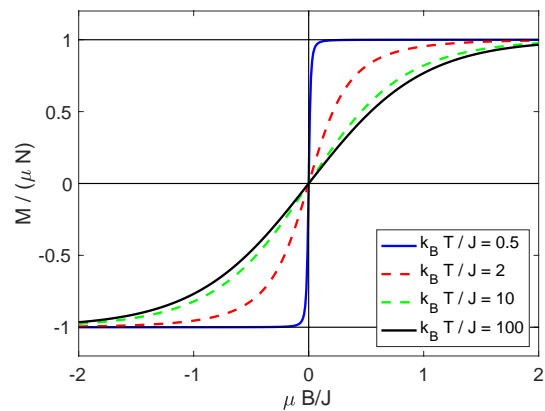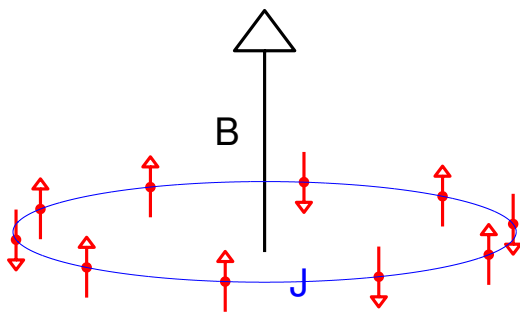# (preliminary draft)

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$$M(T, N, B) = N\mu \frac{\sinh(\mu\beta B)}{\sqrt{\sinh^2(\mu\beta B) + e^{-4J\beta}}}$$

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Contents

Chapter 1

Ising Model

Figure 1.1: *Arrangement of Ising-spins in a 1d chain with pbc.*

We will now examine collective magnetism. The simplest model for this purpose is the Ising model, which is described by the following Hamilton function

$$H = -J \sum_{\langle i,j \rangle} S_i S_j - B \hat{M} \tag{1.1}$$

$$\text{with} \qquad \hat{M} = \mu \sum_i S_i \,, \qquad \left(\mu := -\frac{\mu_B g_e}{2} \right) \tag{1.2}$$

$$H = -J \sum_{\langle i,j \rangle} S_i S_j - \mu B \sum_i S_i \,, \tag{1.3}$$

where the spins S_i can only take the values $S_i = \pm 1$. μ_B is the Bohr magneton and g_e the electronic Landé factor. J is the exchange coupling and the sum over sites is restricted to nearest neighbour sites, such that each neighbouring pairings only counted once! B stands for the magnetic flux density. The Ising model is also used to describe binary alloys. However, the parameters then have a different meaning. The Ising model can be solved exactly in 1d and 2d and in 2d it even has a phase transition. We

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consider periodic boundary conditions [1]

1.1   Exact solution in 1D

The Hamilton function of the Ising model in 1D reads

$$H = -J \sum_{i=1}^{N} S_i S_{i+1} - \mu B \frac{1}{2} \sum_i (S_i + S_{i+1})$$

(pbc): $S_{i+N} = S_i$.

Canonical partition function

The evaluation is particularly simply in the canonical ensemble:

$$Z(T, N, B) = \sum_{\{S_i\}=\pm 1} e^{\beta J \sum_i S_i S_{i+1} + \frac{\mu \beta B}{2} \sum_i (S_i + S_{i+1})}$$

$$= \sum_{\{S_i\}=\pm 1} \prod_{i=1}^{N} e^{j S_i S_{i+1} + \frac{b}{2}(S_i + S_{i+1})} .$$

We introduced the abbreviations $j = \beta J$ and $b = \mu B \beta$. We also define the **Transfermatrix**

$$\mathcal{T}_{s,s'} := e^{j\, ss' + \frac{b}{2}(s + s')} \tag{1.4a}$$

which has the matrix elements
$$\mathcal{T}_{s,s'} = \begin{array}{c|cc} & +1 & -1 \\ \hline +1 & e^{j+b} & e^{-j} \\ -1 & e^{-j} & e^{j-b} \end{array} \tag{1.4b}$$

then: $$Z(T, N, B) = \sum_{\{S_i\}=\pm 1} \prod_{i=1}^{N} \mathcal{T}_{S_i, S_{i+1}} . \tag{1.4c}$$

We first consider the case $N = 2$, where the partition function reads

$$Z(T, N = 2, B) = \sum_{S_1 = \pm 1} \sum_{S_2 = \pm 1} \mathcal{T}_{s_1, s_2} \, \mathcal{T}_{s_2, s_1} = \sum_{s_1} \left(\mathcal{T}^2 \right)_{s_1, s_1} = \text{tr} \left\{ \mathcal{T}^2 \right\}$$

The generalization to $N > 2$ leads obviously to

$$Z(T, N, B) = \text{tr} \left\{ \mathcal{T}^N \right\} .$$

The transfer matrix is real-symmetric and can be expressed in the spectral representation as follows

$$\mathcal{T} = U D U^\dagger ,$$

here U is the unitary matrix of eigenvectors and D the diagoal matrix of eigenvalues (d_1, d_2). Hence we have

$$Z(T, N, B) = \text{tr}\left\{\mathcal{T}^N\right\} = \text{tr}\left\{(UDU^\dagger)^N\right\} = \text{tr}\left\{UD^NU^\dagger\right\} = \text{tr}\left\{D^N\right\}$$
$$= d_1^N + d_2^N .$$

The eigenvalues of the transfer matrix ate

$$d_{1/2} = \frac{e^{j+b} + e^{j-b}}{2} \pm \sqrt{\left(\frac{e^{j+b} - e^{j-b}}{2}\right)^2 + e^{-2j}}$$
$$= e^j \left(\cosh(b) \pm \sqrt{\sinh^2(b) + e^{-4j}} \right)$$

We can use $d_1 > d_2$ in the calculation of the partition function in thermo-dynamic limits

$$Z(T, N, B) = d_1^N \left[1 + \left(\frac{d_2}{d_1}\right)^N\right] .$$

Free energy

The free energy reads

$$F(T, N, B) = -k_B T \ln\left[Z(T, V)\right] = -k_B T N \ln(d_1) - k_B T \ln\left[1 + \underbrace{\left(\frac{d_2}{d_1}\right)^N}_{\to 0}\right]$$
$$= -N k_B T \ln(d_1) .$$

Magnetization

The mean magnetization is

$$M = \mu \left\langle \sum_i S_i \right\rangle .$$

The comparison with the partition function immediately shows

$$
\begin{aligned}
M &= \frac{1}{\beta}\left(\frac{\partial \ln(Z)}{\partial B}\right)\Bigg|_{T,N} = -\left(\frac{\partial F}{\partial B}\right)\Bigg|_{T,N} \\
&= -\mu\beta\left(\frac{\partial F}{\partial b}\right)\Bigg|_{T,N} \\
&= -\mu\beta(-k_B T N)\left(\frac{\partial \ln(d_1)}{\partial b}\right)\Bigg|_{T,N} \\
&= N\mu\frac{\frac{\partial d_1}{\partial b}}{d_1} = N\mu\frac{\sinh(b) + \frac{\sinh(b)\cosh(b)}{\sqrt{\sinh^2(b)+e^{-4j}}}}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}} \\
&= N\mu\sinh(b)\ \frac{1 + \frac{\cosh(b)}{\sqrt{\sinh^2(b)+e^{-4j}}}}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}} \\
&= N\mu\frac{\sinh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}}\ \frac{\sqrt{\sinh^2(b) + e^{-4j}} + \cosh(b)}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}}\ .
\end{aligned}
$$

$$
\text{MAGNETIZATION OF THE 1D ISING MODEL}
$$

$$
M(T,N,B) = N\mu\frac{\sinh(\mu\beta B)}{\sqrt{\sinh^2(\mu\beta B) + e^{-4J\beta}}}\ .
$$

1.1.1   Paramagnet

Without interaction of the magnetic moments ($J = 0$) we obtgain

$$
M(T,N,B) = N\mu\frac{\sinh(\mu\beta B)}{\sqrt{\sinh^2(\mu\beta B) + 1}} = N\mu\tanh(\mu\beta B)\ ,
$$

the well-known result for paramagnetism.

1.1.2 Limits

It depends on the order of the limits. If we first set $B = 0$, we obtain for any finite temperature

$$M(T, N, B = 0) = 0$$

a vanishing magnetization. In the opposite order, i.e. keeping $B > 0$ finite and let T go to zero, i.e. $\beta \to \infty$ we obtain

$$M(T, B \neq 0) = N\mu \frac{\sinh(\mu\beta B)}{\sqrt{\underbrace{\sinh^2(\mu\beta B)}_{\gg 1} + \underbrace{e^{-4J\beta}}_{\ll 1}}}$$

$$\xrightarrow[T \to 0]{} N\mu \, \text{sign}(B) \, .$$

In this limiting case we get perfect alignment of all spins, even if we now let B go to zero.

The Ising model in one dimension has a "phase transition" at $T = 0$.

1.1.3   Magnetization

We use the exchange coupling J as energy unit. Then two independent parameters remain, $k_B T$ and $\tilde{B} := \mu B$. We plot magnetization as a function of $\tilde{B}$
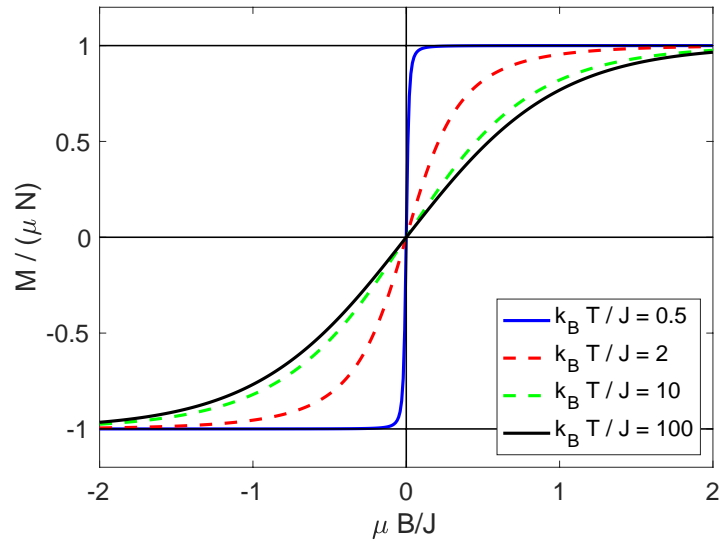

Figure 1.2: Magnetization curve of the 1d Ising model.

We can see from the comparison with the result for the paramagnet that the amount of magnetization increases everywhere due to the influence of the interaction. For low temperatures, the magnetization abruptly enters the fully polarized state.

1.2 Mean field approximation for any dimension

(See *Ising Model for Magnetism (Springer)*)
We will study the concept of the mean-field approximation in terms of the Ising model. We start out from the Ising model expressed as

$$H = -J \sum_{\langle ij \rangle} S_i S_j - B \cdot \hat{M}$$

We recall that the Ising model describes spin-$1/2$ objects. The total magnetisation **M** is related to the spins via

$$\hat{M} = \mu \sum_i S_i \ .$$

Now the Ising model takes only the component along the quantization axis into account and S_i^z takes the values $\frac{\hbar}{2}\sigma_i$, with $\sigma_i \in \{-1, +1\}$. As before, we introduce the variable

$$h = \mu B \ .$$

and obtain

$$H = -J \sum_{\langle ij \rangle} S_i S_j - h \sum_i S_i$$

The mean field approximation is defined for any two dynamical variables A and B by

$$AB \approx \langle A \rangle B + A \langle B \rangle - \langle A \rangle \langle B \rangle \ .$$

In our case, assuming translational invariance, we have

$$S_i S_j \approx \langle S \rangle S_j + S_i \langle S \rangle - \langle S \rangle^2 \ .$$

This leads to the mean-field Hamilton function

$$H_{\text{MFA}} = -J \sum_{\langle ij \rangle} \langle S \rangle S_i - J \sum_{\langle ij \rangle} \langle S \rangle S_j + J \sum_{\langle ij \rangle} \langle S \rangle^2 - h \sum_i S_i$$

$$= -2J \langle S \rangle \sum_{\langle ij \rangle} S_i + J \sum_{\langle ij \rangle} \langle S \rangle^2 - h \sum_i S_i$$

Since we have used the convention that the sum over nearest neighbours avoids double counting, each site i has $z/2$ nearest neighbours, where for

sc.lattices $z = 2d$ is defined as the total number of nearest neighbours.
Hence:

$$H_{\text{MFA}} = -Jz \sum_i \langle S \rangle S_i + JNz \langle S \rangle^2 - h \sum_i S_i .$$

This can also be written as

$$H_{\text{MFA}} = -h' \sum_i S_i + \frac{JNz}{2} \langle S \rangle^2 \tag{1.5}$$

$$\text{with} \qquad h' = h + Jz \langle S \rangle . \tag{1.6}$$

The canonical partition function is then given by

$$Z(T, N, B) = e^{-\frac{\beta NJz}{2} \langle S \rangle^2} \sum_{\{S_i\}} e^{\beta h' \sum_i S_i} , \tag{1.7}$$

The partition function can easily be computed

$$Z(T, N, B) = e^{-\frac{\beta NJz}{2} \langle S \rangle^2} \prod_i \sum_{S_i = \pm 1} e^{h' S_i}$$

$$= \left(e^{\frac{-\beta Jz}{2} \langle S \rangle^2} 2 \cosh(\beta h') \right)^N \tag{1.8}$$

$$\ln \left(Z(T, N, B) \right) = N \left(-\frac{\beta Jz}{2} \langle S \rangle^2 + \ln(2) + \ln \left(\cosh(\beta h') \right) \right) \tag{1.9}$$

1.2.1 Magnetization

Next we compute the mean magnetization

$$\frac{M}{\mu} = \frac{\langle \hat{M} \rangle}{\mu} = \frac{1}{Z} \sum_{\{S_i\}} \left\{ \hat{M} e^{-\frac{\beta NJz}{2} \langle S \rangle^2} e^{\beta h' \hat{M}} \right\} = \frac{k_B T}{Z} \frac{\partial}{\partial h'} Z .$$

$$\frac{M}{\mu} = k_B T \frac{\partial \ln(Z)}{\partial h'} = N \tanh(\beta h') . \tag{1.10}$$

We introduce the magnetization per site

$$m = \frac{M}{\mu N} = \frac{1}{N} \langle \sum_i S_i \rangle = \langle S \rangle . \tag{1.11}$$

and obtain the equation of state

$$
\begin{array}{|c|}
\hline
\text{MAGNETIZATION} \\
\textit{(of the Ising model)} \\
\hline
\end{array}
$$

$$
m = \tanh\left(\beta(Jzm + h)\right) . \tag{1.12}
$$

We are particularly interested in the spontaneous magnetization, i.e. the magnetization for $B \to 0$. So we seek the solution of

$$
m = \tanh\left(\beta Jzm\right) . \tag{1.13}
$$

We introduce an auxiliary temperature T^*, defined by

$$
k_B T^* = Jz . \tag{1.14}
$$

The condition for the spontaneous magnetization can therefore be expressed in a form, independent of the dimension

$$
m = \tanh\left(\frac{T^*}{T}m\right) \tag{1.15}
$$

or rather with $x = \frac{T^*}{T}m$

$$
x = \frac{T^*}{T}\tanh\left(x\right) . \tag{1.16}
$$

The function $\tanh(x)$ starts at $x = 0$ with the value 0 and slope 1, then it increases monotonically with decreasing slope and approaches 1 for $x \to \infty$. equation (1.16) has always the trivial solution $M = 0$. For the non-trivial solution, we need $\frac{T^*}{T} > 1$, or rather $T < T^*$. According to the behaviour of $\tanh(x)$, for $\frac{T^*}{T} > 1$ there is precisely one non-trivial solution. So we see that T^* is indeed the critical/ Curie temperature, i.e

$$
k_B T_C = Jz . \tag{1.17}
$$

In 2D, we have $(\beta_c J) = .25$, as compared to the exact value $\beta_c J = 0.4407$. This not so bad, however, for 1D the mean-field result predicts a phase-transition at $(\beta_c J) = .5$, while the exact result is ∞.
In figure 1.3, the magnetization, obtained from equation (1.13), is depicted as function of T. Interestingly, the curve is independent of the spatial dimension. The later only enters in the value of T_c
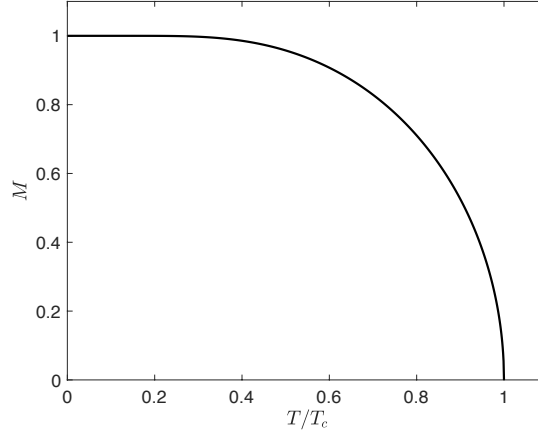
Figure 1.3: *Mean-field result for the Magnetization for arbitrary spatial dimension d*

Critical exponent

For temperatures T slightly below T_c, the magnetization is very small and we can use the Taylor expansion with $\tau = T/T_C$

$$m = \tanh\left(\frac{m}{\tau}\right) = \left(\frac{m}{\tau} - \frac{(m/\tau)^3}{3}\right) = \frac{m}{\tau}\left(1 - \frac{(m/\tau)^2}{3}\right)$$

$$\tau = 1 - \frac{(m/\tau)^2}{3}$$

$$\left(\frac{m}{\tau}\right)^2 = 3\left(1 - \tau\right).$$

Up to this order we have for $T < T_C$

$$m = 3\tau\sqrt{1 - \tau} \propto \varepsilon^{\frac{1}{2}} \tag{1.18}$$

$$\varepsilon := \frac{T_C - T}{T_C} \tag{1.19}$$

The critical exponent is therefore $\beta = 1/2$.

1.2.2   Magnetic susceptibility

Starting from the definition of the susceptibility via

$$\chi = \frac{\partial M}{\partial B}\bigg|_{T,h=0}$$

we obtain with $M = mN\mu$ and $B = h/\mu$ the relation

$$\chi = \mu^2 N \frac{\partial m}{\partial h}\bigg|_{T,h=0}$$

We start out from

$$m = \tanh\left(\beta h + \frac{T_C}{T}m\right)$$

The derivative w.r.t. h is

$$\xi = \frac{\partial m}{\partial h}\bigg|_{T,h=0} = \frac{\beta + \frac{T_C}{T}\xi}{\cosh^2\left(\beta h + \frac{T_C}{T}m\right)}\bigg|_{h=0} = \frac{\beta + \frac{T_C}{T}\xi}{\cosh^2\left(\frac{T_C}{T}m\right)}$$

$$\xi \cosh^2\left(\frac{T_C}{T}m\right) = \beta + \frac{T_C}{T}\xi$$

$$\xi\left(\cosh^2\left(\frac{T_C}{T}m\right) - \frac{T_C}{T}\right) = \beta .$$

Close to T_C the magnetisation is very small and we can Taylor expand the magnetisation resulting in

$$\xi = \frac{\beta}{\cosh^2\left(\frac{T_C}{T}m\right) - \frac{T_C}{T}}$$

$$= \frac{\beta}{1 - \frac{T_C}{T} + \left(\frac{T_C}{T}m\right)^2}$$

$$= \frac{1}{k_B} \frac{1}{T - T_C + T_C\frac{T_C}{T}m^2} .$$

We can replace T by T_C in the last term in the denominator, as it already contains $O(m^2)$

$$\xi = \frac{1}{k_B} \frac{1}{T - T_C + T_C m^2} .$$

For $T \searrow T_C$ the magnetisation is zero and we have

$$\xi = \frac{1}{k_B T_C} \left(\varepsilon\right)^{-1}$$

with $\varepsilon = (T - T_C)/T_C$.
For $T \nearrow T_C$ we use equation (1.18) [previous page] for m and obtain

$$m^2 = 3\tau^2(1 - \tau) = \frac{3}{T_C}(T_C - T) + \mathcal{O}(\Delta T/T_C)^2$$

and have

$$\xi = \frac{1}{k_B} \frac{1}{T - T_C + 3(T_C - T)} = \frac{1}{2k_B T_C}|\varepsilon|^{-1}$$

According to the definition of the critical exponent of the susceptibility

$$\chi \simeq A_\pm |\varepsilon|^{-\gamma_\pm}$$

we have $A_+ = 2A_-$ and $\gamma_+ = \gamma_- = 1$.

1.2.3   Free energy

Next we compute the free energy based equation (1.9) [p. 12]

$$\begin{aligned}
f := \frac{F}{k_B N} &= -\frac{k_B T}{k_B N} \ln(Z) \\
&= -T\left(-\frac{\beta J z}{2}\langle S \rangle^2 + \ln(2) + \ln\left(\cosh(\beta h')\right)\right) \\
&= \frac{Jz}{2k_B}m^2 - T \ln(2) - T \ln\left(\cosh(\beta h + \frac{Jz}{k_B T}m)\right) .
\end{aligned}$$

We have seen before that $k_B T_C = Jz$ so we can express the free energy as

$$\frac{F}{Nk_B} = \frac{1}{2}T_c m^2 - T \ln(2) - T \cosh(\beta h + \frac{T_c}{T}m)) .$$

Along with

$$\cosh(x) = \left(1 - \tanh^2(x)\right)^{-1/2}$$

and the self consistency equation (1.15) [p. 13]

$$m = \tanh\left(\beta h + \frac{T_C}{T}m\right) \tag{1.20}$$

we can express the free energy as

$$\frac{F}{Nk_B} = \frac{T_c m^2}{2} - T \ln(2) + \frac{T}{2}\ln\left(1 - m^2\right) \tag{1.21}$$

Next we compute the Helmholtz free energy, by the following Legendre transform, i.e. by introducing M as natural variable instead of h:

$$A(T, M) = F(T, h) + Mh . \tag{1.22}$$

Then the total differential reads

$$
\begin{aligned}
dA &= dF(T, h) + h dM + M dh \\
&= -S dT - M dh + h dM + M dh \\
&= -S dT + h dM \ .
\end{aligned}
$$

Hence

$$
\left. \frac{\partial A}{\partial M} \right|_T = h \tag{1.23}
$$

$$
\left. \frac{\partial A}{\partial T} \right|_M = -S \ . \tag{1.24}
$$

If we want to have spontaneous magnetisation, i.e. a finite magnetisation M without external field, then according to equation (1.23) we are looking for a finite value of the magnetization M for which

$$
\left. \frac{\partial A(M, T)}{\partial M} \right|_T = 0 \ . \tag{1.25}
$$

Before we can exploit this equation, we need to express h in terms of M (or rather m). To this end we invert

$$
m = \tanh \left(\beta h + \frac{T_C}{T} m \right)
$$

leading to

$$
\beta h + \frac{T_C}{T} m = \tanh^{-1} (m) \ .
$$

Along with

$$
\tanh^{-1} (b) = \frac{1}{2} \ln \left(\frac{1+b}{1-b} \right)
$$

we obtain

$$
\begin{aligned}
\beta h + \frac{T_c}{T} m &= \frac{1}{2} \ln \left(\frac{1+m}{1-m} \right) \\
h &= \frac{k_B T}{2} \ln \left(\frac{1+m}{1-m} \right) - k_B T_c m
\end{aligned}
$$

Then we obtain for the Helmholtz free energy of equation (1.21) [previous page]

$$
\frac{A}{Nk_B} = \frac{T_C m^2}{2} - T\ln(2) + \frac{T}{2}\ln\left(1 - m^2\right) + \frac{mh}{k_B}
$$

$$
= \frac{1}{2}T_c m^2 - T\ln(2) + \frac{T}{2}\ln\left(1 - m^2\right) + \frac{m}{k_B}\left(\frac{k_B T}{2}\ln\left(\frac{1+m}{1-m}\right) - k_B T_c m\right)
$$

$$
= \frac{1}{2}T_c m^2 - T\ln(2) + \frac{T}{2}\ln\left(1 - m^2\right) + \frac{mT}{2}\ln\left(\frac{1+m}{1-m}\right) - T_c m^2 \ .
$$

or rather

$$
\frac{A}{Nk_B T_c} = \frac{A}{NJz} = -\frac{1}{2}m^2 - \tau\ln(2) + \frac{\tau}{2}\left[\ln\left((1-m)(1+m)\right) + m\ln\left(\frac{1+m}{1-m}\right)\right]
$$

$$
= -\frac{1}{2}m^2 - \tau\ln(2) + \frac{\tau}{2}\left((1+m)\ln\left(1+m\right) + (1-m)\ln\left(1-m\right)\right) ,
$$

$$
\tag{1.26}
$$

with $\tau = T/T_c$. According to equation (1.25) [previous page] the magne-
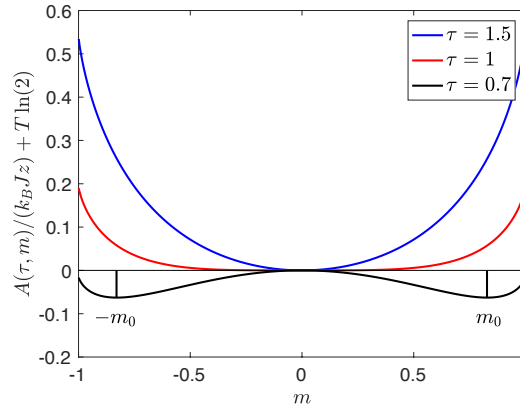
Figure 1.4: *Helmholtz free energy for the Ising model in mean-field approxima-tion versus order parameter without external field.*

tization is given by the points where the slope as function of τ vanishes (see figure 1.4).
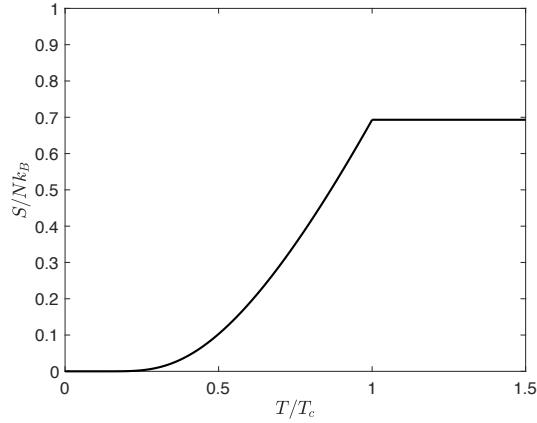
Figure 1.5: *Entropy of the Ising model in MFA.*

1.2.4 Entropy

According to equation (1.23) along with equation (1.26) the entropy is

$$-\frac{S}{Nk_BT_C} = \frac{\partial}{\partial\tau}\left(-\frac{1}{2}m^2 - \tau\ln(2) + \frac{\tau}{2}\Big((1+m)\ln(1+m) + (1-m)\ln(1-m)\Big)\right)\Bigg|_m \frac{d\tau}{dT}\,.$$

Hence

<div style="border:1px solid">

ENTROPY OF THE ISING MODEL
(in MFA for zero field)

$$\frac{S}{Nk_B} = \ln(2) - \frac{1}{2}\Big((1+m)\ln(1+m) + (1-m)\ln(1-m)\Big)\,. \quad (1.27)$$

</div>

It has the correct limiting behaviour: For $T \to 0$, i.e. $m \to 1$ we obtain

$$\frac{S}{Nk_B} = \ln(2) - \frac{1}{2}\left(2\Big(\ln(2) + 0\Big)\right) = 0\,,$$

and for $T \to \infty$, i.e. $m \to 0$ the entropy becomes

$$\frac{S}{Nk_B} = \ln(2) - \frac{1}{2}\Big(\ln(1) + \ln(1)\Big) = \ln(2)\,.$$

Recall that

$$S = k_B \ln(\text{number of micro states}) .$$

For $T \to \infty$ all states can be reach with the same probability. Hence the number of micro states is 2^N and

$$S = N k_B \ln(2) ,$$

kin agreement with the above result.

For the entire T dependence of S we have to insert the self-consistent solution for $m(T)$ in equation (1.15) [p. 13].

1.2.5   Internal energy

The internal energy is defined as the expectation value of the hamiltonian. Using the mean field expression of equation (1.5) [p. 12] we have

$$U = \langle H \rangle = -h' \sum_i \langle S_i \rangle + \frac{JNz}{2} m^2 = N\left(-h'm + \frac{Jz}{2} m^2 \right)$$

with $h' = Jzm + h$ we obtain:

$$\frac{U}{N} \frac{U}{NJ} = -\frac{hm}{J} - zm^2 + \frac{z}{2} m^2$$

$$= -\frac{z}{2} m^2 - \frac{hm}{J} .$$

For zero external field it simplifies to (we also use $z = 2d$)

INTERNAL ENERGY OF THE ISING MODEL
(in MFA for zero field)

$$\frac{U}{NJ} = -d \, m^2 . \tag{1.28}$$

1.2.6 Specific heat

For the specific heat we need

$$C_{h=0} = \left.\frac{\partial U}{\partial T}\right|_{h=0} = -dNJ\,\frac{d\,m^2}{dT}$$

$$\frac{C_{h=0}}{NJ} = -d\,\frac{d}{dT}m^2\ .$$

Above T_C the magnetization is zero and hence $C = 0$. Slightly below T_C we can replace m by equation (1.18) [p. 14], which gives

$$\frac{C_{h=0}}{NJ} = -d\,\frac{d}{dT}3\tau^2(1-\tau)$$

$$= -\frac{3d}{T_C^3}\,\frac{d}{dT}\left(T^2 T_C - T^3\right)$$

$$= -\frac{3d}{T_C^3}\,T\left(2T_C - 3T\right)\ .$$

Hence, approaching T_C from below we obtain

$$\frac{C(T_C)_{h=0}}{NJ} = \frac{3d}{T_C} = \frac{3dk_B}{Jz} = \frac{3dk_B}{J2d}$$

$$\frac{C(T_C)_{h=0}}{N} = \frac{3k_B}{2}\ .$$

Therefore, in MFA, the specific heat has no power-law behaviour close at T_C, but rather a discontinuity from $\frac{3}{2}k_B$ below T_C to 0 above T_C. For the entire T-dependence below T_C we continue

$$\frac{C_{h=0}}{NJ} = -2d\,m\,\frac{dm}{dT}\ . \tag{1.29}$$

First we consider

$$\xi := \frac{dm}{dT}\ .$$

Exploiting equation (1.20) [p. 16] yields

$$\xi = \left.\frac{d}{dT}\tanh\left(\beta h + \beta k_B T_C m\right)\right|_{h=0} \tag{1.30}$$

$$\xi = \left.\frac{(h + k_B T_C m)\frac{d\beta}{dT} + \beta k_B T_C \xi}{\cosh^2\left(\beta(h + k_B T_C m)\right)}\right|_{h=0} \tag{1.31}$$

$$= \frac{-\frac{T_C}{T^2}m + \frac{T_C}{T}\xi}{\cosh^2\left(\frac{T_C}{T}m\right)}\ . \tag{1.32}$$

Then

$$\xi \cosh^2 \left(\frac{T_C}{T} m \right) = -\frac{T_c}{T^2} m + \frac{T_C}{T} \xi$$

$$\xi \left(\cosh^2 \left(\frac{T_C}{T} m \right) - \frac{T_C}{T} \right) = -\frac{T_C}{T^2} m$$

$$\xi = -\frac{1}{T_C} \frac{\frac{m}{\tau}}{\tau \cosh^2 \left(\frac{m}{\tau} \right) - 1}$$

Finally, we have

$$\frac{C_{h=0}}{NJ} = -z \, m \, \xi$$

$$= \frac{z}{T_C} \frac{\frac{m^2}{\tau}}{\tau \cosh^2 \left(\frac{m}{\tau} \right) - 1}$$

$$= \frac{z}{zJ/k_B} \frac{\frac{m^2}{\tau}}{\tau \cosh^2 \left(\frac{m}{\tau} \right) - 1} \ .$$

Finally, we have

$$\frac{C_{h=0}}{N} = k_B \frac{\left(\frac{m}{\tau} \right)^2}{\cosh^2 \left(\frac{m}{\tau} \right) - 1/\tau} \ . \tag{1.33}$$

Together with the self consistent equation for $m(T)$:

$$m(T) = \tanh \left(\frac{T_C}{T} m(T) \right),$$

which have solved numerically before, we can plot the specific heat. We have seen 'statistical physics I'

$$C = \frac{1}{k_B T^2} \left\langle (\Delta H)^2 \right\rangle,$$

i.e. C is large when there are pronounced energy fluctuations, which is the case in the vicinity of T_C. In MFA, above T_C there are no fluctuations because $H \propto m$ and therefore $U = 0$ aboce T_C. This is an artefact of MFA.
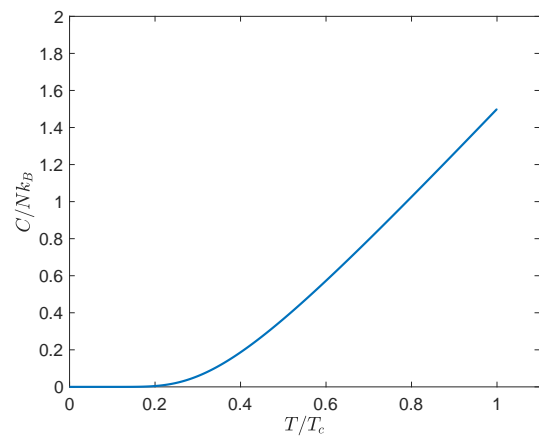
Figure 1.6: *Specific heat of the Ising model in MFA.*

1.3 Exact solution of the 2d Ising model

1.3.1 Transfermatrix approach

We will first briefly explain how the Transfer matrix approach works in the 2d case. To this end we will represent the hamiltonian of the 2d Ising model ($L_x \times L_y$) by writing the two cartesian indices explicitly in the form S_{ij}

$$-\beta H = j \sum_{l=1}^{L_y} \sum_{i=1}^{L_x} S_{i,l} S_{i+1,l} + S_{i,l} S_{i,l+1} + h \sum_l \sum_i S_{il} \, .$$

Now we combine the spins of column l of S_{il} in a vector

$$\mathcal{S}^{(l)} = \begin{pmatrix} S_{1,l} \\ S_{2,l} \\ \ldots \\ S_{L_x,l} \end{pmatrix} \text{ ,i.e. } (\mathcal{S}^{(l)})_i = S_{il}$$

Then the hamiltonian can be written as

$$-\beta H = \sum_l A\big(\mathcal{S}^{(l)}, \mathcal{S}^{(l+1)}\big) \tag{1.34}$$

with the definitions

$$A(\mathcal{S}^{(l)}, \mathcal{S}^{(k)}) = \frac{1}{2}\Big(\tilde{A}(\mathcal{S}^{(l)}, \mathcal{S}^{(k)}) + \tilde{A}(\mathcal{S}^{(k)}, \mathcal{S}^{(l)})\Big) \tag{1.35}$$

$$\tilde{A}(\mathcal{S}^{(l)}, \mathcal{S}^{(k)}) = j \sum_i \Big((\mathcal{S}^{(l)})_i (\mathcal{S}^{(l)})_{i+1} + (\mathcal{S}^{(l)})_i (\mathcal{S}^{(k)})_i \Big) + h \big(\sum_i \mathcal{S}^{(l)}\big)_i \, . \tag{1.36}$$

A is by construction a real symmetric matrix. Inserting indices yields

$$\sum_l \tilde{A}(\mathcal{S}^{(l)}, \mathcal{S}^{(l+1)}) = j \sum_{l,i} \big(S_{i,l} S_{i+1,l} + S_{i,l} S_{i,l+1}\big) + h \sum_{i,l} S_{i,l} \qquad = -\beta H$$

$$\sum_l \tilde{A}(\mathcal{S}^{(l+1)}, \mathcal{S}^{(l)}) = j \sum_{l,i} \big(S_{i,l+1} S_{i+1,l+1} + S_{i,l+1} S_{i,l}\big) + h \sum_{i,l} S_{i,l+1}$$

$(l+1 \to l' \text{ plus pbc} \Rightarrow) \qquad = j \sum_{l',i} \big(S_{i,l'} S_{i+1,l'} + S_{i,l'} S_{i,l+1}\big) + h \sum_{i,l} S_{i,l'} \qquad = -\beta H \, .$$

Hence equation (1.34) is correct. Then

$$Z = \sum_{\{S_{ij}\}} e^{\sum_{l=1}^L A(\mathcal{S}^{(l)}, \mathcal{S}^{(l+1)})} = \prod_{l=1}^L \sum_{\mathcal{S}^{(l)}} e^{A(\mathcal{S}^{(l)}, \mathcal{S}^{(l+1)})} \, .$$

Now, we introduce the transfer matrix $\mathcal{T}$ with matrix elements

$$\mathcal{T}_{\mathcal{S}^{(l)},\mathcal{S}^{(l')}} = e^{A\left(\mathcal{S}^{(l)},\mathcal{S}^{(l')}\right)}$$

Then the partition function can be written as (remember that we use pbc)

$$
\begin{aligned}
Z &= \sum_{\mathcal{S}^{(1)}} \sum_{\mathcal{S}^{(2)}} \cdots \sum_{\mathcal{S}^{(L_y)}} \prod_l \mathcal{T}_{\mathcal{S}^{(l)},\mathcal{S}^{(l+1)}} \\
&= \sum_{\mathcal{S}^{(1)}} \sum_{\mathcal{S}^{(2)}} \cdots \sum_{\mathcal{S}^{(L_y)}} \mathcal{T}_{\mathcal{S}^{(1)},\mathcal{S}^{(2)}} \mathcal{T}_{\mathcal{S}^{(2)},\mathcal{S}^{(3)}} \cdots \mathcal{T}_{\mathcal{S}^{(L_y-1)},\mathcal{S}^{(L_y)}} \mathcal{T}_{\mathcal{S}^{(L_y)},\mathcal{S}^{(1)}} \\
&= \mathrm{tr}\left\{\mathcal{T}^{L_y}\right\} \\
&= \lambda_{\max}^{L_y}.
\end{aligned}
$$

This is the straight-forward generalization of equation (1.4) and is to be understood as follows: The sum over $\mathcal{S}^{(l)}$ runs over the 2^{L_x} configurations, which the vector $\mathcal{S}^{(l)}$ can assume. We introduce an index I that enumerates these configurations and instead of summing over $\mathcal{S}^{(l)}$, we could sum over the index I, that enumerates these configurations (the I-the configuration would be $\mathcal{S}_I$). Then we can define the transfer matrix alternatively by the matrix elements

$$\mathcal{T}_{I,I'} = e^{A(\mathcal{S}_I,\mathcal{S}_{I'})}$$

and then we would have

$$
\begin{aligned}
Z &= \sum_{I^{(1)}} \cdots \sum_{I^{(L_y)}} \mathcal{T}_{I^{(1)},I^{(2)}} \mathcal{T}_{I^{(2)},I^{(3)}}, \ldots, \mathcal{T}_{I^{(L_y-1)},I^{(L_y)}} \mathcal{T}_{I^{(L_y)},I^{(1)}} \\
&= \mathrm{tr}\left\{\mathcal{T}^{L_y}\right\} \\
&= \lambda_{\max}^{N}.
\end{aligned}
$$

As before, the dominant eigenvector ($\lambda_{\max}$) predominates in the thermodynamic limit ($L_y \to \infty$). The eigenvalue problem of the ($2^{L_x} \times 2^{L_x}$)-dimensional transfer matrix for the 2d case, is much more complicated than in the 1d case. It can be found in the book of K. Huang (*Kerson Huang, Statistical Mechanics, Wiley and Sons (1963)*).

1.3.2 Graphical approach

Here we will present instead the exact solution of the 2d Ising model based a graphical representation, however, without external field. The ideas go back to M. Lawrence Glasser, American Journal of Physics 38, 1033 (1970),

and were didactically improved by W. Noting: Qauntum Therory of Magnetism (Springer Verlag).

Starting point is the partition function

$$Z = \sum_{\{S_i\}} \prod_{\langle ij \rangle} e^{j S_i S_j} \ . \tag{1.37}$$

Next we expand the exponential in a Taylor series

$$
\begin{aligned}
e^{j S_i S_j} &= \sum_{n=0}^{\infty} \frac{j^n}{n!} \left(S_i S_j \right)^n \\
&= \sum_{n=0}^{\infty} \frac{j^{2n}}{(2n)!} \underbrace{\left(S_i S_j \right)^{2n}}_{=1} + \sum_{n=0}^{\infty} \frac{j^{2n+1}}{(2n+1)!} \underbrace{\left(S_i S_j \right)^{2n+1}}_{=S_i S_j} \\
&= \cosh(j) \left(1 + \tanh(j) S_i S_j \right)
\end{aligned}
$$

Inserted in equation (1.37) results in

$$Z = \cosh^{2N}(j) \sum_{\{S_i\}} \prod_{\langle ij \rangle} \left(1 + t S_i S_j \right) ,$$

where $t = \tanh(j)$. The power $2N$ arises as there are $2N$ terms in the product in equation (1.37) . For each factor we have the choice to use the term 1 or $t S_i S_j$. In total there are 2^{Nz} such terms, for which we still have to sum over all spin configurations. Graphically, we represent the terms $t S_i S_j$ as lines on a square lattice connecting site i and j. Such a line can be considered as *edge of a a graph* and the sites that are connected by edges are denoted as *vertices*. In graph theory the number of edges connected to a vertex is called *order of the vertex*. In the present context, it can only be an integer $n \in \{1, 2, 3, 4\}$. Each edge, that reaches site (vertex) i carries a factor S_i. Therefore, we obtain a term S_i^n, where n is the order of the vertex. $n \in \{0, 1, 2, 3, 4\}$. If the order is odd, the sum over S_i vanishes, otherwise it gives 2. Hence, only graphs where all vertices have an even order (either 2 or 4) are allowed. By now we have

$$Z = 2^N \cosh^{2N}(j) \sum_G t^{N_e(G)} ,$$

The sum runs over all possible graphs on a square lattice of given size, with periodic boundary conditions, with vertices of even order. $N_e(G)$ is the total number of edges of the graph. The elements of the individual graphs need not to be connected. In figure 1.7 two examples are given,

(a) Allowed graph with $N_e(G) = 20$.   (b) Forbidden graph.

Figure 1.7: *Graphical representation of the partition function of the Ising model.*

one for an allowed and one for a forbidden graph. We can rewrite the sum over allowed graphs also in the form

$$Z = 2^N \, \cosh^{2N}(j) \left(1 + \sum_{n=4}^{\infty} g_n \, t^n \right), \tag{1.38}$$

where n is the number of edges and g_n is the number of allowed graphs with n edges. We have already exploited that the smallest graph (besides the empty graph) has 4 edges. Since each vertex has even order, the allowed graphs contain closed paths, as can be seen in figure 1.7.

1.3.3 Making the graphs unique

The figure also contains a *node*, i.e. a vertex of order 4. Let's try to draw the graph with a pencil on a piece of squared paper. We start at an arbitrary vertex of order 2 and draw a line to one of the two connected vertices. If the next vertex also has order 2, it is obvious how to continue the drawing. When we reach a node, however, we have 3 options to continue: *turn left, go straight, turn right*. It will turn out to be advantageous, to replace the graph by objects that allow to draw them in a unique way. Therefore, we will introduce graphical objects, that make a node unique. To this end a node is split into the three graphical objects, shown in figure 1.8. This splitting results in 3^{N_n} different new graphs, obtained from a graph with N_n nodes. This would increase g_n in a complicated way. To avoid this

Figure 1.8: *Splitting of a node with corresponding weights.*

complication, each new graphical element obtains a weight factor ±1, a shown in figure 1.8. Now the three contributions of each node add up to 1 again and the total count does not change. The new graphs are denoted by $\tilde{G}$. They consist of one or more loops. As a remainder, a *loop* (with e.g. n edges) is a simply connected set of edges, i.e. an object that can be drawn by starting at an arbitrary vortex on the loop, following the edges, and returning at the starting point after n steps. The shortest loop has 4 edges and the number of edges is always even. In the new graphs $\tilde{G}$, the number of edges has not changed, as compared to the original graph, but it has an extra weight factor

$$w(\tilde{G}) = \big(- 1 \big)^{N_c(\tilde{G})} \, ,$$

where $N_c(\tilde{G})$ stands for the number of crossings (decomposition c in figure 1.8) of a graph $\tilde{G}$ of the new type. By now g_n is

$$g_n = \sum_{\tilde{G}}^{N_e(\tilde{G})=n} \big(- 1 \big)^{N_c(\tilde{G})} \, .$$

1.3.4   Decomposing graphs into loops

We are still not able to calculate the sum of all graphs analytically. To this end we need to transform the graphs further. Each graph $\tilde{G}$ with n edges consists of one or more loops, which in total have n edges. If a particular graph $\tilde{G}$ consists of l loops, we can devide the total weight between the loops. A loop L contributes a factor $(-1)^{N_c(L)}$, where $N_c(L)$ is the number of crossings in loop L. The total weight is the product of the weights of the loops of which the graph is formed. Clearly, there is a one-to-one correspondence between all graphs $\tilde{G}$ with n edges and all sets of loops

with a total number n of edges. We define

$$D_l = \begin{cases} \sum_L^{\text{loops with } l \text{ edges}} \left(-1\right)^{N_c(L)} & \text{if } l \text{ is even} \\ 0 & \text{otherwise} \end{cases} . \qquad (1.39)$$

Hence for $n \geq 4$ we may think that we can decompose g_n into the contribution of the loop decomposition:

$$g_n = \sum_{\tilde{G}} \delta_{N_n(\tilde{G})=n} \left(-1\right)^{N_c(\tilde{G})} = \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{l_1 \ldots l_m=4} \delta_{\sum_{\nu=1}^m l_\nu=n} \prod_{\nu=1}^m D_{l_\nu} \qquad (1.40)$$

Here m is the number of loops and l_ν stands for the number of edges of loop ν and D_{l_ν} is the corresponding weight obtained by summing over all realizations of a loop with l_ν edges. The factor $1/m!$ is required as the right hand sight creates a particulcar set of m loops in $m!$ different permutations. We can insert equation (1.40) in equation (1.38) [p. 27] and obtain

$$\sum_{n=4}^{\infty} g_n t^n = \sum_{m=1}^{\infty} \frac{1}{m!} \sum_{l_1 \ldots l_m=4} \underbrace{\sum_{n=4}^{\infty} \delta_{\sum_{\nu=1}^m l_\nu=n}}_{=1} \prod_{\nu=1}^m D_{l_\nu} t^{l_\nu}$$

$$= \sum_{m=1}^{\infty} \frac{1}{m!} \prod_{\nu=1}^m \left(\sum_{l=4} D_l t^l \right)$$

$$= \sum_{m=1}^{\infty} \frac{1}{m!} \left(\sum_{l=4} D_l t^l \right)^m$$

$$= \exp\left(\sum_{l=4} D_l t^l \right) - 1$$

Hence according to equation (1.38) [p. 27] we have

$$\ln(Z) = N \ln(2) + 2N \ln\left(\cosh(j) \right) + \sum_{m=1}^{\infty} D_m t^m . \qquad (1.41)$$

The sum can start at $m = 1$ (instead of $m = 4$) since equation (1.39) counts loops and the shortest loop has length 4 anyways. However, equation (1.40) is not really correct. On the rhs the sum runs over all configurations of independently arranged loops. I.e. there will be configurations where edges occur more than once, like in figure 1.9. Such a configuration is not included in $\tilde{G}$. However, there is a very simple cure. We allow such configurations also in $\tilde{G}$, but in addition to double bonds, say, as in figure 1.9 a) or schematically depicted in figure 1.10 a) we also include configurations that occur if we cross the lines as shown in figure 1.10 b)

Figure 1.9: *Examples of configurations that occur if loops are placed independently. Such configurations are no valid graphs $\tilde{G}$.*

and give them a weight -1. The sum of these configurations adds up to zero. The same holds true, if there are threefold edges as in figure 1.9 b) or even m-fold edges. Generally, in the case of m-fold edges there are $m!$ possible connections (permutations) of the incoming and outgoing lines. The number of crossings is even/odd if the permutation is even/odd. As the number of even permutations is always equal to the number of odd permutations, the signs add up to zero. In the case of figure 1.9 a) the new configurations are depicted in figure 1.11. Now a) represents a double loop generated by placing loops independently, while b) shows a single loop, which is passed twice. Including b) in the allowed single loops ensures the cancelation of forbidden configurations generated by placing loops independently. The same holds true for even more complex structures, such as tripple loops.

If we include the new type of crossings in the loops, then the previous formulas (equation (1.39) [previous page] and equation (1.41) [previous page]) remain unchanged, with the exception that these crossings also contribute to the number of crossings.

$+$ $-$

a) b)

Figure 1.10: *Double occupied edges.*

a) b)

Figure 1.11: *Double occupied edges.*

Counting then number of loops and corresponding crossing

The remaining task is the determination of D_l, which includes the task of counting the crossings. To this end we introduce directed paths. The n-th step of the path is encoded in

$$S^{(n)} = \left(\mathbf{x}^{(n)}, \mathbf{d}^{(n)}\right) \tag{1.42}$$

where $\mathbf{x}^{(n)}$ represents the initial site of the n-th step, and $\mathbf{d}^{(n)} \in \{\pm\mathbf{e}_x, \pm\mathbf{e}_y\}$ the direction of the n-th step. A *path* from $S^{(0)}$ to $S^{(m)}$ is defined by the sequence

$$\mathcal{P} = S^{(0)}, S^{(1)}, \ldots, S^{(m)}$$

Clearly, we have the condition

$$\mathbf{x}^{(n+1)} = \mathbf{x}^{(n)} + \mathbf{d}^{(n)} \ . \tag{1.43}$$

Figure 1.12: *Representative paths and weights.*

As the allowed loops do not contain elements that occur when $\mathbf{d}^{(n+1)} = -\mathbf{d}^{(n)}$, we omit such steps. We define the weight of such a path as

$$w(\mathcal{P}) = \prod_{l=1}^{m} e^{i\frac{1}{2}\Phi(\mathbf{d}^{(l-1)},\mathbf{d}^{(l)})} \,, \tag{1.44}$$

where $\Phi(\mathbf{d}, \mathbf{d}')$ is the angle between the vectors $\mathbf{d}$ and $\mathbf{d}'$, defined as follows.

$$\Phi(\mathbf{d}, \mathbf{d}') = \begin{cases} 0 & \text{if } \mathbf{d}, \mathbf{d}' \text{are parallel} \\ \frac{\pi}{2} & \text{if } \mathbf{d}' \text{ is anti-clockwise rotated from } \mathbf{d} \\ -\frac{\pi}{2} & \text{if } \mathbf{d}' \text{ is clockwise rotated from } \mathbf{d} \\ \text{forbidden} & \text{if } \mathbf{d}, \mathbf{d}' \text{ are anti-parallel} \end{cases} \tag{1.45}$$

In figure 1.12 some examples of allowed loops (paths) are given, for which we want to compute the weight. We start at the lower left corner and follow the arrow. We recall that turning left at a vertex gives $+\frac{\pi}{2}$, a right turn $-\frac{\pi}{2}$ and crossing straight adds zero. In subfigure a) the 4 angles Φ encountered during the path are all $\pi/2$. The four angle add up to 2π. In other words we have performed four left turns The weight is then

$$w = e^{i\frac{1}{2}2\pi} = -1 \,.$$

For example b) the angles are in units of $\frac{\pi}{2}$: $1, 0, -1, -1, -1, 0, 1, 1$, with a sum of 0 and a weight $w = +1$. In other words the number of left and right turns is equal. That is also the case in subfigure c). In example d) a loop is twice passed, so the total angle is 4π and a phase factor $+1$. We find in all cases

$$w(\mathcal{P}) = -(-1)^{N_c(L)} \,,$$

which is the required weight in equation (1.39) [p. 29] apart from a global minus sign.

Now we define a matrix $\mathcal{M}$ with matrix elements

$$\langle S'|\mathcal{M}_m|S\rangle = \text{sum of the weights of all paths from } S \text{ to } S' \text{ in } m \text{ steps .}$$

The value of the matrix element is zero, if there is no path connecting S and S' in m steps. For $m = m_1 + m_2$ we have by definition

$$\langle S'|\mathcal{M}_m|S\rangle = \sum_{S''} \langle S'|\mathcal{M}_{m_1}|S''\rangle\langle S''|\mathcal{M}_{m_2}|S\rangle \, ,$$

which is the common matrix product. Consequently, we have

$$\mathcal{M}_m = \left(\mathcal{M}_1\right)^m .$$

$\mathcal{M}_1$ has the dimension $4N \times 4N$, as each step $S = (\mathbf{x}, \mathbf{d})$ has N possible sites $\mathbf{x}$ and 4 possible directions $\mathbf{d}$. Most of the matrix elements, however, are zero. The fact that a path cannot be retraced is also accounted for in $\mathcal{M}_1$.

We can now easily express the sought-for weight D_m as

$$D_m = -\frac{1}{2m}\sum_S \langle S|\mathcal{M}_m|S\rangle = -\frac{1}{2m}\text{tr}\left\{\mathcal{M}_1^m\right\}$$

---

prove

1. The trace is required to sum over all initial vertices of the loop and to make sure that the loop is really closed

2. Since each vertex of a loop occurs as initial point in the trace, we have to divide by m

3. Each loop can be traversed in two direction, which explains the factor $1/2$.

4. The minus sign has been expained before.

q.e.d. ✓

In total we therefore have according to equation (1.41) [p. 29]

$$\ln(Z) = N \ln(2) + 2N \ln\left(\cosh(j)\right) + \sum_{m=1} D_m t^m$$

$$= N \ln(2) + 2N \ln\left(\cosh(j)\right) - \frac{1}{2}\text{tr}\left\{\sum_{m=1} \frac{(t\mathcal{M}_1)^m}{m}\right\}$$

$$= N \ln(2) + 2N \ln\left(\cosh(j)\right) + \frac{1}{2}\text{tr}\left\{\ln\left(\mathbf{1} - t\mathcal{M}_1\right)\right\}$$

$$= N \ln(2) + 2N \ln\left(\cosh(j)\right) + \frac{1}{2}\ln\det\left[\left(\mathbf{1} - t\mathcal{M}_1\right)\right] .$$

As said before, the size of the matrix $\mathcal{M}_1$ is $4N \times 4N$. The matrix elements are defined via

$$\langle \mathbf{x}, \mathbf{d}|\mathcal{M}_1|\mathbf{x}', \mathbf{d}'\rangle .$$

Since we use pbc, it is advantageous to perform a Fourier transform with respect to $\mathbf{x}$ and $\mathbf{x}'$. The determinant is invariant against such a unitary transformation. Moreover, due to translational invariance of the problem, we obtain

$$\langle \mathbf{q}, \mathbf{d}|\mathcal{M}_1|\mathbf{q}', \mathbf{d}'\rangle = \frac{1}{N}\sum_{\mathbf{x},\mathbf{x}'} e^{-i\left(\mathbf{x}\cdot\mathbf{q} - \mathbf{x}'\cdot\mathbf{q}'\right)} \langle \mathbf{0}, \mathbf{d}|\mathcal{M}_1|\underbrace{\mathbf{x}' - \mathbf{x}}_{\Delta\mathbf{x}}, \mathbf{d}'\rangle$$

$$= \frac{1}{N}\underbrace{\sum_{\mathbf{x}} e^{-i\mathbf{x}\cdot(\mathbf{q}-\mathbf{q}')}}_{=\delta_{\mathbf{q}\mathbf{q}'}}\sum_{\Delta\mathbf{x}} e^{i\mathbf{q}'\cdot\Delta\mathbf{x}}\langle \mathbf{0}, \mathbf{d}|\mathcal{M}_1|\Delta\mathbf{x}, \mathbf{d}'\rangle$$

$$= \delta_{\mathbf{q}\mathbf{q}'}\sum_{\Delta\mathbf{x}} e^{i\mathbf{q}\cdot\Delta\mathbf{x}}\langle \mathbf{0}, \mathbf{d}|\mathcal{M}_1|\Delta\mathbf{x}, \mathbf{d}'\rangle .$$

According to equation (1.43) [p. 31] we have the condition

$$\mathbf{x}' = \mathbf{x} + \mathbf{d}$$

$$\Rightarrow \qquad \Delta\mathbf{x} = \mathbf{x}' - \mathbf{x} = \mathbf{d} .$$

Hence the 4×4 matrix $M(\mathbf{q})$ hat the matrix elements

$$\langle \mathbf{q}, \mathbf{d}|\mathcal{M}_1|\mathbf{q}', \mathbf{d}'\rangle = \delta_{\mathbf{q}\mathbf{q}'}\, e^{i\mathbf{q}\cdot\mathbf{d}}\, \langle \mathbf{0}, \mathbf{d}|\mathcal{M}_1|\mathbf{d}, \mathbf{d}'\rangle$$

$$= \delta_{\mathbf{q}\mathbf{q}'}\, \underbrace{e^{i\mathbf{q}\cdot\mathbf{d}}\, e^{i\frac{1}{2}\Phi(\mathbf{d},\mathbf{d}')}}_{=M_{\mathbf{d},\mathbf{d}'}}$$

The inverse transformation is

$$\langle \mathbf{x}, \mathbf{d} | \mathcal{M}_1 | \mathbf{x}', \mathbf{d}' \rangle = \frac{1}{N} \sum_{\mathbf{q}} e^{i \left(\mathbf{x} - \mathbf{x}' \right) \cdot \mathbf{q}} \langle \mathbf{q}, \mathbf{d} | \mathcal{M}_1 | \mathbf{q}, \mathbf{d}' \rangle \,,$$

and, therefore,

$$\langle \mathbf{x}, \mathbf{d} | \mathcal{M}^n | \mathbf{x}', \mathbf{d}' \rangle = \frac{1}{N} \sum_{\mathbf{q}} e^{i \left(\mathbf{x} - \mathbf{x}' \right) \cdot \mathbf{q}} \langle \mathbf{q}, \mathbf{d} | (\mathcal{M}_1)^n | \mathbf{q}, \mathbf{d}' \rangle$$

$$= \frac{1}{N} \sum_{\mathbf{q}} e^{i \left(\mathbf{x} - \mathbf{x}' \right) \cdot \mathbf{q}} \left((M(\mathbf{q}))^n \right)_{\mathbf{d}, \mathbf{d}'} \,.$$

The remaining 4×4 matrix $M(\mathbf{q})$ has the matrix elements

$$M(\mathbf{q}):$$

$\mathbf{d} \backslash \mathbf{d}'$	$\mathbf{e}_x$	$-\mathbf{e}_x$	$\mathbf{e}_y$	$-\mathbf{e}_y$
$\mathbf{e}_x$	e^{iq_1}	0	λe^{iq_1}	$\lambda^* e^{iq_1}$
$-\mathbf{e}_x$	0	e^{-iq_1}	$\lambda^* e^{-iq_1}$	λe^{-iq_1}
$\mathbf{e}_y$	$\lambda^* e^{iq_2}$	λe^{iq_2}	e^{iq_2}	0
$-\mathbf{e}_y$	λe^{-iq_2}	$\lambda^* e^{-iq_2}$	0	e^{-iq_2}

with the definition $\lambda = e^{i\frac{\pi}{4}}$. This can also be written as

$$M(\mathbf{q}) = D(\mathbf{q}) \tilde{M} \tag{1.46a}$$

$$D(\mathbf{q}) = \mathrm{diag}\left[e^{iq_1}, e^{-iq_1}, e^{iq_2}, e^{-iq_2} \right] \tag{1.46b}$$

$$\tilde{M} = \begin{pmatrix} 1 & 0 & \lambda, \lambda^* \\ 0 & 1 & \lambda^*, \lambda \\ \lambda^*, \lambda & 1 & 0 \\ \lambda, \lambda^* & 0 & 1 \end{pmatrix} \tag{1.46c}$$

Here $\tilde{M}$ is a hermitean matrix bat M is not. As the matrix is blockdiagonal in $\mathbf{q}, \mathbf{q}'$ we have

$$\det\left(\mathbf{1} - t\mathcal{M}_1 \right) = \det\left(t\mathcal{M}_1 - \mathbf{1} \right) = \prod_{\mathbf{q}}^{1bc} \det\left(tM(\mathbf{q}) - \mathbf{1} \right)$$

With $Q_\alpha = t e^{iq_\alpha}$ the matrix argument of the determinant reads

$$tM(\mathbf{q}) - \mathbf{1} = - \begin{pmatrix} Q_1 - 1 & 0 & \lambda Q_1 & \lambda^* Q_1 \\ 0 & Q_1^* - 1 & \lambda^* Q_1^* & \lambda Q_1^* \\ \lambda^* Q_2 & \lambda Q_2 & Q_2 - 1 & 0 \\ \lambda Q_2^* & \lambda^* Q_2^* & 0 & Q_2^* - 1 \end{pmatrix} \,.$$

The determinant yields (according to MATHEMATICA)

$$
\ln\left[\det(\mathbf{1} - t\mathcal{M}_1)\right] = \sum_{\mathbf{q}}^{1bc} \ln\left[(1+t^2)^2 - 2t(1-t^2)\left(\cos(q_1) + \cos(q_2)\right)\right].
$$

Then the free energy per site is

$$
-\beta\frac{F}{N} = \ln(2) + 2\ln(\cosh(j)) + \frac{1}{2N}\sum_{\mathbf{q}}^{1bc}\ln\left[(1+t^2)^2 - 2t(1-t^2)\left(\cos(q_1) + \cos(q_2)\right)\right]
$$

$$(1.47)$$

We introduce the normalized density of states $\rho(\varepsilon)$ corresponding to the dispersion

$$
\varepsilon(\mathbf{q}) = -\left(\cos(q_1) + \cos(q_2)\right) \tag{1.48}
$$

$$
\rho(\varepsilon) = \frac{1}{N}\sum_{\mathbf{q}}^{1bc}\delta(\varepsilon(\mathbf{q}) - \varepsilon) \tag{1.49}
$$

Then the free energies reads

$$
-\beta\frac{F}{N} = \ln(2) + 2\ln(\cosh(j)) + \frac{1}{2}\int d\varepsilon\rho(\varepsilon)\ln\left[(1+t^2)^2 + 2t(1-t^2)\,\varepsilon\right].
$$

$$(1.50)$$

Moreover, we use

$$
\cosh(j) = \frac{1}{\sqrt{1-t^2}}, \qquad \left(t := \tanh(j)\right)
$$

$$
2\ln\left(\cosh(j)\right) = \frac{1}{2}\ln\left((1-t^2)^{-2}\right) = \frac{1}{2}\int d\varepsilon\,\rho(\varepsilon)\ln\left((1-t^2)^{-2}\right)
$$

to obtain

$$
-\beta\frac{F}{N} = \ln(2) + \frac{1}{2}\int d\varepsilon\rho(\varepsilon)\ln\left[\left(\frac{1+t^2}{1-t^2}\right)^2 + \left(\frac{2t}{1-t^2}\right)\varepsilon\right]
$$

$$
= \ln(2) + \frac{1}{2}\int d\varepsilon\rho(\varepsilon)\ln\left[\underbrace{\left(\frac{1+t^2}{1-t^2}\right)^2 - \left(\frac{4t}{1-t^2}\right)}_{=\left(1-\sinh(2j)\right)^2} + \underbrace{\left(\frac{2t}{1-t^2}\right)}_{=\sinh(2j)}(2+\varepsilon)\right].
$$

prove

$$
\frac{2t}{1-t^2} = \frac{2\tanh(j)}{1-\tanh^2(j)}
$$

$$
= \frac{2sh/ch}{\underbrace{(ch^2 - sh^2)}_{=1}/ch^2}
$$

$$
= 2\sinh(j)\cosh(j) = \sinh(2j)
$$

$$
\left(\frac{1+t^2}{1-t^2}\right)^2 - \left(\frac{4t}{1-t^2}\right) = \left(\overbrace{\frac{ch^2+sh^2}{\underbrace{ch^2-sh^2}_{=1}}}^{=\cosh(2j)}\right)^2 - \left(\underbrace{2\frac{2t}{1-t^2}}_{=2\sinh(2j)}\right)
$$

$$
= \cosh^2(2j) - 2\sinh(2j)
$$

$$
= 1 + \sinh^2(2j) - 2\sinh(2j)
$$

$$
= \left(1 - \sinh(2j)\right)^2 .
$$

q.e.d. ✓

The final result for the free energy reads thereore

FREE ENERGY OF THE 2D ISING MODEL
(without external field)

$$
\frac{\ln(Z)}{N} = -\beta\frac{F}{N} = \ln(2) + \frac{1}{2}\int d\varepsilon\rho(\varepsilon)\ln\left[\left(1-\sinh(2j)\right)^2 + \sinh(2j)\,(2+\varepsilon)\right].
$$

(1.51)

It is to be remembered that $j = J\beta > 0$ for the ferrromagnetic model. Therefore, $\sinh(2j) > 0$. According to equation (1.48) , the energies ε are restricted to the interval $([-2, 2]$. The density of states

Figure 1.13: *Free energy of the 2D Ising model.*

$\rho(\varepsilon)$ is that of the 2d tight binding model, which is given by

$$\rho(\varepsilon) = \frac{\theta(|\varepsilon| \leq 2)}{2\pi^2} \, \mathcal{K}\left(1 - \left(\frac{\varepsilon}{2}\right)^2\right) , \tag{1.52}$$

where $\mathcal{K}(x)$ is the elliptic integral of the first kind

$$\mathcal{K}(x) = \int_0^{\frac{\pi}{2}} \frac{\mathrm{d}\varphi}{\sqrt{1 - x^2(\sin\varphi)^2}} . \tag{1.53}$$

The free energy is related to the entropy and internal energy through

$$F = U - TS .$$

As we will easily see later on, for $T \to 0$ we have $U \to -2JN$ and $S \to 0$ (3. law of thermodynamics), hence $F \to -2JN$; while for $k_B T/J \gg 1$ we have $U \to 0$ and $S \to N k_B \ln(2)$, hence $F \to -N k_B T \ln(2)$.

1.3.5 Curie-temperature

If we would have computed the free energy in the presence of an external magnetic field, we could have computed the magnetization and from that directly the transition temperature. In the absence of an external field, the magnetization is always zero, due to symmetry. But in order to allow for a

phase transition the free energy has to have an irregularity. (The argument will be given later.) The argument of the logarithm is non-negative, but it can be zero which yields the required irregularity. For the argument to become zero, both terms $(1 - \sinh(2j))^2$ and $\sinh(2j)(2 + \varepsilon)$ have to be zero. The first condition yields

$$\sinh(2j_C) = 1 \tag{1.54}$$

$$1 - \sinh(2j) = 1 - \frac{e^{2jc} + e^{-2jc}}{2} = 0$$
$$\Rightarrow \quad e^{2jc} + e^{-2jc} - 2 = 0$$
$$e^{4jc} - 2e^{2jc} + 1 = 0 .$$

This quadratic equation has the solutions

$$e^{2jc} = 1 \pm \sqrt{2} .$$

Since $e^{2j} > 0$ the only solution is

$$j_C = J\beta_C = \frac{1}{2} \ln\left(1 + \sqrt{2}\right) = 0.4407 . \tag{1.55}$$

The mean field result was $J\beta_C = 0.25.$ The irregularity of the free energy is a necessary prerequisite for phase transition, but not sufficient for a rigorous prove. Nor does it tell us the order of the phase transition. The rigorous prove requires the dependence of the free energy on the an external field.

1.3.6   Internal energy

$$U = \langle H \rangle = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle \; .$$

Due to the translational invariance all n.n. correlations are the same

$$\frac{U}{NJ} = -2 \langle S_1 S_2 \rangle \; .$$

For high temperatures the spins are uncorrelated resulting in

$$\frac{U}{NJ} = -2 \langle S_1 \rangle \langle S_2 \rangle = 0 \; ,$$

while for $T = 0$, the lowest energy is obtained if all spins are parallel and

$$\frac{U}{NJ} = -2 \; .$$

Now we compute U for arbitrary temperature. To this end, we write $\ln(Z)$ in a more compact form

$$\ln(Z) = \ln(2) + \frac{1}{2} \underbrace{\left\langle \ln \left((1-\kappa)^2 + \kappa(2+\varepsilon) \right) \right\rangle}_{=g(\kappa)} ,$$

the average here is taken w.r.t. $\rho(\varepsilon)$, and $\kappa = \sinh(2\beta J)$. Then

$$\frac{U}{N} = \frac{\langle H \rangle}{N} = -\frac{\partial \ln(Z)}{\partial \beta}$$
$$= -\frac{1}{2} \left(\frac{\partial}{\partial \kappa} g(\kappa) \right) \frac{d\kappa}{d\beta} \; .$$

with

$$\frac{\partial \kappa}{\partial \beta} = \frac{\partial}{\partial \beta} \sinh(2J\beta) = 2J \cosh(2J\beta) = 2J \sqrt{1 + \sinh^2(2J\beta)}$$

we have

$$\frac{U}{N} = -Jg'(\kappa)\sqrt{1+\kappa^2}$$
$$= -J \left\langle \frac{2\kappa + \varepsilon}{(1-\kappa)^2 + \kappa(2+\varepsilon)} \right\rangle \sqrt{1+\kappa^2} \; .$$

(a) Internal energy .

(b) Entropy.

Figure 1.14: *2d Ising model for B = 0.*

In summary we have

$$
\boxed{
\begin{array}{c}
\textsc{Internal energy} \\[2mm]
\dfrac{U}{NJ} = -\left\langle \dfrac{2\kappa + \varepsilon}{(1-\kappa)^2 + \kappa(2+\varepsilon)} \right\rangle \sqrt{1+\kappa^2} \, .
\end{array}
} \qquad (1.56)
$$

1.3.7 Entropy

From $F = U - TS$ we get

$$
\frac{S}{Nk_B} = j\frac{U}{NJ} - \beta\frac{F}{N} = j\left(\frac{U}{NJ}\right) + \left(\frac{\ln(Z)}{N}\right) \, .
$$

Hence, we can express the entropy in terms of equation (1.56) and equation (1.51) [p. 37].

We see no critical behaviour in the entropy, which is the first derivative of the free energy w.r.t. T. The latter is continuous at T_C. According to section (3.2.3) [Seite 110] it is therefore not a first order phase transition.

1.3.8   Specific heat

The order of the phase transition can also be inferred from the specific heat at $B = 0$.

$$\frac{C}{N} = \frac{1}{N}\frac{\partial U}{\partial T}\bigg|_N = \frac{1}{N}\frac{\partial U}{\partial \kappa}\underbrace{\frac{\partial \kappa}{\partial \beta}}_{=2J\sqrt{1+\kappa^2}}\underbrace{\frac{\partial \beta}{\partial T}}_{=-\frac{1}{k_B T^2}}$$

$$= \left[\frac{\partial}{\partial \kappa}\left(-Jg'(\kappa)\sqrt{1+\kappa^2}\right)\right]\left(-k_B\beta^2\left(2J\sqrt{1+\kappa^2}\right)\right)$$

The final result reads

$$\frac{C(T)}{Nk_B} = 2j^2\left[(1+\kappa^2)g''(\kappa) + \kappa g'(\kappa)\right] . \tag{1.57a}$$

with

$$g'(\kappa) = \left\langle \frac{2\kappa + \varepsilon}{(1-\kappa)^2 + \kappa(2+\varepsilon)} \right\rangle \tag{1.57b}$$

$$g''(\kappa) = \left\langle \frac{2}{(1-\kappa)^2 + \kappa(2+\varepsilon)} \right\rangle - \left\langle \left(\frac{2\kappa + \varepsilon}{(1-\kappa)^2 + \kappa(2+\varepsilon)}\right)^2 \right\rangle \tag{1.57c}$$

We see in figure 1.15 that the specific heat diverges at T_C. In order to unravel the type of divergency we perform a Taylor expansion in T about T_C, i.e. $T = T_C + \Delta T$. This corresponds to

$$j = j_C + \Delta j$$
$$\kappa = \sinh(2J_C + \Delta \kappa = 1 + \Delta \kappa$$

In the last step we have used equation (1.54) [p. 39]. The only divergent behaviour can come from g' or g''. The other terms can, therefore, be replaced by $T = T_C$. I.e.

$$\frac{C(T_C + \Delta T)}{Nk_B} = 2j_C^2\left[2g''(\kappa_c + \Delta \kappa) + g'(\kappa_c + \Delta \kappa)\right] .$$

 There is a critical behaviour in the second derivative of F, i.e. the specific heat. Therefore, the Ising model has a second order phase transition.

Figure 1.15: *Specific heat of the 2d Ising model.*

Type of divergency

The divergency originates from the term $\frac{1}{(1-\kappa)^2+\kappa(\varepsilon+2)}$ at the vicinity of $\varepsilon = -2$. The dos $\rho(\varepsilon)$ in principle also has a divergency at $\varepsilon = 0$ but it is integrable and does not result in a divergence in the specific heat. To study the divergency at $\varepsilon = -2$ we split

$$\rho(\varepsilon) = \underbrace{\rho(-2)}_{=\rho_0}+\Delta\rho(\varepsilon) \ .$$

Then the expectation values become

$$\langle F(\varepsilon)\rangle = \langle F(\varepsilon)\rangle_{\rho_0} + \langle F(\varepsilon)\rangle_{\Delta\rho} \ .$$

The second term cause no divergency, hence we merely need to consider terms of the form

$$\langle F(\varepsilon)\rangle_{\rho_0} \ . \tag{1.58}$$

Proof

$$\lim_{\varepsilon \to -2} \frac{\Delta\rho(\varepsilon)(2 + \varepsilon + 2\Delta\kappa)}{(\Delta\kappa)^2 + (1 + \Delta\kappa)(\varepsilon + 2)}$$

$$= \lim_{\eta \to 0} \frac{\Delta\rho(-2 + \eta)(\eta + 2\Delta\kappa)}{(\Delta\kappa)^2 + (1 + \Delta\kappa)\eta}$$

$$\overset{\text{L'Hospital}}{=} \lim_{\eta \to 0} \frac{\Delta\rho'(-2 + \eta)(\eta + 2\Delta\kappa) + \Delta\rho(-2 + \eta)}{(\Delta\kappa)^2 + (1 + \Delta\kappa)\eta}$$

$$= \lim_{\eta \to 0} \frac{(2\Delta\kappa\Delta\rho'(-2 + \eta) + \Delta\rho(-2 + \eta)}{(\Delta\kappa)^2}$$

$$= \frac{2}{\Delta\kappa} \underbrace{\lim_{\eta \to 0} \Delta\rho'(-2 + \eta)}_{=0} + \frac{1}{(\Delta\kappa)^2} \underbrace{\lim_{\eta \to 0} \Delta\rho(-2 + \eta)}_{=0}$$

$$= 0 \ .$$

or for g'' we need

$$\lim_{\varepsilon \to -2} \Delta\rho(\varepsilon) \left(\frac{2 + \varepsilon + \Delta\kappa}{\left(\Delta\kappa\right)^2 + (1 + \Delta\kappa)(\varepsilon + 2)} \right)^2$$

$$= \lim_{\eta \to 0} \frac{\Delta\rho(-2 + \eta)(\eta + \Delta\kappa)^2}{\left((\Delta\kappa)^2 + (1 + \Delta\kappa)\eta\right)^2}$$

$$\overset{L'Hospital}{=} \lim_{\eta \to 0} \frac{\Delta\rho'(-2 + \eta)(\eta + \Delta\kappa)^2 + 2\Delta\rho(-2 + \eta)(\eta + \Delta\kappa)}{2\left((\Delta\kappa)^2 + (1 + \Delta\kappa)\eta\right)(1 + \Delta\kappa)}$$

$$\overset{L'Hospital}{=} \lim_{\eta \to 0} \frac{\Delta\rho'(-2 + \eta)(\Delta\kappa)^2 + 2\Delta\kappa\Delta\rho(-2 + \eta)}{2\left((\Delta\kappa)^2\right)(1 + \Delta\kappa)}$$

$$= \frac{(\Delta\kappa)^2}{2\left((\Delta\kappa)^2\right)(1 + \Delta\kappa)} \underbrace{\lim_{\eta \to 0} \Delta\rho'(-2 + \eta)}_{=0} + \frac{2\Delta\kappa}{2\left((\Delta\kappa)^2\right)(1 + \Delta\kappa)} \underbrace{\lim_{\eta \to 0} \Delta\rho(-2 + \eta)}_{=0}$$

$$= 0 \ .$$

q.e.d. ✓

For the first term in equation (1.57) we need

$$g'(1 + \Delta\kappa) = \left\langle \frac{\varepsilon + 2 + \Delta\kappa}{(2 + \varepsilon)(1 + \Delta\kappa) + (\Delta\kappa)^2} \right\rangle_{\rho_0} ,$$

for which we find

$$g'(1 + \Delta\kappa) = \frac{1}{1 + \Delta\kappa} \cdot \{4\rho_0 + \Delta\kappa\rho_0 \ln(4) - 2\rho_0\Delta\kappa \ln(\Delta\kappa) + O(\Delta\kappa)\}$$
$$\xrightarrow[\Delta\kappa \to 0]{} 4\rho_0 = O(1) \; .$$

Proof

First we will transform the denominator

$$(2 + \varepsilon)(1 + \Delta\kappa) + (\Delta\kappa)^2 = (1 + \Delta\kappa)\left(2 + \varepsilon + \frac{(\Delta\kappa)^2}{1 + \Delta\kappa}\right)$$
$$= (1 + \Delta\kappa)\left(2 + \varepsilon + (\Delta\kappa)^2 + O((\Delta\kappa)^3)\right)$$

Then

$$\frac{\varepsilon + 2 + \Delta\kappa}{(2 + \varepsilon)(1 + \Delta\kappa) + (\Delta\kappa)^2}$$
$$= \frac{1}{1 + \Delta\kappa} \cdot \frac{\varepsilon + 2 + \Delta\kappa}{2 + \varepsilon + (\Delta\kappa)^2 + O((\Delta\kappa)^3}$$
$$= \frac{1}{1 + \Delta\kappa} \cdot \frac{\varepsilon + 2 + (\Delta\kappa)^2 + O((\Delta\kappa)^3) + \Delta\kappa(1 - \Delta\kappa) + O((\Delta\kappa)^3)}{2 + \varepsilon + (\Delta\kappa)^2 + O((\Delta\kappa)^3)} \; .$$

I.e.

$$\frac{\varepsilon + 2 + \Delta\kappa}{(2 + \varepsilon)(1 + \Delta\kappa) + (\Delta\kappa)^2} = \frac{1}{1 + \Delta\kappa} \cdot \left\{1 + \frac{\Delta\kappa(1 - O((\Delta\kappa)^2))}{2 + \varepsilon + (\Delta\kappa)^2(1 + O(\Delta\kappa))}\right\} \; .$$
$$(1.59)$$

So we have

$$g'(1 + \Delta\kappa) = \left\langle \frac{\varepsilon + 2 + \Delta\kappa}{(2 + \varepsilon)(1 + \Delta\kappa) + (\Delta\kappa)^2} \right\rangle_{\rho_0}$$

$$= \frac{1}{1 + \Delta\kappa} \cdot \left\{\langle 1 \rangle_{\rho_0} + \Delta\kappa(1 - O((\Delta\kappa)^2)) \left\langle \frac{1}{2 + \varepsilon + (\Delta\kappa)^2(1 + O(\Delta\kappa))} \right\rangle_{\rho_0}\right\}$$

The definition of the expectation value is

$$\langle f(\varepsilon) \rangle_{\rho_0} := \int_{-2}^{2} f(\varepsilon)\rho_0 d\varepsilon \; = \; \rho_0 \int_{-2}^{2} f(\varepsilon)d\varepsilon \; .$$

Therefore

$$\langle 1 \rangle_{\rho_0} = 4\rho_0 \; .$$

$$\left\langle \frac{1}{2 + \varepsilon + (\Delta\kappa)^2 \left(1 + O(\Delta\kappa) \right)} \right\rangle_{\rho_0}$$

$$= \rho_0 \int_{-2}^{2} \frac{1}{2 + \varepsilon + (\Delta\kappa)^2 \left(1 + O(\Delta\kappa) \right)} d\varepsilon$$

$$= \rho_0 \ln \left(2 + 2 + (\Delta\kappa)^2 \left(1 + O(\Delta\kappa) \right) \right) - \rho_0 \ln \left(2 - 2 + (\Delta\kappa)^2 \left(1 + O(\Delta\kappa) \right) \right)$$

$$= \rho_0 \ln (4) - \rho_0 \ln \left((\Delta\kappa)^2 \right) + O(\Delta\kappa)$$

In total we have

$$g'(1 + \Delta\kappa) = \left\langle \frac{\varepsilon + 2 + \Delta\kappa}{(2 + \varepsilon)(1 + \Delta\kappa) + (\Delta\kappa)^2} \right\rangle_{\rho_0}$$

$$= \frac{1}{1 + \Delta\kappa} \cdot \left\{ 4\rho_0 + \Delta\kappa\rho_0 \ln (4) - 2\rho_0\Delta\kappa \ln (\Delta\kappa) + O(\Delta\kappa) \right\}$$

$$\xrightarrow[\Delta\kappa\to0]{} 0 \; .$$

q.e.d. ✓

Similarly, for the second term of g'' we find with equation (1.59) [previous

page]

$$\left\langle \left(\frac{2\kappa + \varepsilon}{(1-\kappa)^2 + \kappa(2+\varepsilon)} \right)^2 \right\rangle_{\rho_0}$$

$$= \left(\frac{1}{1+\Delta\kappa} \right)^2 \cdot \left\langle \left(1 + \frac{\Delta\kappa(1 - O((\Delta\kappa)^2))}{2+\varepsilon+(\Delta\kappa)^2(1+O(\Delta\kappa))} \right)^2 \right\rangle_{\rho_0}$$

$$= O(1) + O(\Delta\kappa\ln(\Delta\kappa)) + O((\Delta\kappa)^2) \int_{-2}^{2} \frac{1}{2+\varepsilon+(\Delta\kappa)^2} d\varepsilon$$

$$= O(1) + O(\Delta\kappa\ln(\Delta\kappa)) + O((\Delta\kappa)^2)\left(O(1) + O(\frac{1}{(\Delta\kappa)^2}) \right)$$

$$= O(\Delta\kappa\ln(\Delta\kappa)) + O(1) + O(((\Delta\kappa)^2)$$

Again no divergency. The only divergent term stems from the first part of g'', which yields

$$\left\langle \frac{2}{(\Delta\kappa)^2 + (1+\Delta\kappa)(2+\varepsilon)} \right\rangle_{\rho_0} = \int_{-2}^{2} \frac{\rho_0}{(\Delta\kappa)^2 + (1+\Delta\kappa)(2+\varepsilon)} d\varepsilon$$

$$= \rho_0 \ln\left[(\Delta\kappa)^2 + (1+\Delta\kappa)(2+2) \right] - \rho_0 \ln\left[(\Delta\kappa)^2 + (1+\Delta\kappa)(2-2) \right]$$

$$= \rho_0 \ln\left[4 + O(\Delta\kappa) \right] - 2\rho_0 \ln(|\Delta\kappa|);$$

$$= O(1) - 2 \ln(|\Delta\kappa|);$$

The specific heat obviously has a logarithmic divergency, which corresponds to the critical exponent

$$\alpha = \alpha' = 0 . \tag{1.60}$$

For the definition of the critical exponents see section (3.3) [Seite 111].

1.3.9 Spontaneous magnetization

So far it has not been possible to find the exact solution of the 2d Ising model in an external magnetic field. This is only doable for infinitesimal B values, which is enough to determine the spontaneous magnetization. It amounts to computing the spin-spin correlation $\langle S_i S_j \rangle$ and use

$$\lim_{l\to\infty} \langle S_i S_{i+l} \rangle \longrightarrow \left(\langle S_i \rangle \right)^2 = \left(\frac{M}{N} \right)^2 .$$

The graphical solution amounts to count all graphs as before but with the peculiarity that the vertices i and j have an odd order. The result reads

Figure 1.16: *Spontaneous magnetization of Ising spins.*

SPONTANEOUS MAGNETIZATION OF THE 2D ISING MODEL

$$\frac{M}{N} = \begin{cases} \left(1 - \sinh^{-4}(2j)\right)^{1/8} & \text{for } T \leq T_C \\ 0 & \text{otherwise} \end{cases} \qquad (1.61)$$

The order parameter, the magnetization, is continuous, which corroborates the statement, that it is a second order phase transition.

1.3.10   Proof

We seek the number of paths from the center $\mathbf{x} = 0$ to site $\mathbf{x}$, where the Manhattan distance is n. We consider only cases with $n > 1$, actually we are interested in $n - 1$ to ∞. We are interested in the weighted sum over all paths from the center to site $\mathbf{x}$. Schematically this can be written as

$$Z_{0\mathbf{x}} = \sum_{m=n}^{\infty} W_{0,\mathbf{x}}^{(m)} \,,$$

where $W_{0,\mathbf{x}}^{(m)}$ stands for the contributions that contain m steps. We will again use the previous matrix $M^{(m)}$. Here, however, we are not counting

loops and therefore the weights are not entirely correct and it is not yet clear what we have to do with the directions of the last step, which points from the final point **x** to an arbitrary direction. It is, therefore, useful, to split off the last step. Then it seem reasonable to start with the form

$$W_{0,x}^{(m)} = \sum_{d_0} \sum_{x',d'} \left(M^{(m-1)} \right)_{(0,d_0),(x',d')} \left(M^{(1)} \right)_{(x',d'),(x,d'')}$$

There is one constraint:

$$x' = x - d' \ .$$

The last term adds a factor $th(j)$ plus a phase, that depends on the yet undefined **d″**. The phase-factors are only correct in closed loops to add up to the sign, representing crossings. Therefore, we will add graph elements to from a closed loop, such that no additional crossings occur. There are 16 possibilities depending on **d** and
vvd′

1.3.11 Critical exponent

For $T \searrow T_C$ we have

$$\frac{M}{N} = \left(1 - \left[\sinh \left(2j_C + 2J\Delta\beta \right) \right]^{-4} \right)^{\frac{1}{8}}$$

$$= \left(1 - \underbrace{\left[\sinh \left(2j_C \right)}_{\stackrel{(1.54)}{=} 1} + \cosh \left(2j_C \right) J\Delta\beta \right]^{-4} \right)^{\frac{1}{8}} \ .$$

In addition, we have

$$\cosh \left(2j_C \right) = \sqrt{1 + \sinh^2(2j_C)} = \sqrt{2} \ .$$

Hence

$$\frac{M}{N} = \left(1 - \left[1 + \sqrt{2}J\Delta\beta \right]^{-4} \right)^{\frac{1}{8}}$$

$$= \left(1 - 1 + 4\sqrt{2}J\Delta\beta \right)^{\frac{1}{8}}$$

$$= \left(4\sqrt{2}J\Delta\beta \right)^{\frac{1}{8}}$$

$$= \propto \left(\frac{1}{T} - \frac{1}{T_C} \right)^{\frac{1}{8}}$$

$$\propto \varepsilon^{\frac{1}{8}}$$

Chapter 2

Magnetism

2.1   Hamiltonian

The hamiltionian reads

$$H = \sum_j \left(\mathbf{p}_j + e\mathbf{A}(\mathbf{r}_j) \right)^2 + H_{\text{Coul}} - \sum_j m_j^s B(\mathbf{r}_j) + H_{rel} \qquad (2.1)$$

So far, this hamiltonian describes any arbitrary system, from isolated atoms up to any crystal. The first term describes the coupling of the electrons to the electromagnetic field in combination with the kinetic energy of the electrons, the second contains Coulomb interaction of the electrons to the atomic core and the electron-electron interaction and last term covers the interaction of the magnetic moment of the electronic spins to the external field. The spin of electron j, denoted by $\mathbf{S}_j$ corresponds to a magnetic moment

$$\mathbf{m}_j^s = -\frac{g_e e}{2m}\mathbf{S}_j = -\frac{g_e \mu_B}{\hbar}\mathbf{S}_j \qquad (2.2)$$

with $g_e = 2.0023$ being the Landé Factor for the electron, and the Bohr magneton

$$\mu_B = \frac{e\hbar}{2m} \ . \qquad (2.3)$$

The last term in equation (2.1) covers relativistic effects, such as the spin orbit coupling, which we will briefly discuss later on. In the hamiltonian the dipol-dipol interaction of the spins is neglected, as is of minor importance. First, we transform the first part of the hamiltonian

$$\left(\mathbf{p}_j + e\mathbf{A}(\mathbf{r}_j) \right)^2 = \mathbf{p}_j^2 + e\mathbf{p}_j\mathbf{A}(\mathbf{r}_j) + e\mathbf{A}(\mathbf{r}_j)\mathbf{p}_j + e^2\mathbf{A}^2(\mathbf{r}_j)$$

We use the Coulomb gauge, in which

$$\text{div}\mathbf{A}(\mathbf{r}) = 0$$

holds. Moreover, we will only consider a homogeneous magnetic field $\mathbf{B}$, for which in the Coulomb gauge we can write

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r} \ .$$

In this case

$$\mathbf{p}_j\mathbf{A}(\mathbf{r}_j) = \frac{1}{2}\mathbf{p}_j \cdot \left(\mathbf{B} \times \mathbf{r}_j \right) \ .$$

We have to take into account that **P** and **r** are operators, while **B** is a classical vector. Then the spin-term simplifies to

$$\sum_j m_j^s B(\mathbf{r}_j) = \mathbf{B} \sum_j m_j^s \,.$$

Moreover, we need

$$\begin{aligned}
\mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) &= p_i \varepsilon_{ijk} B_j r_k \\
&= -B_j \varepsilon_{jik} p_i r_k \\
&= B_j \varepsilon_{jki} r_k p_i \,.
\end{aligned}$$

IN the last step we have used that r_k and p_j commute for different indices, which is guaranteed be the Levi Civita tensor. Hence

$$\mathbf{p}_j \cdot (\mathbf{B} \times \mathbf{r}_j) = \mathbf{B} \cdot (\mathbf{r}_j \times \mathbf{p}_j) = \mathbf{B} \cdot \mathbf{L}_j \,. \tag{2.4}$$

Similarly, we find

$$\begin{aligned}
(\mathbf{B} \times \mathbf{r}) \cdot \mathbf{p} &= \varepsilon_{ijk} B_j r_k p_i \\
&= B_j \varepsilon_{jki} r_k p_i \,.
\end{aligned}$$

We still need

$$\begin{aligned}
\mathbf{A}^2(r) &= \frac{1}{4} \left(\mathbf{B} \times \mathbf{r} \right)^2 \\
&= \frac{1}{4} \varepsilon_{ijk} \varepsilon_{imn} B_i r_j B_m r_n \\
&= \frac{1}{4} \left(B_i r_j B_i r_j - B_i r_i B_j r_j \right) \\
&= \frac{1}{4} \left(\mathbf{B}^2 \mathbf{r}^2 - (\mathbf{B} \cdot \mathbf{r})^2 \right) \,.
\end{aligned}$$

In total we therefore find

$$H = \frac{1}{2m} \sum_j \mathbf{p}_j^2 + \frac{e}{2m} \mathbf{B} \sum_j \cdot \mathbf{L}_j + \frac{e^2 B^2}{8m} \sum_j \left(\mathbf{B}^2 \mathbf{r}_j^2 - (\mathbf{B} \cdot \mathbf{r}_j)^2 \right) + H_{\text{Coul}} - \mathbf{m}^s \cdot \mathbf{B} \,,$$

where $\mathbf{m}^s$ is the total magnetic moment of all spins. We also relate the angular momentum with the magnetic moment

$$\begin{aligned}
\mathbf{m}_j^L &= -\frac{e}{2m} \mathbf{L}_j = -\frac{\mu_B}{\hbar} \mathbf{L}_j \\
\mathbf{m}^L &= -\frac{e}{2m} \sum_j \mathbf{L}_j = -\frac{\mu_B}{\hbar} \sum_j \mathbf{L}_j \,.
\end{aligned}$$

Then the hamiltonian simplifies to

$$H = \frac{1}{2m} \sum_j \mathbf{p}_j^2 + H_{dia} + H_{\text{Coul}} - \mathbf{m}^{perm} \cdot \mathbf{B} \, ,$$

$$H_{dia} = \frac{e^2 B^2}{8m} \sum_j \left(\mathbf{B}^2 \mathbf{r}_j^2 - (\mathbf{B} \cdot \mathbf{r}_j)^2 \right) \, ,$$

with the total *permanent* magnetic moment defined by

$$\mathbf{m}^{perm} = \mathbf{m}^s + \mathbf{m}^L = -\frac{\mu_B}{\hbar} \left(\mathbf{L} + g_e \mathbf{S} \right) \, . \qquad (2.5)$$

It results in *paramagnetism*.

The permanent moments tend to align in the magnetic field, while thermal fluctuations have the opposite effect. There is yet another term in the hamiltonian equation (2.1) [p. 52] that contains magnetic moments resulting from the electronic motion: the diamagnetic term H_{dia}. One can show that the total magnetic moment, defined as

$$\mathbf{m} = \mathbf{m}^{perm} + \mathbf{m}^{ind} \, ,$$

can be obtained by

$$\mathbf{m} = -\nabla_{\mathbf{B}} H \, .$$

Then we see that the induced magnetic moment is given by

$$\mathbf{m}^{ind} = -\frac{e^2}{4m} \sum_j \left(\mathbf{r}_j^2 - \mathbf{r}_j \mathbf{r}_j^T \right) \mathbf{B} \, .$$

W.l.o.g. we can choose $\mathbf{B} = B \mathbf{e}_z$ then

$$\mathbf{m}^{ind} = -B \frac{e^2}{4m} \sum_j \left(\mathbf{r}_j^2 \mathbf{e}_z - z_j \mathbf{r}_j \right)$$

2.1.1   Diamagnetism of atoms

We consider atoms or ions with closed shells, e.g. helium or other noble gases. in this case $S = 0$, $L = 0$. Then the only term contribution to a magnetic moment is the diamagnetic term. We will treat this term in first order perturbation theory, i.e. we first determine the ground state of the system for $B = 0$ and use the corresponding eigenvectors to determine the first order energy correction

$$\Delta E_1 = \langle H_{dia} \rangle \, ,$$

	He	Ne	Ar	Kr	Xe
χ per mole in 10^{-6}cm^3/mole	-1.9	-7.2	-15.4	-28.0	-43.0

from which we obtain the resulting moment

$$\langle \mathbf{m}^{ind} \rangle = - B \frac{e^2}{4m} \sum_j \left(\langle \mathbf{r}_j^2 \rangle \mathbf{e}_z - \langle z_j \mathbf{r}_j \rangle \right) .$$

where $r_{j,\nu}$ is the ν-the cartesian component of the vector $\mathbf{r}_j$. We consider

$$\langle z_j \mathbf{r}_j \rangle = \sum_\nu \mathbf{e}_\nu \langle z_j r_{j,\nu} \rangle ,$$

For closed atomic shells, the ground state wavefunction is rotational invariant, therefore

$$\langle z_j r_{j,\nu} \rangle = \delta_{\nu,z} \langle z_j^2 \rangle = \delta_{\nu,z} \frac{1}{3} \langle r_j^2 \rangle$$

So in total , the atomic induced magnetic moment is

$$\mathbf{m}_{ind} = -\mathbf{B} \frac{e^2}{6m} \sum_j \langle r_j^2 \rangle$$

The magnetic moment is always in the opposite direction of the applied magnetic field, i.e. *diamagnetic reaction*, it reduced the total magnetic field. It is called *Langevin diamagnetism*.
From the magnetic moment, we determine the magnetic susceptibility

$$\chi_{\nu\mu} = \mu_0 \frac{\partial \langle \mathbf{m}_\nu \rangle}{\partial B_\mu} = -\delta_{\mu\nu} \frac{\mu_0 e^2}{6m} \langle \sum_j r_j^2 \rangle$$

To estimate the order of magnitude, we replace $\langle r_j^2 \rangle$ by the square of the Bohr radius. One obtains

$$\chi \text{per mole} = \approx -3 \times 10^{-6} \frac{cm^3}{\text{mol}} .$$

For noble gases this value value is This diamagnetic contribution is also present in in open shell systems, but then it is orders of magnitude smaller than the contribution of the other term.

2.2   Density matrix and thermodynamic relations

We consider the canonical ensemble with fixed particle number N, which we will not explicitly mention as natural variable in the arguments. We only write T and $\mathbf{B}$

$$\rho(T, \mathbf{B}) = \frac{1}{Z(T, \mathbf{B})} e^{-\beta H}$$
$$Z = \mathrm{tr}\, e^{-\beta H} .$$

The free energy reads

$$F(T, \mathbf{B}) = -k_B T \ln(Z(T, \mathbf{B})) . \tag{2.6}$$

The internal energy follows from

$$U = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln(Z)$$
$$= \frac{\partial}{\partial \beta} (\beta F)$$
$$= F - \underbrace{\beta(k_B T^2)}_{=T} \underbrace{\frac{\partial}{\partial T} F}_{=-S}$$
$$U = F - TS .$$

This is equivalent to

$$S = \frac{1}{T}(U - F)$$
$$= k_B \, \mathrm{tr} \left\{ \varrho \left(\beta H \right) \right\} + k_B \ln(Z)$$
$$= k_B \left(\mathrm{tr} \left\{ \varrho \left(\beta H \right) \right\} + \ln(Z) \right) .$$

Then we use

$$\ln(\rho) = \ln \left(\frac{e^{-\beta H}}{Z} \right) = \ln \left(e^{-\beta H} \right) - \ln(Z) = -\beta H - \ln(Z)$$
$$\beta H = - \left(\ln(\rho) + \ln(Z) \right) .$$

Inserting above yields

$$
\begin{aligned}
S &= k_B \left(-\operatorname{tr}\left\{ æ\left(\ln(æ) + \ln(Z) \right) \right\} + \ln(Z) \right) \\
&= k_B \left(-\operatorname{tr}\left\{ æ\ln(æ) \right\} - \underbrace{\operatorname{tr}\left\{ æ \right\}}_{=1} \ln(Z)) + \ln(Z) \right) \\
&\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}_{=0} \\
&= \operatorname{tr}\left\{ -k_B æ\ln(æ) \right\} \\
&= -k_B \langle \ln(\rho) \rangle \ .
\end{aligned}
$$

Hence the entropy is the trace of the quantum entropy operator.
For the total differential of F we have

$$
\begin{aligned}
dF &= \left. \frac{\partial F(T, \mathbf{B})}{\partial T} \right|_{\mathbf{B}} dT + \left. \nabla_{\mathbf{B}} F(T, \mathbf{B}) \right|_{T} \cdot d\mathbf{B} \\
&= -S dT - \mathbf{M} \cdot d\mathbf{B}
\end{aligned}
$$

Prove of the last step

$$
\begin{aligned}
\left. \nabla_{\mathbf{B}} F(T, \mathbf{B}) \right|_{T} &= -k_B T \nabla_{\mathbf{B}} \ln(Z) \\
&= -\frac{k_B T}{Z} \nabla_{\mathbf{B}} Z \\
&= -\frac{k_B T}{Z} \operatorname{tr}\left(\left. \nabla_{\mathbf{B}} e^{-\beta H} \right|_{T} \right) \\
&= \underbrace{-\frac{k_B T}{Z}(-\beta)}_{=\frac{1}{Z}} \operatorname{tr}\left(e^{-\beta H} \underbrace{\left. \nabla_{\mathbf{B}} H \right|_{T}}_{=-\mathbf{m}} \right) \\
&= -\operatorname{tr}\left(\frac{e^{-\beta H}}{Z} \mathbf{m} \right) = -\mathbf{M}
\end{aligned}
$$

Hence

$$
\left. \frac{\partial F}{\partial \mathbf{B}} \right|_{T} = -\mathbf{M} \ . \tag{2.7}
$$

Oftentimes the magnetization is defined as total mean magnetic moment per volume.

2.2.1   Magnetic response functions

Specific heat in analogy to the case of gases

$$C_{\mathbf{B}} = \left.\frac{\partial U}{\partial T}\right|_{\mathbf{B}} = \left.T\frac{\partial S}{\partial T}\right|_{\mathbf{B}} = \left.-T\frac{\partial^2 F}{\partial T^2}\right|_{\mathbf{B}} . \tag{2.8}$$

Derivation as before without magnetic field.
Magnetic susceptibility

$$\chi_{T,\nu\mu} = \left.\mu_0 \frac{\partial M_\nu}{\partial B_\mu}\right|_T = -\mu_0 \frac{\partial^2 F}{\partial B_\nu \partial B_\mu} \tag{2.9}$$

In many times, the susceptibility is also expressed per volume.

2.2.2   Internal energy

We have defined the internal energy as $U = \langle H \rangle$, which is the energy of the material including the interaction of the electro magnetic field. It was derived from the purely electronic part. However, the field energy itself is not included. It is common to define a second internal energy U' that also includes the field energy

$$U' = U + \mathbf{M} \cdot \mathbf{B} . \tag{2.10}$$

resulting in

$$dU' = TdS + \mathbf{B} \cdot d\mathbf{M} .$$

It is the Legendre transformation in the pair $(\mathbf{M}, \mathbf{B})$.
With

$$\left.\frac{\partial U'}{\partial S}\right|_{\mathbf{M}} = T$$

$$\left.\frac{\partial U'}{\partial \mathbf{M}}\right|_S = \mathbf{B} .$$

It results in the Maxwell relation

$$\left.\frac{\partial \mathbf{B}}{\partial S}\right|_{\mathbf{M}} = \left.\frac{\partial T}{\partial \mathbf{M}}\right|_S .$$

2.3 Paramagnetism of independent moments

We consider the situation, where the permanent magnetic moments of the atoms do not interact. Then the hamiltonian has the structure

$$H = \sum_i H^{(i)} \ .$$

where i enumerates the atoms. All atoms shall be the same, so all $H^{(i)}$ are the same. In the following we suppress the index i. The hamiltonian $H^{(i)}$ has the form

$$H^{(i)} = H_0 + \underbrace{\gamma(\mathbf{LS})}_{\text{spin-orbit coupling}} + \underbrace{\frac{\mu_B B}{\hbar}\left(J^z + S^z\right)}_{\text{Zeeman term}} \ . \tag{2.11}$$

Here $J^z = L_z + S^z$. w.l.o.g. we have assumed that $\mathbf{B} = B\mathbf{e}_z$. In addition we have used $g_e \approx 2$.
H_0 commutes with L^2, S^2, L^z, S^z. Which is also true for the total hamiltonian without spin-orbit coupling. For the calculation of the partition function we have, since there is no interaction between the atoms

$$Z^N = \left(Z^1\right)^N ,$$

i.e. it suffices to consider a single atom.

2.3.1 Weak spin-orbit coupling

In this case we ignore the spin-orbit term and the eigenvectors are given by

$$|\kappa, L, S, L_z, S_z\rangle \ ,$$

where γ covers all other quantum numbers. The corresponding eigenvalues are based on equation (2.11) with J^z replaced by $L^z + S^z$.

$$E(\kappa, L, S, L_z, S_z) = E_0(\kappa, L, S) + \frac{\mu_B B}{\hbar}\left(L_z + 2S_z\right) \ ,$$

The canonical partition function reads

$$Z = \prod_{i=1}^{N} Z^{(i)} = \left(Z^{(1)}\right)^N \tag{2.12}$$

$$Z^{(1)} = \sum_{\kappa, L, S, L_z, S_z} e^{-\beta E_0(\kappa, L, S) - \frac{\beta \mu_B B}{\hbar}(L_z + 2S_z)} \tag{2.13}$$

$$Z^{(1)} = \sum_{\kappa, L, S} e^{-\beta E_0(\kappa, L, S)} \sum_{L_z, S_z} e^{-\frac{\beta \mu_B B}{\hbar}(L_z + 2S_z)} \ . \tag{2.14}$$

Typically, the Zeeman splitting is small compared to the other energy differences, when changing κ, L, S. For moderate temperature we only need to consider the ground state quantum numbers (κ_0, L_0, S_0) (Hund's rule) and obtain (we use $L_z = \hbar l_z$ and $S_z = \hbar s_z$, with $l_z, s_z \in \mathbb{N}$)

$$Z^{(1)} = e^{-E_0(\kappa_0, L_0, S_0)} \underbrace{\sum_{l_z = -L_0}^{L_0} e^{-b L_z} \sum_{s_z = -S_0}^{S_0} e^{-2b S_z}}_{= \mathcal{Z}(L_0, S_0)}$$

Here $b = \beta B \mu_B$. If there is a gap between the ground state multiplet and the first excited one of ΔE, then the next to leading order contribution $((\kappa_1, L_1, S_1))$ is

$$Z^{(1)} = e^{-\beta E_0(\kappa_0, L_0, S_0)} \mathcal{Z}(L_0, S_0) + e^{-E_0(\kappa_1, L_1, S_1)} \mathcal{Z}(L_1, S_1)$$
$$= e^{-\beta E_0(\kappa_0, L_0, S_0)} \left(\mathcal{Z}(L_0, S_0) + e^{-\beta \Delta E} \mathcal{Z}(L_1, S_1) \right)$$

If $|\Delta E| \gg k_B T$ then we can neglect the higher order terms and

$$Z^{(1)} = e^{-\beta E_0(\kappa_0, L_0, S_0)} \mathcal{Z}(L_0, S_0) \tag{2.15}$$

The key elements are sums of the form

$$z_M(\eta) = \sum_{m=-M}^{M} e^{-\eta m} = e^{\eta M} \sum_{m=0}^{2M} e^{-\eta m} = e^{\eta M} \frac{1 - e^{-\eta(2M+1)}}{1 - e^{-\eta}}$$
$$= \frac{e^{\eta(M+1/2)} - e^{-\eta(M+1/2)}}{e^{\eta/2} - e^{-\eta/2}}$$
$$= \frac{\sinh(\eta(M+1/2))}{\sinh(\eta/2)}$$

Then we obtain immediately

$$\frac{F}{N} = -k_B T \ln(Z^1)$$
$$= E_0(\kappa_0, L_0, S_0) - k_B T \ln\left(z_{L_0}(b) \right) - k_B T \ln\left(z_{S_0}(2b) \right) .$$

Next we compute the magnetisation

$$\mathbf{M} = -\frac{\partial F}{\partial \mathbf{B}} \bigg|_T$$

Since $\mathbf{B} = \mathbf{e}_z$ we obtain

$$\mathbf{M} = -\mathbf{e}_z \frac{\partial F}{\partial B}\bigg|_T$$

E_0 is independent of the magnetic field. We need

$$\frac{\partial}{\partial B} z_M(\eta) = \frac{z'_M(\eta)}{z_M(\eta)} \frac{d\eta}{dB}$$

For the latter derivative we need

$$\frac{db}{dB} = \beta \mu_B$$
$$\frac{d(2b)}{dB} = 2\beta \mu_B \ .$$

Next we compute

$$z'_M(\eta) = \frac{d}{d\eta} \frac{\sinh(\eta(M + 1/2))}{\sinh(\eta/2)}$$
$$= (M + \frac{1}{2}) \frac{\cosh(\eta(M + 1/2))}{\sinh(\eta/2)} - \frac{1}{2} \frac{\sinh(\eta(M + 1/2)) \cosh(\eta/2)}{\sinh^2(\eta/2)} \ .$$

Then

$$\frac{z'_M(\eta)}{z_M(\eta)} = (M + \frac{1}{2}) \coth(\eta(M + 1/2)) - \frac{1}{2} \coth(\eta/2)$$
$$= M \left(\frac{2M+1}{2M} \coth(\frac{M\eta(2M+1)}{2M})) - \frac{1}{2M} \coth(\frac{M\eta}{2M}) \right) \ .$$

Finally we have

$$\frac{z'_M(\eta)}{z_M(\eta)} = M \, \mathcal{B}_M(M\eta) \ , \tag{2.16}$$

with

BRILLOUIN FUNCTION

$$\mathcal{B}_M(x) = \frac{2M+1}{2M} \coth(\frac{x(2M+1)}{2M})) - \frac{1}{2M} \coth(\frac{x}{2M}) \right) \qquad (2.17)$$

$$(2.18)$$

Then the final result reads

$$\frac{\mathbf{M}}{N} = \mathbf{e}_z \mu_B B \left(L_0 \mathcal{B}_{L_0}(bL_0) + 2S_0 \mathcal{B}_{S_0}(2bS_0) \right) . \tag{2.19}$$

Properties of the Brillouin function

For small or large arguments, $\coth(x)$ behave like

$$x \ll 1 : \qquad\qquad \coth(x) = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} O(x^5)$$

$$x \to \infty : \qquad\qquad \coth(x) \to 1 .$$

Hence, we have for $x \ll 1$ (MATHEMATICA)

$$\mathcal{B}_M(x) = \frac{M+1}{3M} x - \frac{2M^3 + 4M^2 + 3M + 1}{90M^3} x^3 . \tag{2.20}$$

And for $x \to \infty$

$$\mathcal{B}_M(x) \to \frac{2M+1}{2M} - \frac{1}{2M} = 1 .$$

In summary

$$\eta \ll 1 : \qquad\qquad \mathcal{B}_M(\eta) = \frac{M+1}{3M} \eta$$

$$\eta \to \pm\infty : \qquad\qquad \mathcal{B}_M(\eta) \to \pm 1 .$$

This yields for the magnetization in equation (2.19)

$$b \ll 1 : \qquad \frac{\mathbf{M}}{N} = \mathbf{e}_z \mu_B \left(L_0 \frac{L_0 + 1}{3L_0}(bL_0) + 2S_0 \frac{S_0 + 1}{3S_0}(2bS_0) \right)$$

$$= \mathbf{e}_z \frac{\mu_B^2 B}{3k_B T} \left(L_0(L_0 + 1) + 4S_0(S_0 + 1) \right)$$

The susceptibility then reads

<table>
<tr><td align="center">CURIE LAW</td></tr>
<tr><td align="center">$$\chi_{\mu\nu} = \delta_{\mu\nu} \frac{C}{T} , \tag{2.21}$$</td></tr>
</table>

with

$$C = \frac{\mu_0 \mu_B^2}{3k_B} \left(L_0(L_0 + 1) + 4S_0(S_0 + 1) \right)$$

We still need to consider the large b limit. Here we have

$$b \to \infty : \qquad \frac{\mathbf{M}}{N} \to \pm \mathbf{e}_z \mu_B \left(L_0 + 2S_0 \right) .$$

Brillouin function for $M = 1/2$ and $M = \infty$

An important special case is given for spin-1/2, then

$$
\begin{aligned}
\mathcal{B}_{1/2}(x) &= 2\coth(2x) - \coth(x) \\
&= \frac{2\left(e^{2x} + e^{-2x}\right)}{e^{2x} - e^{-2x}} - \frac{e^x + e^{-x}}{e^x - e^{-x}} \cdot \frac{e^x + e^{-x}}{e^x + e^{-x}} \\
&= \frac{2e^{2x} + 2e^{-2x} - e^{2x} - e^{-2x} - 2}{(e^x - e^{-x})(e^x + e^{-x})} \\
&= \frac{e^{2x} + e^{-2x} - 2}{(e^x - e^{-x})(e^x + e^{-x})} .
\end{aligned}
$$

So we finally have

$$\mathcal{B}_{1/2}(x) = \tanh(x) \qquad (2.22)$$

For large spin ($M \gg 1$) with $\varepsilon = 1/2M \ll 1$ find

$$
\begin{aligned}
\mathcal{B}_M(x) &= (1 + \varepsilon)\coth\left(x + \varepsilon x\right) - \varepsilon \coth(\varepsilon x) \\
&= \coth(x) + \mathcal{O}(\varepsilon) - \frac{\varepsilon}{\varepsilon x} + \mathcal{O}(\varepsilon)
\end{aligned}
$$

Hence

$$\mathcal{B}_{M \to \infty}(x) = \coth(x) - \frac{1}{x} : \qquad (2.23a)$$

This is the classical limit.

2.3.2 Strong spin-orbit coupling

To avoid confusion we mark operators by hats. If the spin-orbit coupling is strong compared to the magnetic field, then we cannot ignore the spin-orbit term. In this case, H still commutes with L and S, but no longer with

Figure 2.1: .

L^z and S^z. Instead, based on the relations

$$\hat{J} = \hat{L} + \hat{S} \tag{2.24}$$

$$\hat{L}\hat{S} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right), \tag{2.25}$$

H now commutes with L^2, S^2, J^2, J_z. The eigenvectors are therefore

$$|\kappa, L, S, J, J_z\rangle .$$

The corresponding eigenvalues are given by equation (2.11) [p. 59] as

$$E(\kappa, L, S, J, J_z) = E_0(\kappa, L, S) + \frac{B\mu_B}{\hbar}\left(J_z - \langle \hat{S}^z \rangle\right) .$$

Here $\langle \hat{S}^z \rangle$ is the expectation value of of $\hat{S}^z$ in one of the eigenstates $|\kappa, L, S, J, J_z\rangle$, while J_z is already the eigenvalue of the operator $\hat{J}^z$. The computation of the expectation value $\langle \hat{S}_z \rangle$ yields eventually

$$E(\kappa, L, S, J, J_z = E_0(\kappa, L, S) + \frac{\mu_B B}{\hbar}\underbrace{\left(1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right)}_{=g_J} J_z$$

$$= E_0(\kappa, L, S) + \mu_B B g_J m ,$$

with $J_z = \hbar m$ and $m \in \{-J, -J+1, \ldots, J\}$

To compute the expectation value we proceed as follows. We start out with the identity

$$\hat{S}\left(\hat{L} \cdot \hat{S}\right) - \left(\hat{L} \cdot \hat{S}\right)\hat{S} = -i\hbar \hat{S} \times \hat{L} . \tag{2.26}$$

which follows from

$$\hat{S}_\nu \hat{L}_\mu S_\mu - \hat{L}_\mu \hat{S}_\mu \hat{S}_\nu = \hat{S}_\nu \hat{S}_\mu \hat{L}_\mu - \hat{S}_\mu \hat{S}_\nu \hat{L}_\mu = [\hat{S}_\nu, \hat{S}_\mu] \hat{L}_\mu$$
$$= i\hbar \varepsilon_{\nu\mu\rho} \hat{S}_\rho \hat{L}_\mu = -i\hbar \varepsilon_{\nu\rho\mu} \hat{S}_\rho \hat{L}_\mu$$
$$= -i\hbar (\hat{S} \times \hat{L})_\nu$$

. Next we multiply equation (2.26) with $\times \hat{J}$ and obtain

$$\hat{S}\left(\hat{L} \cdot \hat{S}\right) \times \hat{J} - \left(\hat{L} \cdot \hat{S}\right)\hat{S} \times \hat{J} = -i\hbar (\hat{S} \times \hat{L}) \times \hat{J} \tag{2.27}$$

Now, $(\hat{L} \cdot \hat{S})$ commutes with all components of the vector operator $\hat{J}$, since according to equation (2.27) $\hat{L} \cdot \hat{S}$ is given by $\frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$ which can be seen as follows

$$[\hat{L} \cdot \hat{S}, J^\alpha] = \frac{1}{2}\left(\underbrace{[J^2, J^\alpha]}_{=0} - [L^2, J^\alpha] - [S^2, J^a]\right)$$
$$= -\frac{1}{2}\left([L^2, L^\alpha + S^\alpha] + [S^2, L^a + S^\alpha]\right)$$
$$= -\frac{1}{2}\left([L^2, L^\alpha] + [S^2, S^\alpha]\right)$$
$$= 0 .$$

Then we can move $\hat{L} \cdot \hat{S}$ in the first term of equation (2.27) to the right of $\hat{J}$, resulting in

$$(\hat{S} \times \hat{J})\left(\hat{L} \cdot \hat{S}\right) - \left(\hat{L} \cdot \hat{S}\right)(\hat{S} \times \hat{J}) = -i\hbar (\hat{S} \times \hat{L}) \times \hat{J}$$

If we now compute expectation values in the eigenvectors $|\kappa, L, S, J, J_z\rangle$, we can replace the operators $(\hat{L} \cdot \hat{S})$ by the eigenvalues $\frac{1}{2}(J(J+1) - L(L+1) - S(S+1))$ and the remaining expectation value on the left hand side is zero. Hence, we obtain from the right hand side

$$\langle (\hat{S} \times \hat{L}) \times \hat{J} \rangle = 0 , \tag{2.28}$$

which is valid in the eigenstates. From

$$
\begin{aligned}
\left[\left(\hat{\boldsymbol{S}}\times\hat{\boldsymbol{L}}\right)\times\hat{\boldsymbol{J}}\right]_i &= \varepsilon_{ijk}\left(\hat{\boldsymbol{S}}\times\hat{\boldsymbol{L}}\right)_j\hat{J}_k \\
&= \varepsilon_{ijk}\varepsilon_{jmn}\hat{S}_m\hat{L}_n\hat{J}_k \\
&= \varepsilon_{jki}\varepsilon_{jmn}\hat{S}_m\hat{L}_n\hat{J}_k \\
&= \left(\delta_{km}\delta_{in}-\delta_{kn}\delta_{im}\right)\hat{S}_m\hat{L}_n\hat{J}_k \\
&= \hat{S}_k\hat{L}_i\hat{J}_k - \hat{S}_i\hat{L}_k\hat{J}_k \\
&= \hat{L}_i\hat{S}_k\hat{J}_k - \hat{S}_i\hat{L}_k\hat{J}_k \ .
\end{aligned}
$$

we obtain for the double vector product

$$
\begin{aligned}
\left(\hat{\boldsymbol{S}}\times\hat{\boldsymbol{L}}\right)\times\hat{\boldsymbol{J}} &= \hat{\boldsymbol{L}}\left(\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}\right) - \hat{\boldsymbol{S}}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{J}}\right) \\
&= \left(\hat{\boldsymbol{J}}-\hat{\boldsymbol{S}}\right)\left(\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}\right) - \hat{\boldsymbol{S}}\left(\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{J}}\right) \\
&= \hat{\boldsymbol{J}}\left(\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}\right) - \hat{\boldsymbol{S}}\left(\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\hat{\boldsymbol{J}}\right) \\
&= \hat{\boldsymbol{J}}\left(\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}\right) - \hat{\boldsymbol{S}}\,\hat{\boldsymbol{J}}^2 \ .
\end{aligned}
$$

From equation (2.28) we therefore obtain

$$
\left(\hat{\boldsymbol{S}}\times\hat{\boldsymbol{L}}\right)\times\hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}\left(\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}\right) - \hat{\boldsymbol{S}}\,\hat{\boldsymbol{J}}^2 = 0 \ .
$$

and for the expectation value in the eigenstates $|\kappa, L, S, J, J^z\rangle$ we have

$$
\left\langle \hat{J}_z\left(\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}\right)\right\rangle - \left\langle \hat{S}_z\,J^2\right\rangle = 0 \ .
$$

Next we use

$$
\begin{aligned}
\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}} &= \hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}} + \hat{S}^2 \\
&= \frac{1}{2}\left(\hat{J}^2 - \hat{S}^2 - \hat{L}^2\right) + \hat{S}^2 \\
&= \frac{1}{2}\left(\hat{J}^2 + \hat{S}^2 - \hat{L}^2\right) \ .
\end{aligned}
$$

and obtain

$$
J_z\,\frac{1}{2}\left\langle \hat{J}^2 + \hat{S}^2 - \hat{L}^2\right\rangle - \left\langle \hat{S}_z\,J(J+1)\right\rangle = 0
$$

$$
J_z\,\frac{1}{2}\left(J(J+1) + S(S+1) - L(L+1)\right) - \left\langle \hat{S}_z\right\rangle\,J(J+1) = 0 \ .
$$

The expectation value $\langle S_z\rangle$ in the eigenstates $|\kappa, L, S, J, J^z\rangle$ is therefore:

$$
\langle S_z\rangle = J_z\,\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \ .
$$

Hence, the eigenvalues are

$$E(\kappa, L, S, J, J_z) = E_0(\kappa, L, S) + \frac{\mu_B B}{\hbar} \underbrace{\left(1 + \frac{1}{2}[J(J+1) + S(S+1) - L(L+1)] \right)}_{=g_J} J_z .$$

q.e.d. ✓

The remaining calculation is similar to the previous one and one obtains

$$\frac{F}{N} = E_0 - k_B T \ln \left(z_J(b) \right)$$

with $b = g_J \mu_B \beta B$. Then

$$\hat{M} = \mathbf{e}_z N J g_J \mu_B B \, \mathcal{B}_J(bJ) .$$

For high T and small B, the susceptibility yields

<table>
<tr><td align="center">CURIE LAW</td><td></td></tr>
</table>

$$\chi_{\mu\nu} = \delta_{\mu\nu} \frac{C}{T} . \tag{2.29}$$

with

$$C = \frac{N \mu_0 \mu_B^2 g_J^2 J(J+1)}{3 k_B} ,$$

and for large b we have

$$\frac{\mathbf{M}}{N} \xrightarrow[b \to \infty]{} \pm \mathbf{e}_z g_J \mu_B J .$$

Plot of the Brillouin function

Entropy

For the entropy we obtain

$$\frac{S}{N} = -\left.\frac{\partial F/N}{\partial T}\right|_{\mathbf{B}} = k_B \ln\left(z_J(b)\right) + k_B T \frac{z_J'(b)}{z_J(b)}\frac{db}{dT}$$

$$\frac{db}{dT} = -g_J\mu_B B \frac{1}{k_B T^2} = -\beta^2 g_J\mu_B B = -\beta b \ .$$

$$S = k_B\left(\ln\left(z_J(b)\right) - b\frac{z_J'(b)}{z_J(b)}\right)$$

Along with equation (2.16) we obtain

$$\frac{S}{N} = k_B\left(\ln\left(\frac{\sinh(b(J+1/2))}{\sinh(b/2)}\right) - bJ\mathcal{B}_J(bJ)\right)\ .$$

For $b \ll 1$ (i.e. $T \to \infty$) we find

$$\frac{S}{N} = k_B\left(\ln\left(\frac{b(J+1/2)}{b/2}\right) - (bJ)^2\frac{J+1}{3J}\right)$$
$$= k_B \ln\left(2J+1\right)\ .$$

The argument is the number of eigenvalues of J_z.

2.3.3   Plot of S and specific heat

2.4 Magnetism of the free electron model

The free electron gas is based on the following assumptions: no electron-electron interactions, the electrons experience no potential due to the crystal, they are confined to a box. In addition, we apply a constant homogeneous external magnetic field.

2.4.1 Pauli paramagnetism

First, we restrict the discussion to the coupling of the electronic spin to the magnetic field, i.e. we ignore the angular moment. The energy one-particle eigenvalues are

$$\varepsilon_\sigma(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} + \sigma b \; ,$$

$$b = \frac{\mu_B g_e}{2} B \; .$$

with the quantized wave vectors $\mathbf{k}$. The mean occupation of the one-particle orbitals is given by the Fermi-Dirac distribution

$$n_F(\varepsilon_\sigma(\mathbf{k})|T, \mu)$$

The mean total number of electrons in the Zeeman level represented by σ is

$$N_\sigma = \sum_{\mathbf{k}} n_F(\varepsilon_\sigma(\mathbf{k})|T, \mu) = \int d\varepsilon \rho(\varepsilon) n_F(\varepsilon + \sigma b|T, \mu) \; .$$

As derived in appendix (4.3) the 3D dos is

$$\rho(\varepsilon) = D\sqrt{\varepsilon} \; , \tag{2.30a}$$

$$\text{with} \quad D = \frac{V m^{3/2}}{\hbar^3 \pi^2 \sqrt{2}} \; . \tag{2.30b}$$

Then

$$N_\sigma = D \int_0^\infty d\varepsilon \sqrt{\varepsilon} \, n_F(\varepsilon + \sigma b|T, \mu) \; .$$

For small magnetic field we can use a Taylor expansion in b abound $b = 0$

$$N_\sigma = D \int_0^\infty d\varepsilon \sqrt{\varepsilon} \left(n_F(\varepsilon|T, \mu) + \sigma b \frac{\partial}{\partial \varepsilon} n_F(\varepsilon|T, \mu) + \mathcal{O}(b^2) \right)$$

$$= D \int_0^\infty d\varepsilon \sqrt{\varepsilon} \, n_F(\varepsilon|T, \mu) + \sigma b D \int_0^\infty d\varepsilon \sqrt{\varepsilon} \, n_F'(\varepsilon|T, \mu) + \mathcal{O}(b^2)$$

The total particle number follows as

$$N = N_+ + N_- = 2D \int_0^\infty d\varepsilon \sqrt{\varepsilon} \, n_F(\varepsilon|T,\mu) + \mathcal{O}(b^2)$$

$$= 2D \int_0^\infty d\varepsilon \sqrt{\varepsilon} \, n_F(\varepsilon|T,\mu) + \mathcal{O}(b^2) \,. \tag{2.31}$$

For small b and low temperature we can use the Sommerfeld expansion, outlined in appendix (4.1),

---
SOMMERFELD EXPANSION

$$I = \int_0^\infty f(\varepsilon) n_F(\varepsilon|\mu,T) d\varepsilon$$

$$= \int_0^\mu f(\varepsilon) d\varepsilon + 2 \sum_{n=1}^{\text{odd}} \left(1 - \frac{1}{2^n}\right) \zeta(n+1) \left(k_B T\right)^{n+1} f^{(n)}(\mu) \,, \tag{2.32}$$

---

which reads to leading order

$$I = \int_0^\mu f(\varepsilon) d\varepsilon + \frac{\pi^2}{6} \left(k_B T\right)^2 f'(\mu) + \mathcal{O}((\frac{k_B T}{\mu})^4) \,.$$

For the total particle number we obtain

$$N = 2D \left(\int_0^\mu \sqrt{\varepsilon} + \frac{\pi^2}{6} \frac{d}{d\mu} \sqrt{\mu} \left(k_B T\right)^2 + \dots \right)$$

$$= 2D \left(\frac{2}{3} \mu^{3/2} + \frac{\pi^2}{12} \mu^{-1/2} (k_B T)^2 + \dots \right) \,.$$

$$\frac{3N}{4D} = \mu^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2 + \dots \right) \tag{2.33}$$

For $T = 0$ the chemical potential is equivalent to the Fermi energy ε_F and we have

$$\frac{3N}{4D} = \varepsilon_F^{3/2} \,, \tag{2.34}$$

or rather

$$\varepsilon_F = \left(\frac{3N\hbar^3(2\pi)^2}{4V(2m)^{3/2}}\right)^{2/3} = \left(\frac{3N\pi^2}{V}\right)^{2/3}\frac{\hbar^2}{2m}.$$

FERMI ENERGY IN THE FREE ELECTRON GAS

$$\varepsilon_F = \left(3\pi^2 n\right)^{2/3}\frac{\hbar^2}{2m}. \tag{2.35}$$

This defines the Fermi wave number k_F, through

$$\varepsilon_F = \left(3\pi^2 n\right)^{2/3}\frac{\hbar^2}{2m} = \frac{\hbar^2 k_F^2}{2m}$$

$$k_F = \left(3\pi^2 n\right)^{1/3} = \left(\frac{3\pi^2}{v}\right)^{1/3},$$

where v is the average volume per electron. Hence

$$k_F \propto \frac{1}{r},$$

where r is the mean distance between the electrons. Inserting equation (2.34) in equation (2.33) yields apart from higher order terms

$$\varepsilon_F = \mu\left(1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right)^{2/3}$$

$$\mu = \varepsilon_F\left(1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right)^{-2/3}.$$

We can solve this equation iteratively, starting with $\mu = \varepsilon_F$. The first iteration yields

$$\mu = \varepsilon_F\left(1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right)^{-2/3}.$$

For low temperatures, $\frac{k_B T}{\varepsilon_F} < 1$ we can as well write

$$\mu = \varepsilon_F \left(1 - \frac{\pi^2}{8} \frac{2}{3} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \mathcal{O}\left(\left(\frac{k_B T}{\varepsilon_F} \right)^4 \right) \right) .$$

Further iterations do not change the second order term and we generally have

---

CHEMICAL POTENTIAL
(*free electron gas*)

$$\mu = \varepsilon_F \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right) + \mathcal{O}\left(\left(\frac{k_B T}{\varepsilon_F} \right)^4 \right) \qquad (2.36)$$

The partition function for non-interacting particles has already been derived previously. For one-particle energies ε_ν it was

$$\ln(Z) = \sum_\nu \ln \left(1 + e^{-\beta(\varepsilon_\nu - \mu)} \right) .$$

In the present case the index ν stands for the wave vector $\mathbf{k}$ and the spin direction. Hence

$$\ln(Z) = \sum_\sigma \int_0^\infty \rho(\varepsilon) \, \ln \left(1 + e^{-\beta(\varepsilon + \sigma b - \mu)} \right) . \qquad (2.37)$$

The corresponding grand potential reads

$$\Omega(T, \mathbf{B}) = -k_B T \ln(Z) = -k_B T \sum_\sigma \int_0^\infty \rho(\varepsilon) \, \ln \left(1 + e^{-\beta(\varepsilon + \sigma b - \mu)} \right) .$$

The magnetization in z-direction is obtain via

$$M = -\frac{\partial \Omega}{\partial B} \bigg|_T$$

$$= k_B T \sum_\sigma \left(-\frac{\beta \sigma \mu_B g_e}{2} \right) \int_0^\infty d\varepsilon \, \rho(\varepsilon) \, \frac{e^{-\beta(\varepsilon + \sigma b - \mu)}}{1 + e^{-\beta(\varepsilon + \sigma b - \mu)}}$$

$$= -\frac{\mu_B g_e}{2} \sum_\sigma \sigma \int_0^\infty d\varepsilon \, \rho(\varepsilon) \, n_F(\varepsilon + \sigma b | T, \mu)$$

$$= -\frac{\mu_B g_e}{\hbar} \underbrace{\frac{\hbar(N_+ - N_-)}{2}}_{= \langle S^z_{\text{total}} \rangle}$$

In agreement with equation (2.2) [p. 52]. Again we assume that b is small and employ a Taylor expansion.

$$
\begin{aligned}
M &= -\frac{\mu_B g_e}{2} \sum_\sigma \sigma \int_0^\infty d\varepsilon \left(\rho(\varepsilon) n_F(\varepsilon|T,\mu) + \sigma b n_F'(\varepsilon|T,\mu) + O(b^2) \right) \\
&= -\frac{\mu_B g_e}{2} 2b \int_0^\infty d\varepsilon \rho(\varepsilon) n_F'(\varepsilon|T,\mu) + O(b^2) \\
&= -\frac{(\mu_B g_e)^2}{2} B \int_0^\infty d\varepsilon \rho(\varepsilon) n_F'(\varepsilon|T,\mu) + O(b^2) .
\end{aligned}
$$

Then the susceptibility reads

$$
\begin{aligned}
\chi_T &= \mu_0 \frac{\partial M}{\partial B}\bigg|_T\bigg|_{B=0} \\
&= -\mu_0 \frac{(\mu_B g_e)^2}{2} \int_0^\infty d\varepsilon \rho(\varepsilon) n_F'(\varepsilon|T,\mu) .
\end{aligned}
$$

This can also be written as

$$
\begin{aligned}
\chi_T &= -\mu_0 \mu_B^2 \left(\frac{g_e}{2}\right)^2 2 \int d\varepsilon \rho(\varepsilon) n_F'(\varepsilon|T,\mu) \\
&= \mu_0 \mu_B^2 \left(\frac{g_e}{2}\right)^2 2 \frac{\partial}{\partial\mu} \int d\varepsilon \rho(\varepsilon) n_F(\varepsilon|T,\mu) .
\end{aligned}
$$

Comparison with equation (2.31) [p. 70] yields

$$
\chi_T = \mu_0 \mu_B^2 \left(\frac{g_e}{2}\right)^2 \frac{\partial N}{\partial\mu}\bigg|_{T,B=0} \tag{2.38}
$$

We use the Sommerfeld expansion, derived in appendix (4.1) to expand the integral in powers of $k_B T/\mu$.

$$
\begin{aligned}
\chi &= -\mu_0 \frac{(\mu_B g_e)^2}{2} \int_0^\infty d\varepsilon \rho(\varepsilon) n_F'(\varepsilon|T,\mu) \\
&= \mu_0 \frac{(\mu_B g_e)^2}{2} \int_0^\infty d\varepsilon \rho'(\varepsilon) n_F(\varepsilon|T,\mu) \\
&= \mu_0 \frac{(\mu_B g_e)^2}{2} \left(\int_0^\mu d\varepsilon \rho'(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \rho''(\mu) + \mathcal{O}\left(\left(\frac{k_B T}{\mu}\right)^4\right) \right) \\
&= \mu_0 \frac{(\mu_B g_e)^2}{2} \left(\rho(\mu) + \frac{\pi^2}{6}(k_B T)^2 \rho''(\mu) + \mathcal{O}\left(\left(\frac{k_B T}{\mu}\right)^4\right) \right) .
\end{aligned}
$$

The final result reads

$$\chi = \mu_0 \frac{(\mu_B g_e)^2}{2} \rho(\mu) \left(1 + \frac{\pi^2}{6}(k_B T)^2 \frac{\rho''(\mu)}{\rho(\mu)} + \dots \right) \qquad (2.39)$$

Now we recall, that $\rho(\varepsilon) = D\sqrt{\varepsilon}$, resulting in $\rho''(\mu)/\rho(\mu) = -1/(4\mu^2)$.

MAGNETIC SUSCEPTIBILITY
(*free electron gas*)

$$\chi_P = \mu_0 \frac{(\mu_B g_e)^2}{2} \rho(\mu) \left(1 - \frac{\pi^2}{24}\left(\frac{k_B T}{\mu} \right)^2 + \dots \right). \qquad (2.40)$$

We see that indeed $k_B T/\mu$ is the relevant small parameter. This describes the Pauli-spin-paramagnetism, which is almost temperature independent for low T; in strong contrast to the Curie $1/T$ behaviour. The reason for the discrepancy lies in the fermi-statistics. Only the spin of the electrons in the vicinity of μ can contribute. The number of thermally excited electrons is $k_b T \rho(\mu)$ which compensates the $1/T$ behaviour.

2.4.2 Langevin Diamagnetismus

So far we have only considered the spin degrees of freedom of the free electron gas. The orbital moments also contribute to the magnetization, which results in the

---

LANDAU DIAMAGNETISM
(*free electron gas*)

$$\chi_L = -\frac{1}{3}\chi_P \qquad (2.41)$$

For the derivation see appendix **??**

2.5 Collective magnetism

2.5.1 Heisenberg hamiltonian

In many crystaline systems, the electrons can be split into those that are localized at the atomic sites and others which can move freely through the crystal. The former result in localized magnetic moments or spins $\mathbf{S}_i$, if they do not belong to closed shells. We have discussed these local spins $\mathbf{S}_i$ before, but there we have focussed on systems where these spins do not interact. The Coulomb interaction between the electrons can lead to various types of exchange interactions between these spins. The exchange can either result from exchange processes of the electrons that form the local spins on neighboring sites *direct exchange* or it can be mediated by additional electrons *indirect exchange*. In the latter case, the interaction can be long ranged, like in the case of the so-called *RKKY* (Ruderman-Kittel-Kasuya-Yosida). In RKKY the interaction decays like $1/|\mathbf{R}_i - \mathbf{R}_j|^3$ with the distance between the spins at site $\mathbf{R}_i$ and $\mathbf{R}_j$. In addition, the exchange interaction changes sign as function of distance, i.e. depending on the distance between the localized spins it can be ferromagnetic and anti-ferromagnetic. In all cases, the interaction can be described by a prominent model for collective magnetism, the

---

<div style="border:1px solid black; padding:10px;">

HEISENBERG MODEL

$$H = -\sum_{jj'} \left(J_{jj'}^z S_j^z S_{j'}^z + J_{jj'}^{xy} \left(S_j^x S_{j'}^x + S_j^y S_{j'}^y \right) \right) + b \sum_j S_j^z \; . \qquad (2.42)$$

</div>

Here $J_{jj'} = J((\mathbf{R}_j - \mathbf{R}_{j'}))$, with $J_{jj} = 0$. $J_{jj'}$ can always be chosen symmetric, since by substituting $j \leftrightarrow j'$ we find

$$H_H = -\sum_\alpha \sum_{jj'} J_{jj'} S_j^\alpha S_{j'}^\alpha = -\sum_\alpha \sum_{jj'} J_{j'j} S_{j'}^\alpha S_j^\alpha = -\sum_\alpha \sum_{jj'} J_{j'j} S_j^\alpha S_{j'}^\alpha$$

Hence

$$H = \frac{1}{2}\left(-\sum_\alpha \sum_{jj'} J_{jj'} S_j^\alpha S_{j'}^\alpha + -\sum_\alpha \sum_{jj'} J_{j'j} S_j^\alpha S_{j'}^\alpha \right) = -\sum_\alpha \sum_{jj'} \left(\frac{J_{jj'} + J_{j'j}}{2}\right) S_j^\alpha S_{j'}^\alpha \; .$$

We also introduce the ladder operators

$$S_j^\pm = S_j^x \pm i S_j^y \; . \qquad (2.43)$$

In these operators, the hamiltonian reads

$$H = -\sum_{jj'} \left(J_{jj'}^z S_j^z S_{j'}^z + J_{jj'}^{xy} S_j^+ S_{j'}^- \right) + b \sum_j S_j^z \ .$$

The order of the operators $S_j^+ S_{j'}^-$ is irrelevant, since $j \neq j'$ and in that case they commute. There are three important limiting cases depending on the anisotropy of the crystal in spin-space.

- $(|J^z| \ll |J^{xy}|)$ results in the so-called *xy- model*

XY-MODEL

$$H = -\sum_{jj'} J_{jj'}^{xy} S_j^+ S_{j'}^- + b \sum_j S_j^z \ . \tag{2.44}$$

- $(|J^z| \gg |J^{xy}|)$ results in the so-called *Ising model*, which is discussed in great detail chapter chapter (1) [page 4]

- $(J^z = J^{xy})$ represents the isotropic Heisenberg model

HEISENBERG MODEL
(isotropic case)

$$H = -\sum_{jj'} J_{jj'} \mathbf{S}_j \mathbf{S}_{j'} + b \sum_j S_j^z \ . \tag{2.45}$$

Very often the exchange coupling $J_{jj'} = J(|\mathbf{R}_j - \mathbf{R}_{j'}|)$ decreases very rapidly with distance and it suffices to take only nearest neighbour (nn) interactions into account, i.e.

$$-\sum_{jj'} J_{jj'} \approx -J \sum_{\langle jj' \rangle} \ . \tag{2.46}$$

In general, J can be positive or negative. In the first (second) case, ferromagnetic (anti-ferromagnetic) spin alignment is favoured. If the exchange coupling between localized spins is mediated by itinerant electrons, the so-called *RKKY-interaction* (Ruderman-Kittel-Kasuya-Yosida) results, which is long ranged and oscillating as function of distance, i.e. depending on the distance between the localized spins it can be ferromagnetic and anti-ferromagnetic.

2.5.2 Mermin-Wagner Theorem

There are only a few exact results available for the Heisenberg model. Presumably the most important one is due to Mermin and Wagner and states:
In one and two dimensions, continuous symmetries cannot be broken spontaneously at finite temperature in systems with sufficiently short-ranged interactions.
We add an external field

$$\mathbf{B}_j = b\mathbf{e}_z e^{i\mathbf{Q}\mathbf{R}_j} ,$$

to the isotrop ferromagnetic Heisenberg model. This B-field couples to different types of magnetic order (e.g. ferro, anti-ferro), depending on the choice of the wave vector $\mathbf{Q}$. We consider the order parameter

$$\mathcal{S}_{\mathbf{Q}}(T,b) = \frac{1}{\hbar N}\langle \mathbf{S}_{\mathbf{Q}}^z \rangle_{T,b} . \tag{2.47}$$

The operator $S_{\mathbf{Q}}^z$ stands for the Fourier transform of S_j^z, defined in equation **(??)** [p. **??**].
After a straightforward but tedious calculation, which can be found in appendix **??**, the result reads

$$1D) \qquad |\mathcal{S}_{\mathbf{Q}}(T,b)| \leq \left(\frac{|b|}{T^2}\right)^{1/3} \qquad\qquad \xrightarrow[b\to 0]{} 0 \qquad (2.48a)$$

$$2D) \qquad |\mathcal{S}_{\mathbf{Q}}(T,b)| \leq \frac{const}{\sqrt{T|\ln(|b|)|}} \qquad\qquad \xrightarrow[b\to 0]{} 0 \qquad (2.48b)$$

$$3D) \qquad |\mathcal{S}_{\mathbf{Q}}(T,b)| \leq \frac{const}{\sqrt{T}} \qquad\qquad\qquad\qquad (2.48c)$$

For finite T the rhs in 1D 2D goes to zero for vanishing field ($b \to 0$). Hence there is no finite order parameter possible, irrespective of the wve vector $\mathbf{Q}$ (order). For 3D, however, the Mermin-Wagner theorem does not rule out spontaneous magnetization for finite T.

2.5.3 Exact ground-state of the ferromagnetic Heisenberg model

Here we consider only the homogeneous ferromagnetic ($J_{jj'} > 0$) Heisenberg model with a homogenous magnetic field pointing in the z-direction. We readily see that the ground state is given by the state, where all spins are maximally aligned in the negative z-direction

$$|0\rangle = \otimes_{j=1}^{N} |-S\rangle_j \tag{2.49}$$

with

$$S_j^z |m\rangle_j = \hbar m |m\rangle_j \tag{2.50a}$$
$$S_j^2 |m\rangle_j = \hbar^2 S(S+1) |m\rangle_j \ . \tag{2.50b}$$

Applying the hamiltonian to $|0\rangle$ yields

$$H|0\rangle = -\sum_{jj'} J_{jj'} S_j^z S_{j'}^z |0\rangle - \sum_{jj'} J_{jj'} S_j^+ \underbrace{S_{j'}^- |0\rangle}_{=0} \bigg) + b \sum_j S_j^z |0\rangle$$

$$= -\sum_{jj'} J_{jj'} \hbar^2 S^2 |0\rangle - b \sum_j \hbar S |0\rangle$$

$$= -\hbar \left(N \sum_l J(|\mathbf{R}_l|) \hbar S^2 + b \sum_j S \right) |0\rangle$$

$$= -\hbar N \left(\hbar \tilde{J}(0) S^2 + bS \right) |0\rangle$$

$$\tilde{J}(0) = \sum_l J(|\mathbf{R}_l|) \ .$$

We have introduced the Fourier transform of the exchange coupling.

$$\tilde{J}(\mathbf{k}) = \sum_l J(|\mathbf{R}_l|) e^{i\mathbf{k}\mathbf{R}_l} \ . \tag{2.51}$$

Obviously, $|0\rangle$ is an eigenvector. We consider

$$\left(\mathbf{S}_j + \mathbf{S}_j \right)^2 = \mathbf{S}_j^2 + \mathbf{S}_{j'}^2 + 2\mathbf{S}_j \mathbf{S}_{j'}$$

$$-\mathbf{S}_j \mathbf{S}_{j'} = \frac{1}{2} (\mathbf{S}_j^2 + \mathbf{S}_{j'}^2) - \frac{1}{2} (\mathbf{S}_j + \mathbf{S}_j)^2$$

All spins have magnitude S. We consider an arbitrary vector $|\psi\rangle$, which is an eigenstate of all $\mathbf{S}_j^2$ with eigenvalue $S(S+1)$ but otherwise arbitrary. Then

$$-\langle \mathbf{S}_j \rangle \mathbf{S}_{j'} = S(S+1) - \frac{1}{2} \left\langle (\mathbf{S}_j + \mathbf{S}_j)^2 \right\rangle$$

Now $\mathbf{S}' := \mathbf{S}_j + \mathbf{S}_j$ is an effective spin where the eigenvalues of $\mathbf{S}'^2$ are given bei $S'(S'+1)$ with $S' \in \hbar\{0, 1, \ldots, 2S\}$. Consequently,

$$\frac{1}{2}\left\langle (\mathbf{S}_j + \mathbf{S}_j)^2 \right\rangle \leq 2S(2S+1) \ .$$

Then

$$-\langle \mathbf{S}_j \rangle \mathbf{S}_{j'} \geq S(S+1)S(2S+1) = S^2$$

Finally that means if $J_{jj'} \geq 0 \forall j, j'$

$$\langle H_0 \rangle = \sum_{jj'} J_{jj'}\left(-\langle \mathbf{S}_j \rangle \mathbf{S}_{j'} \right)$$

$$\geq -S^2\hbar^2 \sum_{jj'} J_{jj'}$$

$$\langle H_0 \rangle \geq -N\hbar^2 \tilde{J}(0) \ .$$

For the Zeeman term we see readily

$$\langle H_Z \rangle \geq -bS\hbar$$

Hence in total we have for the energy

$$E \geq -N\hbar^2 \tilde{J}(0) - bS\hbar = E_0$$

Since there is no energy lower than the ferromagnetic state, it is the groundstate. Moreover, we see that

$$S_{total}^z = \sum_j \mathbf{S}_j^z |0\rangle = \hbar N S |0\rangle \ .$$

The groundstate is an eigenstate of S_{total}^z and also of

$$\mathbf{S}_{total}^2 = \sum_{j \neq j'} \mathbf{S}_j \mathbf{S}_{j'} + \sum_j \mathbf{S}_j^2$$

$$\mathbf{S}_{total}^2 |0\rangle = \sum_{j \neq j'} \mathbf{S}_j \mathbf{S}_{j'} \mathbf{S}_{total}^2 |0\rangle + N\hbar^2 S(S+1)|0\rangle$$

$$\mathbf{S}_{total}^2 |0\rangle = \sum_{j \neq j'} \hbar^2 S^2 |0\rangle + \underbrace{S_j^+ S_{j'}^- |0\rangle}_{=0} + NS(S+1)\hbar^2|0\rangle$$

$$= \left(N(N-1)\hbar^2 S^2 + NS(S+1)\hbar^2 \right)|0\rangle$$

$$= \hbar^2 \left(N^2 S^2 - \cancel{NS^2} + \cancel{NS^2} + NS \right)|0\rangle$$

$$= \hbar^2 \, NS(NS+1)|0\rangle$$

So it $|0\rangle$ an eigenstate of $\mathbf{S}_{total}$ with maximum magnitude $NS\hbar$.

2.5.4   Spin waves in the ferromagnetic Heisenberg model

Next we study the low-laying excited states. To this end we first consider the hamiltonian in Fourier space. The details of the Fourier transform as introduced in equation (**??**) [p. **??**] are

$$S_k^\alpha = \sum_j S_j^\alpha e^{i\mathbf{k}\mathbf{R}_j} \,, \qquad \alpha \in \{x, y, z\} \tag{2.52a}$$

$$S_j^\alpha = \frac{1}{N} \sum_k^{1.Bz} S_k^\alpha e^{-i\mathbf{k}\mathbf{R}_j} \tag{2.52b}$$

We recall the commutation relations

$$\left[S_j^\alpha S_{j'}^\beta\right] = \delta_{jj'} i\hbar \varepsilon_{\alpha\beta\gamma} S_j^\gamma \,, \tag{2.53a}$$

$$\left[S_j^z S_{j'}^\pm\right] = \pm \delta_{jj'} \hbar S_j^\pm \,, \tag{2.53b}$$

$$\left[S_j^-, S_{j'}^+\right] = -2\hbar \delta_{jj'} S_j^z \,, \tag{2.53c}$$

$$\left[S_j^+, S_{j'}^+\right] = 0 \,. \tag{2.53d}$$

Then

$$\left[S_{\mathbf{k}}^z S_{\mathbf{k'}}^\pm\right] = \pm \hbar S_{\mathbf{k}+\mathbf{k'}}^\pm \,, \tag{2.54a}$$

$$\left[S_{\mathbf{k}}^-, S_{\mathbf{k'}}^+\right] = -2\hbar S_{\mathbf{k}+\mathbf{k'}}^z \,, \tag{2.54b}$$

$$\left[S_j^+, S_{j'}^+\right] = 0 \,. \tag{2.54c}$$

Proof

$$\left[S_j^z S_{j'}^\pm\right] = \left[S_j^z S_{j'}^x\right] \pm i\left[S_j^z S_{j'}^y\right]$$

$$= \delta_{jj'} i\hbar \left(\varepsilon_{zxy} S_j^y \pm i\varepsilon_{zyx} S_j^x \right.$$

$$= \delta_{jj'} \hbar \left(i \underbrace{\varepsilon_{zxy}}_{=+1} S_j^y \mp \underbrace{\varepsilon_{zyx}}_{=-1} S_j^x \right)$$

$$= \delta_{jj'} \hbar \left(iS_j^y \pm S_j^x \right)$$

$$= \pm \delta_{jj'} \hbar \left(S_j^x \pm iS_j^y \right) \,.$$

$$\left[S_{\mathbf{k}}^z S_{\mathbf{k}'}^{\pm}\right] = \sum_{jj'} e^{i\left(\mathbf{k}\mathbf{x}_j + \mathbf{k}'\mathbf{x}_{j'}\right)} \left[S_j^z S_{j'}^{\pm}\right]$$

$$= \pm\hbar \sum_{jj'} e^{i\left(\mathbf{k}\mathbf{x}_j + \mathbf{k}'\mathbf{x}_{j'}\right)} \delta_{jj'} S_j^{\pm}$$

$$= \pm\hbar \sum_j e^{i\left(\mathbf{k}+\mathbf{k}'\right)\mathbf{x}_j} S_j^{\pm}$$

$$= \pm\hbar S_{\mathbf{k}+\mathbf{k}'}^{\pm} .$$

$$\left[S_j^-, S_{j'}^+\right] = \left[\left(S_j^x - iS_j^y\right), \left(S_{j'}^x + iS_{j'}^y\right)\right]$$

$$= i\left[S_j^x, S_{j'}^y\right] - \left[S_j^y, S_{j'}^x\right]$$

$$= 2i\delta_{jj'}\left(i\hbar S_j^z\right)$$

$$= -2\hbar \delta_{jj'} S_j^z .$$

$$\left[S_{\mathbf{k}}^-, S_{\mathbf{k}'}^+\right] = \sum_{jj'} e^{i\left(\mathbf{k}\mathbf{x}_j + \mathbf{k}'\mathbf{x}_{j'}\right)} \underbrace{\left[S_j^-, S_{j'}^+\right]}_{=-2\hbar\delta_{jj'} S_j^z}$$

$$= -2\hbar \sum_j e^{i\left(\mathbf{k}+\mathbf{k}'\right)\mathbf{x}_j} S_j^z$$

$$= -2\hbar S_{\mathbf{k}+\mathbf{k}'}^z$$

q.e.d. ✓

and obtain

$$
\begin{aligned}
H &= -\sum_{jj'} J_{jj'}\left(S_j^z S_{j'}^z + S_j^+ S_{j'}^-\right) + b\sum_j S_j^z \\
&= -\frac{1}{N^2}\sum_{kk'}\sum_{jj'} J\underbrace{(\mathbf{R}_{j'}-\mathbf{R}_j)}_{=\mathbf{R}_l}\, e^{-i\left(\mathbf{R}_j\mathbf{k}+\mathbf{R}_{j'}\mathbf{k}'\right)}\left(S_k^z S_{k'}^z + S_k^+ S_{k'}^-\right) \\
&\quad + b\frac{1}{N}\sum_k \underbrace{\sum_j e^{i\mathbf{R}_j\mathbf{k}}}_{=N\delta_{k,0}}\, S_k^z \\
&= -\frac{1}{N^2}\sum_{kk'}\sum_{jl} J(|\mathbf{R}_l|)e^{-i\left(\mathbf{R}_j\mathbf{k}+(\mathbf{R}_j+\mathbf{R}_l)\mathbf{k}'\right)}\left(S_k^z S_{k'}^z + S_k^+ S_{k'}^-\right) + bS_{k=0}^z \\
&= -\frac{1}{N}\sum_{kk'}\sum_l J(|\mathbf{R}_l|)e^{-i\mathbf{k}'\mathbf{R}_l}\underbrace{\sum_j e^{-i\mathbf{R}_j(\mathbf{k}+\mathbf{k}')}}_{=N\delta_{k',-k}}\left(S_k^z S_{k'}^z + S_k^+ S_{k'}^-\right) + bS_{k=0}^z \,.
\end{aligned}
$$

Eventually, we have with equation (2.51)

$$
H = -\frac{1}{N}\sum_k \tilde{J}(k)\left(S_k^z S_{-k}^z + S_k^+ S_{-k}^-\right) + bS_{\mathbf{k}=0}^z \,. \tag{2.55}
$$

There exist exact eigenstates for the low-lying excitations given by

$$
|\tilde{\psi}(q)\rangle = S_q^+|0\rangle \,. \tag{2.56}
$$

First we will prove that these states are indeed eigenstates

$$
\begin{aligned}
H|\tilde{\psi}(q)\rangle &= HS_q^+|0\rangle \\
&= S_q^+ \underbrace{H|0\rangle}_{=E_0|0\rangle} + [H, S_q^+]|0\rangle \\
&= E_0|\tilde{\psi}(q)\rangle + [H, S_q^+]|0\rangle \,.
\end{aligned}
$$

For the commutator we first evaluate the Zeeman part of the hamiltonian

$$
[H_Z, S_q^+]|0\rangle = b[S_{q=0}^z, S_q^+]|0\rangle = b\hbar S_{q+0}^+|0\rangle = \hbar b|\tilde{\psi}(q)\rangle \,.
$$

For the Heisenberg part of the hamiltonian we obtain

$$[H_H, S_q^+] = -\frac{1}{N}\sum_k \tilde{J}(k)\left([S_k^z S_{-k}^z, S_q^+] + [S_k^+ S_{-k}^-, S_q^+] \right)$$

$$= -\frac{1}{N}\sum_k \tilde{J}(k)\left(S_k^z[S_{-k}^z, S_q^+] + [S_k^z, S_q^+]S_{-k}^z + S_k^+[S_{-k}^-, S_q^+] \right)$$

$$= -\frac{\hbar}{N}\sum_k \tilde{J}(k)\left(\underbrace{S_k^z S_{q-k}^+}_{=S_{q-k}^+ S_k^z + \underbrace{[S_k^z, S_{q-k}^+]}_{=\hbar S_q^+}} + S_{q+k}^+ S_{-k}^z - 2S_k^+ S_{q-k}^z \right)$$

$$= -\frac{\hbar}{N}\sum_k \tilde{J}(k)\left(S_{q-k}^+ S_k^z + S_{q+k}^+ S_{-k}^z - 2S_k^+ S_{q-k}^z \right) - \frac{\hbar^2}{N}\left(\sum_k \tilde{J}(k) \right) S_q^+ \ .$$

The last term vanishes because

$$\sum_k \tilde{J}(\mathbf{k}) = \sum_l J(|\mathbf{R}_l|)\underbrace{\sum_k e^{i\mathbf{k}\mathbf{R}_l}}_{=N\delta_{l,0}} = NJ_{ll} = 0 \ .$$

We also have

$$S_k^z|0\rangle = \sum_l e^{i\mathbf{k}\mathbf{R}_l}\underbrace{S_l^z|0\rangle}_{=-\hbar S|0\rangle} = -\hbar S\left(\sum_l e^{i\mathbf{k}\mathbf{R}_l} \right)|0\rangle = -\hbar SN\delta_{k,0}|0\rangle \ .$$

Hence

$$[H_H, S_q^+]|0\rangle = \frac{\hbar^2 SN}{N}\sum_\mathbf{k} \tilde{J}(\mathbf{k})\left(S_{\mathbf{q}-\mathbf{k}}^+ \delta_{\mathbf{k},0} + S_{\mathbf{q}+\mathbf{k}}^+ \delta_{\mathbf{k},0} - 2S_\mathbf{k}^+ \delta_{\mathbf{k}-\mathbf{q}} \right)|0\rangle$$

$$= \hbar^2 S\left(2\tilde{J}(0) - 2\tilde{J}(q) \right) S_q^+|0\rangle$$

$$= 2\hbar^2 S\left(\tilde{J}(0) - \tilde{J}(q) \right)|\tilde{\Psi}(q)\rangle$$

Putting all terms together proves that $|\tilde{\psi}(q)\rangle$ is an eigen vector

$$H|\tilde{\Psi}(q)\rangle = \left(E_0 + \hbar\omega_q \right)|\tilde{\Psi}(q)\rangle \ , \tag{2.57}$$

with eigenvalue

$$\omega_q = b + 2\hbar S\left(\tilde{J}(0) - \tilde{J}(q) \right) \ . \tag{2.58}$$

For nearest neighbour exchange interactions,

$$\tilde{J}(q) = J \sum_{\mathbf{ffi}} e^{i\mathbf{ffi}\mathbf{q}} = 2J \sum_{\nu=1}^{D} \cos(q_\nu) \,,.$$

The sum runs over the cartesian coordinates. Hence

$$\tilde{J}(0) - \tilde{J}(q) = 2J \sum_{\nu} (1 - \cos(q_\nu)) \,.$$

For $b = 0$ and small values of q_α the leading order of the Taylor expansion yields

$$\hbar w_q = 2\hbar^2 S\big(\tilde{J}(0) - \tilde{J}(q)\big) = D\mathbf{q}^2 \,.$$

The excitation has a quadratic dispersion with a *spin wave stiffness* $D = 2\hbar^2 SJ$. The excitation energy tends continuously to zero for small q. This is a typical feature of a *Goldstone mode*, which tries to restore the broken symmetry.

Properties of the single magnon state

We will study further properties of the one-magnon excitation. We start out with the scalar product of one-magnon states for different wavevectors

$$\begin{aligned}
\langle \tilde{\Psi}(q) | \tilde{\Psi}(q') \rangle &= \langle 0 | S^-_{-q} S^+_{q'} | 0 \rangle \\
&= \langle 0 | S^+_{q'} \underbrace{S^-_{-q} | 0 \rangle}_{=0} + \langle 0 | \big[S^-_{-q}, S^+_{q'} \big] | 0 \rangle \\
&= -2\hbar \langle 0 | \underbrace{S^z_{q'-q} | 0 \rangle}_{=\delta_{q,q'}(-SN\hbar)|0\rangle} \\
&= \delta_{q,q'} 2SN\hbar^2 \,.
\end{aligned}$$

The one-magnon states are orthogonal and the correctly normalized vectors are

---

$$\textsc{One-magnon states}$$

eigenvector:	$\|\psi(\mathbf{q})\rangle = \dfrac{1}{\hbar\sqrt{2NS}} S^+_q \|0\rangle \,.$	(2.59a)
excitation energy:	$w_q = b + 2S\big(\tilde{J}(0) - \tilde{J}(q)\big)$	(2.59b)

The one-magnon vectors are also eigenvectors of

$$S^z_{total} = \sum_l S^z_l = S^z_{q=0} \ .$$

The proof is as follows

$$S^z_{q=0} S^+_q |0\rangle = S^+_q \underbrace{S^z_{q=0}|0\rangle}_{=-SN\hbar|0\rangle} + \underbrace{\left[S^z_{q=0}, S^+_q \right]}_{=\hbar S^+_{q+0}} |0\rangle$$

$$= \hbar \big(- NS + 1 \big) S^+_q |0\rangle$$

The eigenvalue of S^z_{total} has been changed by $+\hbar$. Now it is interesting to compare that with the expectation value of S^z_j of the spin at site $\mathbf{R}_j$

$$\langle \psi(\mathbf{q}) | S^z_j | \psi(\mathbf{q}) \rangle = \frac{1}{N} \sum_k e^{-i\mathbf{k}\mathbf{R}_j} \langle \psi(\mathbf{q}) | S^z_k | \psi(\mathbf{q}) \rangle \ . \qquad (2.60)$$

We need

$$\langle 0 | S^-_{-q} S^z_k S^+_q |0\rangle = \langle 0 | S^-_{-q} S^+_q \underbrace{S^z_k |0\rangle}_{=-NS\hbar\delta_{k,0}|0\rangle} + \langle 0| S^-_{-q} \left[S^z_k S^+_q \right] |0\rangle$$

$$a = -SN\hbar\delta_{k,0} \underbrace{\langle 0| S^-_{-q} S^+_q |0\rangle}_{=\langle\psi(\mathbf{q})|\psi(\mathbf{q})\rangle} + \hbar \underbrace{\langle 0| S^-_{-q} S^+_{k+q} |0\rangle}_{=\langle\psi(\mathbf{q})|\psi(\mathbf{q}+\mathbf{k})\rangle}$$

$$= \langle \psi(\mathbf{q})|\psi(\mathbf{q})\rangle \delta_{\mathbf{k},\mathbf{0}} \, \hbar \left(- SN + 1 \right) \ .$$

Hence

$$\langle S^z_{\mathbf{k}} \rangle = \frac{\langle 0| S^-_{-\mathbf{q}} S^z_{\mathbf{k}} S^+_{\mathbf{q}} |0\rangle}{\langle 0| S^-_{-q} S^+_q |0\rangle} = \delta_{k,0}\hbar \left(- SN + 1 \right) \ .$$

Inserting in equation (2.60) yields

$$\langle \psi(\mathbf{q}) | S^z_j | \psi(\mathbf{q}) \rangle = -\hbar \big(S - \frac{1}{N} \big) \sum_k e^{-\mathbf{k}\mathbf{R}_j} \delta_{k,0} = -\hbar S + \frac{\hbar}{N} \ .$$

The value of S^z_j is increased by $\hbar/N$ at each site, irrespective of the index j.

2.5.5 Mean field approximation of the isotropic Heisenberg model

The derivation of the MFA results is very similar to that in the Ising model. The hamiltonian in MFA for an homogeneous magnetic field is

$$H^{\text{MFA}} = -\frac{1}{2} \sum_{jj'} J_{jj'} \big(\langle \mathbf{S}_j \rangle \mathbf{S}_{j'} + \mathbf{S}_j \langle \mathbf{S}_{j'} \rangle \big) + \frac{1}{2} \sum_{jj'} J_{jj'} \langle \mathbf{S}_j \rangle \langle \mathbf{S}_{j'} \rangle - \mathbf{b} \sum_j \mathbf{S}_j \ .$$

$$(2.61)$$

We consider only the restricted MFA, where we retain the translational symmetry of the hamiltonian, i.e.

$$\langle \mathbf{S}_j \rangle = \mathbf{S} \qquad \forall j$$

It is obvious in an isotropic model to assume that the mean field will point into the same direction as the external field. Without loss of generality, we assume that the external field defines the z-direction ($\mathbf{b} = b\mathbf{e}_z$). With $\mathcal{S} = \langle S_j^z \rangle$ Then

$$H^{\text{MFA}} = -\underbrace{\left(\sum_{j'} J_{jj'}\right)}_{=\tilde{J}(0)} \mathcal{S} \sum_j S_j^z + \mathcal{S}^2 \frac{1}{2} \underbrace{\sum_{jj'} J_{jj'}}_{=N\tilde{J}(0)} - b \sum_j S_j^z$$

$$= -\underbrace{\left(\tilde{J}(0)\,\mathcal{S} + b\right)}_{=b'} \sum_j S_j^z + \frac{N\tilde{J}(0)}{2}\,\mathcal{S}^2 \,.$$

We have employed equation (2.51) [p. 78] and emphasize that S_j^z is an operator.

The partition function is readily computed in the eigen basis of the S_i^z operators. Since the spins are no longer interacting and the effective field b' is translational invariant, the partition function of N spins Z_N is simply the N-th power of Z_1, or rather (see also equation (1.7) [p. 12] of the Ising model)

$$\ln(Z_N) = N \ln(Z_1)$$

$$Z_1 = e^{-\frac{\beta \tilde{J}(0)}{2}\mathcal{S}^2} \sum_{\sigma=-S}^{S} e^{h'\sigma}$$

$$= e^{-\frac{\beta \tilde{J}(0)}{2}\mathcal{S}^2} e^{-Sh'} \sum_{\sigma=0}^{2S} e^{h'\sigma}$$

$$= e^{-\frac{\beta \tilde{J}(0)}{2}\mathcal{S}^2} e^{-Sh'} \frac{e^{h'(2S+1)} - 1}{e^{h'} - 1} y$$

$$= e^{-\frac{\beta \tilde{J}(0)}{2}\mathcal{S}^2} \frac{\sinh\left(h'(2S+1)/2\right)}{\sinh(h'/2)}$$

with $h' = \beta b'$. Hence

$$\frac{\ln(Z_N)}{N} = -\beta \frac{\tilde{J}(0)}{2}\mathcal{S}^2 + \ln\left[\sinh\left(h'(2S+1)/2\right)\right] - \ln\left[\sinh\left(h'/2\right)\right]$$

and for the free energy $\frac{F}{N} = -k_B T \frac{\ln(Z_N)}{N}$ we obtain

FREE ENERGY OF THE ISOTROPIC HEISENBERG MODEL
(*in mean-field approximation*)

$$\frac{F}{N} = \frac{\tilde{J}(0)\mathcal{S}^2}{2} - k_B T \left(\ln\left[\sinh\left(h'(2S+1)/2 \right) \right] - \ln\left[\sinh\left(h'/2 \right) \right] \right)$$

$$(2.62)$$

Like in the Ising case, the easiest way to compute the order parameter $\mathcal{S}$ is via

$$\mathcal{S} = \frac{1}{N}\frac{d}{dh'}\ln(Z) = \frac{d}{dh'}\left(\ln\left[\sinh\left(h'(2S+1)/2 \right) \right] - \ln\left[\sinh\left(h'/2 \right) \right] \right)$$

$$= \frac{2S+1}{2}\coth\left(h'(2S+1)/2 \right) - \frac{1}{2}\coth\left(h'/2 \right) .$$

In terms of the Brillouin function, defined in equation (2.17) [p. 61], we have

ORDER PARAMETER OF THE ISOTROPIC HEISENBERG MODEL
(*in mean-field approximation*)

$$\frac{\mathcal{S}}{S} = \mathcal{B}_S(Sh') \qquad\qquad (2.63\text{a})$$

$$h' = \beta\left(\tilde{J}(0)\mathcal{S} + b \right) . \qquad\qquad (2.63\text{b})$$

For $S = 1/2$ we obtain according to equation (2.22) [p. 63]

$$2\mathcal{S} = \mathcal{B}_{1/2}(\frac{h'}{2}) = \tanh\left(\frac{h'}{2}\right) . \qquad\qquad (2.64)$$

This result agrees with that of the MFA result in equation (1.12) [p. 13] for the nn Ising model, if we take into account

$$\tilde{J}(0) = \sum_l J(|\mathbf{R}_l|) = zJ .$$

Then equation (2.64) becomes

$$2S = \tanh\left(\beta\left(\frac{zJ}{4}2S + \frac{b}{2}\right)\right).$$ (2.65)

We also have to take into account for the spin-1/2 case

$$H_H^{\text{MFA}} = -\tilde{J}_H(0)\langle S_1\rangle \sum_i S_i^z - b_H \sum_j S_j.$$

If the spin eigenvalues are $S_i = \frac{1}{2}\sigma_i$, with $\sigma_i = \pm 1$ then

$$H_H^{\text{MFA}} = -\frac{\tilde{J}_H(0)}{4}\langle \sigma_1\rangle \sum_i \sigma_i^z - \frac{b_H}{2} \sum \sigma_j$$

So we have the following relations between the Heisenberg- and the Ising parameters

$$J_I = \frac{J_H}{4}, \qquad\qquad\qquad b_I = \frac{b_H}{2}.$$

With these parameters equation (2.65) turns into

$$\langle \sigma_1\rangle = \tanh\left(\beta\left(zJ_I\langle \sigma_1 + b_I\rangle\right)\right).$$

which is identical to that of the Ising modelequation (1.12) [p. 13].

2.5.6   Curie temperature

According to equation (2.20) [p. 62] the equation for the order parameter without external field reads for $T \leq T_C$

$$\frac{S}{S} = \mathcal{B}_S(\underbrace{\beta\tilde{J}(0)S^2}_{=\alpha}\underbrace{\frac{S}{S}}_{=x})$$

$$x = \frac{S+1}{3S}\,\alpha\,x - \underbrace{\frac{2S^3 + 4S^2 + 3S + 1}{90S^3}}_{=D}\alpha^3\,x^3.$$

Removing the trivial solution ($x = 0$) we are left with

$$Dx^2 = (\frac{S+1}{3S}\alpha - 1)$$

$$x \propto \left(\frac{S(S+1)}{3}\tilde{J}(0)\beta - 1\right)^{1/2}.$$

There is a temperature (Curie temperature), at which x goes to zero. The condition for it yields

$$k_B T_C = \tilde{J}(0) \frac{S(S+1)}{2} \; . \tag{2.66}$$

Then the order parameter slightly below T_C can also be written as

$$x \propto \left(\frac{T_C}{T} - 1 \right) \simeq \varepsilon^{1/2} \; .$$

Hence the critical exponent for the order parameter is again $\beta = 1/2$.

2.5.7 Internal energy

Like in the Ising case we obtain for the internal energy

$$U = \left\langle H^{MFA} \right\rangle = -\frac{N\tilde{J}(0)}{2} \mathcal{S}^2 \; , \tag{2.67}$$

which is zero above T_C and slighty below T_C it has the form

$$\frac{U}{N} = \frac{\tilde{J}(0)}{2D} \left(T - T_C \right) \, ,$$

resulting in a specific heat close to T_C

$$\frac{C}{N} = \begin{cases} \frac{\tilde{J}(0)}{2D} > 0 & \text{for } T < T_C \\ 0 & \text{for } T > T_C \; . \end{cases}$$

Like in the Ising case there is a discontinuous jump the the specific heat, but no power law behaviour

2.5.8 Magnetic susceptibility

$$\chi = \mu_0 \frac{\partial M}{\partial h} \bigg|_T \bigg|_{h=0}$$

Since the equation has the same structure as in the Ising case, we again find

$$\chi \simeq A_\pm |\varepsilon|^{-\gamma_\pm}$$

with $A_+ = 2A_-$ and $\gamma_+ = \gamma_- = 1$.

Chapter 3

Phase transitions

3.1 Phases

We can generalise the formalism introduced in statistical physics I to incorporate different coexisting phases.

3.1.1 Isolated systems

We begin with isolated systems, where the total volume, total energy, and the partical number per component is conserved. Let's assume that there are N_p coexisting phase, which we enumerate by $(v = 1, \ldots, N_p)$ and α component, enumerated by $(j = 1, \ldots, \alpha)$. The conditions for isolated systems are therefore

$$\sum_{v=1}^{N_p} V_v = V \tag{3.1a}$$

$$\sum_{v=1}^{N_p} U_v = U \tag{3.1b}$$

$$\sum_{v=1}^{N_p} N_{jv} = N_j \text{, for } j = 1, \ldots, \alpha . \tag{3.1c}$$

Here V_v (U_v) is the total volume (energy) of the particles in phase v. N_j is the total number of particles of component j and N_{jv} the number of component j that is in phase v. We also introduce the following vectors

$$\mathbf{N} = (N_{j=1}, N_{j=1}, \ldots, N_\alpha)^T \tag{3.2}$$

$$\mathbf{N}_v = (N_{j=1,v}, N_{j=1,v}, \ldots, N_{\alpha,v})^T . \tag{3.3}$$

The entropy as extensive quantity is

$$S(U, V, \mathbf{N}) = \sum_{\nu=1}^{N_p} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \tag{3.4}$$

For an isolated system (micro-canonical ensemble) the entropy represents the thermodynamic potential and in equilibrium it has to be maximal. So we have to maximize the entropy based on the constraints in equation (3.1) [previous page] . This is best achieved by Lagrange multipliers, i.e. we define

$$\mathcal{L} = \sum_\nu S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) - \lambda^V \sum_\nu V_\nu - \lambda^U \sum_\nu U_\nu - \sum_j \lambda_j^N \sum_\nu N_{j\nu} \tag{3.5}$$

and form the differential

$$d\mathcal{L} = \sum_{\nu=1}^{N_p} \left[\left. \frac{\partial}{\partial U_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \right|_{V_\nu, \mathbf{N}_\nu} - \lambda^U \right] dU_\nu \tag{3.6a}$$

$$+ \sum_{\nu=1}^{N_p} \left[\left. \frac{\partial}{\partial V_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \right|_{U_\nu, \mathbf{N}_\nu} - \lambda^V \right] dV_\nu \tag{3.6b}$$

$$+ \sum_{\nu=1}^{N_p} \sum_{j=1}^{\alpha} \left[\left. \frac{\partial}{\partial N_{j\nu}} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \right|_{U_\nu, V_\nu, N_{i\nu}, i \neq j} - \lambda_j^N \right] dN_{j\nu} \stackrel{!}{=} 0 . \tag{3.6c}$$

First of all, the variations in volume, energy, and particle number are independent from each other and, therefore, we have the individual conditions

$$\sum_{\nu=1}^{N_p} \left[\left. \frac{\partial}{\partial U_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \right|_{U_\nu, \mathbf{N}_\nu} - \lambda^U \right] dU_\nu = 0 \tag{3.7a}$$

$$\sum_{\nu=1}^{N_p} \left[\left. \frac{\partial}{\partial V_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \right|_{V_\nu, \mathbf{N}_\nu} - \lambda^V \right] dV_\nu = 0 \tag{3.7b}$$

$$\sum_{\nu=1}^{N_p} \sum_{j=1}^{\alpha} \left[\left. \frac{\partial}{\partial N_{j\nu}} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \right|_{U_\nu, V_\nu, N_{i\nu}, i \neq j} - \lambda_j^N \right] dN_{j\nu} = 0 . \tag{3.7c}$$

According to the constraints equation (3.1) [previous page] , there is one condition for the variables U_ν, i.e. we can choose U_ν for $\nu = 1, 2, \ldots, N_p - 1$ as we like and U_{N_p} follows from the constraint. Then we can always demand that

$$\lambda^U = \left. \frac{\partial}{\partial U_{N_p}} S_{N_p}(U_{N_p}, V_{N_p}, \mathbf{N}_{N_p}) \right|_{U_{N_p}, \mathbf{N}_{N_p}} , \tag{3.8}$$

as long as we are eventually able to fulfil the constraint equation (3.7a) .
Then the remaining constraint reads

$$\sum_{\nu=1}^{N_p-1} \left[\frac{\partial}{\partial U_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) - \lambda^U \right] dU_\nu = 0; .$$

Here all dU_ν are independent and the square brackets have to vanish in-
dividually. In total we have

$$\lambda^U = \frac{\partial}{\partial U_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \bigg|_{V_\nu, \mathbf{N}_\nu} \qquad = \frac{1}{T_\nu} . \tag{3.9a}$$

Similarly, we obtain from the other constraints

$$\lambda^V = \frac{\partial}{\partial V_\nu} S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \bigg|_{U_\nu, \mathbf{N}_\nu} \qquad = \frac{p_\nu}{T_\nu} . \tag{3.9b}$$

and

$$\frac{\partial}{\partial N_{j\nu}} \lambda_j^V = S_\nu(U_\nu, V_\nu, \mathbf{N}_\nu) \bigg|_{U_\nu, V_\nu, N_{i\nu}, i \neq j} \qquad = -\frac{\mu_{j\nu}}{T_\nu} , \qquad \text{for } j = 1, \ldots, \alpha . \tag{3.9c}$$

So we find that in an isolated system in equilibrium all phases have the
same temperature T, the same pressure p and the same chemical potential
μ_j for component j. But in general, we still have $\mu_j \neq \mu_{j'}$.

3.1.2   Closed system with $p = fixed, T = fixed$

Another important system is that where pressure and temperature are
fixed experimentally. In this case the Free Enthalphy $G(p, T, \mathbf{N}$ is the rel-
evant thermodynamic potential. The equilibrium condition is G has to be
minimal, or rather $dG = 0$. Again G is extensive, i.e. additive w.r.t. the
phases

$$G = \sum_{\nu=1}^{N_p} G_\nu(T, p, \mathbf{N}_\nu) \tag{3.10}$$

Here, we have already exploited that all phases have the same temperature
and pressure, which is given at the outset. So the only d.o.f. that can be

varied are the particle numbers, still under the constrain, used before. A similar derivation now yields

$$\lambda_j^N = \frac{\partial}{\partial N_{jv}} G_v(T, p, \mathbf{N}_v) \bigg|_{T,p,N_{i,v},i\neq j} = \mu_{j,v} \,. \tag{3.11}$$

and we find that in closed system, where T and p is fixed, the chemical potential of component j is the same in all phases.

3.1.3 Number of degrees of freedom

The chemical potentials will depend on T, p, and in principle on the particle numbers

$$\mu_{jv} = \mu_{jv}(T, p, \{N_{jv}\}) \tag{3.12}$$

Now, the chemical potentials are intensive quantities, i.e. scaling the extensive quantities in its argument, by a common factor does not change the chemical potential. Let's consider an intensive function f that shall depend on T, p, and some particle numbers N_l. Scaling the total size by λ results in particle numbers λN_l. As T and p are intensive, we have

$$f(T, p, \{\lambda N_l\}) = f(T, p, \{N_l\}) \,.$$

This is the case if f only depends on the concentrations $c_j = N_j / \sum_i N_i$, since scaling all N_j by a common factor does not change the concentration. By phase we mean a spatial area within which no abrupt changes of any physical quantity occur, but at the boundary of which such changes can be observed. The system consists of one or more components/ component. Component means the minimum number of independent chemical substances that we need to produce the phase. The stat of the system is described by a number of state variables depending on the type of system. By degrees of freedom F we mean the number of state variables that we can vary independently of each other without any of the phases disappearing. First of all, we want to assume that no chemical reactions take place in the system. The state of each phase is clearly defined when we specify T, p, and the mole fraction of component/component j in phase v.

$$c_j^{(v)} := \frac{N_{jv}}{N_v} \tag{3.13}$$

i.e. the fraction of particles in phase v that belong to component j. Then

$$\sum_j c_j^{(v)} = 1 \,, \qquad \forall v \,. \tag{3.14}$$

Scaling the total size of the system by a common factor λ, i.e. in particular $N_{j\nu} \to \lambda N_{j\nu}$, does not change the phases. So along with the intensitivity of the chemical potentials, we know by now that the latter depend on the mole fractions and not the absoluter particle numbers

$$\mu_{j\nu} = \mu_{j\nu}(T, p, \{c_j^{(\nu)}\}) \tag{3.15}$$

The number of state variables is $Z_v = 2 + \alpha N_p$, but they are not independent. According to equation (3.11) we have the equilibrium conditions, which include the conditions for the particle numbers in equation (3.1c)

$$\mu_{j\nu}(T, p, \{N_{j\nu}\}) = \mu_{j\nu'}(T, p, \{N_{j\nu}\}) \, , \forall \nu \neq \nu' \text{and } \forall j \, .$$

These are $N_p - 1$ conditions for each component, i.e. in total $\alpha(N_p - 1)$ constraints. In addition we have the N_p normalization constraints in equation (3.14) . So the total number of constraints is

$$Z_c = \alpha N_p - \alpha + N_p \, ,$$

and therefore the number of d.o.f. is the number of state variables minus the number of constraints resulting in

---

GIBBS' PHASE RULE

$$f = 2 + \alpha - N_p \, . \tag{3.16}$$

Example: H_2O Phase diagram
For water: $T_{tp} = 273,16000K(0,01000C)$, $p_{tp} = 611,657Pa$. $T_c = 647.096K$, $p_c = 22.064MPa$ and $\rho_c = 356kg/m^3$.

solid-liquid: melting, freezing

liquid-gas: condensation, vaporization

solid-gas: sublimation, deposition

Anomaly of water: increasing reduces the volume and the density increases. By increasing pressure, solid water becomes liquid. Hence, the density of solid water (ice) is smaller than of liquid water. That is the reason why ice floats on water.
What is a one component liquid, i.e. $\alpha = 1$.

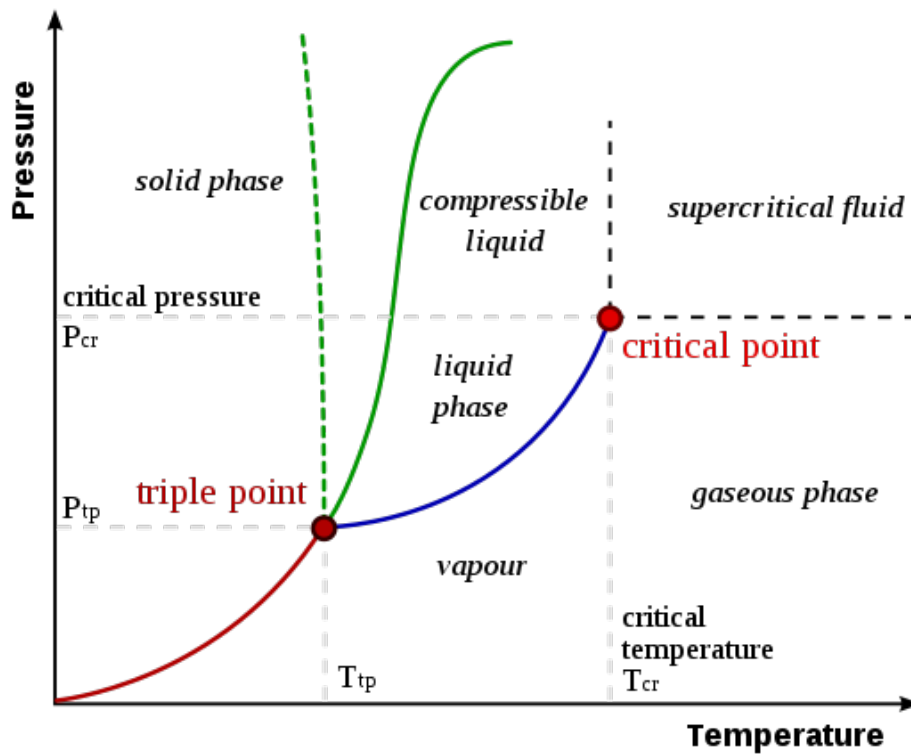Figure 3.1: **Phase diagram of water, taken from 'wikipedia'. The dashed green line is the melting-point line of water (negative slope, anomalous). The solid green line is the melting-point line of most other substances (positive slope, normal).**

Pure phase (solid,liquid,gas), $N_p = 1$

The number of d.o.f. is

$$f = 2 + 1 - 1 = 2 \,,$$

which means we can vary T and p independently.

Two coexisting phases, $N_p = 2$

- boiling curve (liquid to gas)

- condensation curve (liquid to gas)

- melting curve (solid to liquid)

- solidification curve (liquid to solid)

- sublimation curve (solid to gas)

- resublimation curve (gas to solid)

melting-point line (solid to liquid) Condensation curve () Siedekurve (liquid to gas)
sublimation (solid to gas) resublimation (gas to solid)
The number of d.o.f. is

$$f = 2 + 1 - 2 = 1 \,,$$

which means, we have to vary T and p on a curve, $p(T)$, e.g. melting-point line.

Three coexisting phases, $N_p = 3$, triple point

Here $f = 0$. There is no degree of freedom.
It also follows, that for a one-component substance there are at most 3 phases, otherwise the number of d.o.f. become negative.

3.1.4 Clausius-Clapeyron

As a further application of the previous discussion, we consider the coexistence line between liquid and gas (Condensation curve) of a one-component system, such as water.

If we choose T and P as the two independent d.o.f. then according to equation (3.11) [p. 93] we have

$$\mu_{fl}(T, p) = \mu_g(T, p) .\tag{3.17}$$

This relation allows to determine to condensation curve $p(T)$ on which the fluid and the gas phase coexist. Away from this curve, only one phase exists, namely the one where the chemical potential is smaller. This is due to the Gibbs-Duhem relation

$$G(T, p, N) = \mu N .$$

In the case of a single phase, the system will minimize the Free Enthalpy. Since N is fiixed, the phase with the smaller chemical potential has a smaller Free Enthalpy.

The free Enthalpy is related to the free energy $F(T, V, N)$ via a Legendre transformation, where V is replaced by p. We start out with

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

This relation can be inverted for given T, N and p we obtain

$$V = V(p, T, N)$$

$$G(T, p, N) = F(T, V(p, T, N), N) + pV .\tag{3.18}$$

Then

$$\begin{aligned} dG &= dF + pdV + Vdp \\ &= -SdT - pdV + \mu dN + pdV + Vdp \\ dG &= -SdT + \mu dN + Vdp . \end{aligned}$$

Furthermore we have seen before

$$dG = \mu dN - SdT + Vdp ,$$

or rather

$$dG - \mu dN = -SdT + Vdp .$$

On the other hand the Gibbs-Duhem relation yields

$$dG = \mu dN + Nd\mu \Rightarrow dG - \mu dN = Nd\mu .$$

Combining the two relation yields

$$-SdT + Vdp = Nd\mu \ .$$

This is generally valid and it also applies individually to different phases, i.e.

$$-S_\nu dT + V_\nu dp = N_\nu d\mu_\nu$$
$$-\frac{S_\nu}{N_\nu}dT + \frac{V_\nu}{N_\nu}dp = d\mu_\nu \ .$$

We introduce entropy and volume per particle

$$s_\nu = \frac{S_\nu}{N_\nu} \tag{3.19}$$

$$v_\nu = \frac{V_\nu}{N_\nu} \ , \tag{3.20}$$

and obtain

$$-s_\nu dT + v_\nu dp = d\mu_\nu \ . \tag{3.21}$$

Now we consider changes dp, dT along the coexistence line. There we have due to equation (3.17) [previous page]

$$d\mu_{fl}(T, p) = d\mu_g(T, p) \ .$$

Along with equation (3.21) we obtain

$$-s_{fl}dT + v_{fl}dp = -s_g dT + v_g dp$$
$$\frac{dp}{dT} = \frac{s_g - s_{fl}}{v_g - v_{fl}} = \frac{\Delta s}{\Delta v} \ .$$

Finally, we define the molar vaporation enthalpy

$$q = T(s_g - s_{fl})$$

and find the

CLASIUS-CLAPEYRON RELATION

$$\frac{dp}{dT} = \frac{q}{T(v_g - v_{fl})} \ . \tag{3.22}$$

In the derivation of the Clausius-Clapeyron relation we have assumed that $S_g \neq S_{fl}$ and $V_g \neq V_{fl}$, which means, although

$$\mu_g(T,p) = \mu_{fl}(T,p)$$

that

$$\left.\frac{\partial \mu_g}{\partial T}\right|_p \neq \left.\frac{\partial \mu_{fl}}{\partial T}\right|_p$$

$$\left.\frac{\partial \mu_g}{\partial p}\right|_T \neq \left.\frac{\partial \mu_{fl}}{\partial p}\right|_T .$$

Such a phase transition is a first order phase transition.
The Clausius-Clapeyron relation is only valid for first order phase transitions.

3.1.5   Real gases (van der Waals equation)

In an earlier chapter we have discussed the ideal gas and its equation of state

$$pV = Nk_BT .$$

We also introduced finite eigen-volumes of the moelcules and obtained

$$p(V - V_0) = Nk_BT .$$

Finally, we also want to include the intermolecular forces. For molecules in the bulk of the material, these forces vanish on average, as they act with equal strength in opposite directions. This is not the case in the surface layer, where the partners outside the surface are missing. This results in an effective force, pulling the molecules in the surface layer into the bulk. I.e. the intermolecular forces act at the surface like an additional pressure (internal pressure). It has the form

$$a\frac{N^2}{V^2}$$

resulting in

VAN DER WAALS EQUATION
(extensive form)

$$\left(p + a'\frac{N^2}{V^2}\right)\left(V - \overbrace{Nb'}^{V_0}\right) = Nk_BT \ . \tag{3.23}$$

It can also be expressed in term of molar volume v, pressure and temperature, i.e. the intensive form

---

VAN DER WAALS EQUATION
(intensive representation)

$$\left(p + \frac{a'}{v^2}\right)\left(v - b'\right) = k_BT \ . \tag{3.24}$$

Here, b' is the eigen-volume of one molecule.

We multiply equation (3.24) by v^2 and find that it becomes a cubic equation in v

$$\left(pv^2 + a'\right)\left(v - b'\right) - k_BTv^2 = 0$$

$$pv^3 + a'v - b'pv^2 - a'b' - k_BTv^2 = 0 \ .$$

Next we introduce suitable units p_{cr}, v_{cr}, T_{cr} and the corresponding dimensionless quantities π, ν, t via

$$p = \pi p_{cr}$$
$$v = \nu v_{cr}$$
$$T = t T_{cr} \ ,$$

resulting in

$$\pi v^3 + \frac{a' v_{cr}}{p_{cr} v_{cr}^3} v - \frac{b' p_{cr} v_{cr}^2}{p_{cr} v_{cr}^3} \pi v^2 - \frac{a' b'}{p_{cr} v_{cr}^3} - \frac{k_B T_{cr} v_{cr}^2}{p_{cr} v_{cr}^3} t v^2 = 0$$

$$\pi v^3 + \underbrace{\left(\frac{a'}{p_{cr} v_{cr}^2} \right)}_{=T_1} v - \underbrace{\left(\frac{b'}{v_{cr}} \right)}_{=T_2} \pi v^2 - \underbrace{\left(\frac{a' b'}{p_{cr} v_{cr}^3} \right)}_{=T_3} - \left(\frac{k_B T_{cr}}{p_{cr} v_{cr}} \right) t v^2 = 0$$

$$\pi v^3 + T_1 v - T_2 \pi v^2 - T_3 - \underbrace{\left(\frac{k_B T_{cr}}{p_{cr} v_{cr}} \right)}_{=T_4} t v^2 = 0 \; .$$

Now we have the freedom to choose the parameters p_{cr}, v_{cr}, and T_{cr} suitably. We use

$$T_2 = \left(\frac{b'}{v_{cr}} \right) = \frac{1}{3} \tag{3.25}$$

$$T_3 = \left(\frac{a' b'}{p_{cr} v_{cr}^3} \right) = 1 \tag{3.26}$$

$$T_4 = \left(\frac{k_B T_{cr}}{p_{cr} v_{cr}} \right) = \frac{8}{3} \tag{3.27}$$

then

> CRITICAL VALUES
> (*van der Waals*)
>
> $$v_{cr} = 3b' \tag{3.28}$$
>
> $$\Rightarrow \quad p_{cr} = \frac{a' b'}{v_{cr}^3} = \frac{a'}{27 b'^2} \tag{3.29}$$
>
> $$\Rightarrow \quad T_1 = \frac{a'}{p_{cr} v_{cr}^2} = \frac{a'}{\frac{a'}{27 b'^2} 9 b'^2} = 3 \tag{3.30}$$
>
> $$k_B T_{cr} = \frac{8}{3} p_{cr} v_{cr} = \frac{8}{3} \frac{a'}{27 b'^2} 3 b' = \frac{8 a'}{27 b'} \; . \tag{3.31}$$

So we have

$$\pi v^3 + 3v - \frac{\pi v^2}{3} - 1 = \frac{8}{3}tv^2 \tag{3.32}$$

$$\left(\pi + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right) = \frac{8}{3}t . \tag{3.33}$$

Solving for π yields

$$\pi = \frac{8t}{3v - 1} - \frac{3}{v^2}$$

The term $(3v - 1)$ originated from $V - V_0$, and therefore it is always positive, as the total volume has to be greater than the eigenvolume.

If we plot $\pi(v)$ for fixed t (isotherm) then we find different behaviour for $t < 1, t = 1$ and $t > 1$.

- For $t < 1$ the curve has a minimium and a maximum in the physical interval $v > 1/3$.

- For $t = 1$ minimum and maximum coincide at $v = 1$, with $\pi(v = 1) = 1$.

- For $t > 1$ the curve is monotonically decreasing in the physical interval.

As we will see soon, if the curve has a maximum and a minimum then there is a phase transition. If it is monotonically decreasing, there is no phase transition. Hence, the parameters p_{cr}, v_{cr}, and T_{cr} represent the critical point.

Inserting the critical values into the equation of state for the ideal gas in form of the following ratio then we obtain

$$Z := \frac{p_{cr}v_{cr}}{k_B T_{cr}} = \frac{\frac{a'}{27b'^2}3b'}{\frac{8a'}{27b'}} = \frac{3}{8} . \tag{3.34}$$

Experimentally one finds for all real gases am kritischen Punkt $Z < 3/8$, while the ideal gas yields $Z = 1$. In this respect the van der Waals model is clearly better. Alternatively, equation (3.34) can be written with $\rho_c = 1/v_{cr}$ as

$$p_{cr} = \frac{3}{8}k_B T_{cr}\rho_{cr} . \tag{3.35}$$

3.1.6 Maxwell-Construction

We have just seen that the equation of state for the van der Walls model read in dimensionless units i

$$\left(\pi - \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right) = \frac{8}{3}t \;.$$

As we have seen, for $t < 1$ there are regions in the $\pi - v$-diagramm where the isotherm compressiblility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\Big|_T\right) = -\frac{1}{p_{cr}v}\left(\frac{\partial v}{\partial \pi}\Big|_T\right) < 0 \qquad (3.36)$$

becomes negative. This implies that the system is mechanically unstable, it would shrink by itself. The reason is that the van der Waals model describes a single phase of a one-component system. It is applicable for large volume, in the gas phase, and for small volume, in the liquid phase, but in between there is a phase transition, where 2 phases coexist, which cannot be described by the vdW equation. What happens in reality is the following. We have seen before that generally in the coexistence line between liquid and gas, the number of d.o.f. is merely 1 and it is describe d by $p = p(T)$. On isotherms, T is fixed and hence p is fixed.

In the pV-diagram all isotherms for $(T < T_c)$ in the two-phase region are horizontal lines.

We denote the pressure on the coexistece line by $p_{\alpha\beta}$.
In the pure phase regions the vdW model is still valid.
we have the condition

$$\mu_{fl}(T, p) = \mu_g(T, p) \;,$$

i.e. pressure is a function of temperature alone and independent of the volume. Hence for the isotherm compression, discussed before, the pressure in when reducing the volume in the two-phase region, does not change
In the coexistence region we have

$$\mu_{fl}(T, P_{\alpha\beta}) = \mu_g(T, P_{\alpha\beta})$$

In addition, at the points α and β, we have pure phases and therefore $N_\alpha = N$ and $N_\beta = N$ and consequently

$$\mu_{fl}(T, P_{\alpha\beta})N_\alpha = \mu_g(T, P_{\alpha\beta})N_\beta$$

The Gibbs-Duhem relation then yields

$$G_\alpha = G_\beta$$
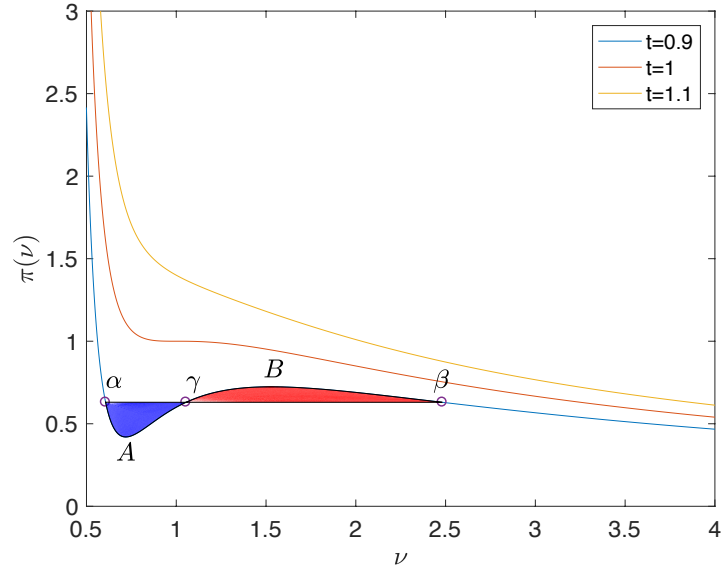$$F_\alpha + p_\alpha V_\alpha = F_\beta + p_\beta V_\beta$$

Figure 3.2: **Maxwell construction.**

or rather

$$F_\alpha - F_\beta = -p_{\alpha\beta}(V_\alpha - V_\beta) \ . \tag{3.37}$$

This is the result, if we assume a coexistence of two phases. Alternatively, if we stick to one phase then the vdW equation determines the pressure curve, the one given in figure 3.2 with the wavy look. In that case, the differential of the free energy is, since N is fixed and T is fixed (isotherm),

$$dF = SdT - pdV + \mu dN = -pdV \ ,$$

and the integral yields

$$F_\alpha - F_\beta = \int_\beta^\alpha dF = -\int_{V_\beta}^{V_\alpha} p(T, V', N)dV' \ .$$

$$F_\alpha - F_\beta = \int_{V_\alpha}^{V_\beta} p(T, V', N)dV' \tag{3.38}$$

By combining equation (3.37) and equation (3.38) we find

$$\int_{V_\alpha}^{V_\beta} p(T, V', N) dV' = p_{\alpha\beta}(V_\beta - V_\alpha) \tag{3.39}$$

I.e., the area under the vdW curve $p(t, V, N$ in the interval (V_α, V_β) has to be same as the area of the $p(V) = p_{\alpha\beta}$ curve in the two-phase region. Consequently, the subareas A and B have to be same.

Finally, we will show that the pure phase is unstable w.r.t. to the mixed phase. To this end we compare two states with the same T and V but different pressures $p_{\alpha\beta}$ the vdW pressure $p(T, V, N)$. Since T and V is fixed, we haver to compare the free energies.

In the pure phase compute the free energy for a given V in the interval (V_α, V_β). To this end we use $dF = -pdV$ and integrate from V_α to V

$$F_{vdW}(V, T) = F_\alpha - \int_{V_\alpha}^{V} p(V', T) dV' . \tag{3.40}$$

In the two-phase region the free energy is the linear combination of the free energy of the two phases according to there relative size, i.e.

$$F_{mp} = c_{fl} F_{fl} + c_g F_g \tag{3.41}$$
$$= c_{fl} F_\alpha + c_g F_\beta , \tag{3.42}$$

with $c_{fl} = N_{fl}/N$ and $c_g = N_g/N$, hence $c_{fl} + c_g = 1$. Then

$$F_{mp} = F_\alpha + (c_{fl} - 1)F_\alpha + c_g F_\beta$$
$$= F_\alpha - c_g F_\alpha + c_g F_\beta$$
$$F_{mp} = F_\alpha + c_g (F_\beta - F_\alpha) . \tag{3.43}$$

Finally, we want to express c_g in terms of volume. The total volume is split accordingly,

$$V = c_{fl} V_{fl} + c_g V_g = (1 - c_g) V_\alpha + c_g V_\beta$$
$$V - V_\alpha = c_g (V_\beta - V_\alpha)$$

and we obtain the relative portions of the phases

$$c_g = \frac{V - V_\alpha}{V_\beta - V_\alpha} \tag{3.44a}$$
$$c_{fl} = \frac{V_\beta - V}{V_\beta - V_\alpha} . \tag{3.44b}$$

We then have

$$F_{mp} = F_\alpha + \frac{V - V_\alpha}{V_\beta - V_\alpha}(F_\beta - F_\alpha) \ . \tag{3.45}$$

Here we can also use equation (3.37) resulting in

$$F_{mp} = F_\alpha - p_{\alpha\beta}\frac{V - V_\alpha}{V_\beta - V_\alpha}(V_\beta - V_\alpha) = F_\alpha + p_{\alpha\beta}(V - V_\alpha) \tag{3.46}$$

The difference of the free energies is according to equation (3.40) and equation (3.46)

$$F_{vdW}(V, T) - F_{mp}(V, T) = p_{\alpha\beta}(V - V_\alpha) - \int_{V_\alpha}^{V} p(V', T)dV' \geq 0$$

The reason can be seen in figure 3.2. As long as $V \in (V_\alpha, V_\gamma)$ it is obvious that the integral over $p(V', T)$ is smaller than the area of the rectangle formed obtained if p is replaced by $p_{\alpha\beta}$. For $V > V_\gamma$ we can modify the equation as follows

$$F_{vdW}(V, T) - F_{mp}(V, T)$$
$$= p_{\alpha\beta}(V_\gamma - V_\alpha) + p_{\alpha\beta}(V - V_\gamma) - \left(\int_{V_\alpha}^{V_\gamma} p(V', T)dV' + \int_{V_\gamma}^{V} p(V', T)dV' \right)$$
$$= \underbrace{p_{\alpha\beta}(V_\gamma - V_\alpha) - \int_{V_\alpha}^{V_\gamma} p(V', T)dV'}_{=A} - \int_{V_\gamma}^{V} (p(V', T) - p_{\alpha\beta})dV'$$

For $V \in (V_\gamma, V_\beta)$ the integrand is positive and

$$\int_{V_\gamma}^{V} (p(V', T) - p_{\alpha\beta})dV' \leq B$$

since B is the value of the integral over the entire interval $(V_\gamma, V_\beta$. According to the Maxwell construction $B = A$, hence the integral is les then A so in total we find

$$F_{vdW}(V, T) - F_{mp}(V, T) \geq 0 \ ,$$

as we have claimed before.

3.2 Phasetransitions

In case of the liquid-case mixture we haver seen that the transition occurs at fixed T and fixed p, the latter is

$$p_{\alpha,\beta}(T): \qquad \text{vapor pressure}$$

In the transition region we have a mixture of the liquid and the gas state. The percentage portion is given by equation (3.44) .

The supplied heat leads to transformation of a fraction of the fluid into gas. This process is isotherm, since heat is only used overcome the binding energy present in the fluid. Only if the entire fluid is vaporized, further heat transfer results in a temperature rise. Heat transfer that occurs at a constant system temperature but changes the state variable is called latent heat with respect to the variable.

Such phase transitions, that involve *latent heat* are *first order phase transitions*. *Latent heat* in contrast to *sensible heat* does not lead to a change in temperature.

Only for first order phase transitions, the Clausius-Claperyron equation is applicable, as it requires that entropy and volume per particle are different in the two phases.

We recall that

$$S = -\left.\frac{\partial G}{\partial T}\right|_p \tag{3.47}$$

$$V = -\left.\frac{\partial G}{\partial p}\right|_T. \tag{3.48}$$

A characteristic feature of first order phase transition is discontinuity of the **first** derivative of the thermodynamic potential when crossing the co-existence line in the phase diagram. Along the line it is continuous.

Next we exploit in addition the following relations

$$S = -\left.\frac{\partial F}{\partial T}\right|_V, \tag{3.49}$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_T. \tag{3.50}$$

which allow to compute specific heat and compressibility in term of the

free enthalpy or free energy

$$0 \leq C_p = T \frac{\partial S}{\partial T}\bigg|_p = -T \frac{\partial^2 G}{\partial T^2}\bigg|_p \qquad\qquad \Rightarrow \frac{\partial^2 G}{\partial T^2}\bigg|_p \leq 0 \qquad (3.51)$$

$$0 \leq \kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T = -\frac{1}{V}\frac{\partial^2 G}{\partial p^2}\bigg|_T \qquad\qquad \Rightarrow \frac{\partial^2 G}{\partial T^2}\bigg|_p \leq 0 \qquad (3.52)$$

$$0 \leq C_V = T \frac{\partial S}{\partial T}\bigg|_V = -T \frac{\partial^2 F}{\partial T^2}\bigg|_V \qquad\qquad \Rightarrow \frac{\partial^2 F}{\partial T^2}\bigg|_V \leq 0 \qquad (3.53)$$

$$0 \leq \frac{1}{\kappa_T} = -V \frac{\partial p}{\partial V}\bigg|_T = V \frac{\partial^2 F}{\partial V^2}\bigg|_T \qquad\qquad \Rightarrow \frac{\partial^2 F}{\partial T^2}\bigg|_p \geq 0 \ . \qquad (3.54)$$

Hence we have

$$\frac{\partial^2 G}{\partial T^2}\bigg|_p \leq 0 \qquad\qquad\qquad \frac{\partial^2 G}{\partial p^2}\bigg|_T \leq 0 \qquad\qquad (3.55)$$

$$\frac{\partial^2 F}{\partial T^2}\bigg|_p \leq 0 \qquad\qquad\qquad \frac{\partial^2 F}{\partial V^2}\bigg|_T \geq 0 \ . \qquad\qquad (3.56)$$

I.e. G is concave in both variables p and T. Due to $F = G - pV$, it follows that F is also concave in T, but convex in p.

3.2.1   Free energy for T and N fixed

Since $F > 0$ is convex in V and $\frac{\partial F}{\partial V} = -p < 0$, $F(V)$ is a left curving line that is always positive and it is strictly monotonically decreasing (slope zero would mean $p = 0$).

The Legendre transform of the free energy $F(V, T, N)$ (in the variable V) is the free enthalpy

$$G(p, T, N) = F(V(p), GT, N) + pV$$

$$= F(V(p), GT, N) - \frac{\partial F}{\partial V}\bigg|_T V$$

For $T > T_c$ the second derivative $\frac{\partial F^2}{\partial V^2} = -\frac{\partial p}{\partial V}$ is greater than zero for all V. For $T < T_c$, however, there is an interval (V_α, V_β) in which the second derivative is zero and $F(V)$ is a linear function in V. Hence,

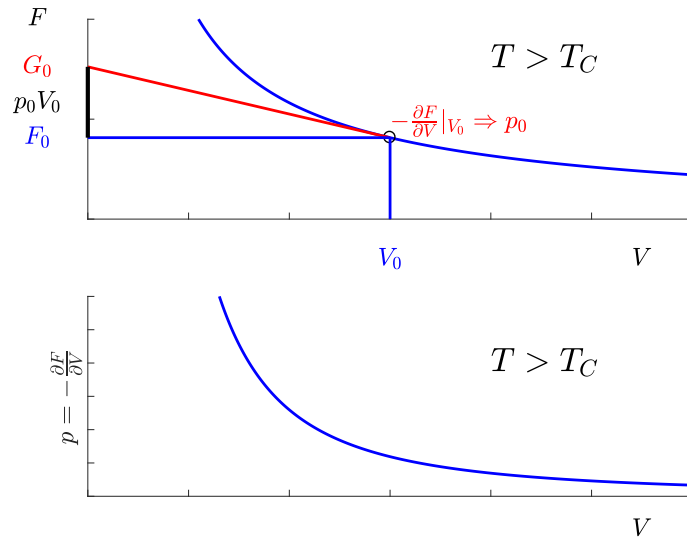$$\frac{\partial F}{\partial V}\bigg|_T = -p = const = -p_{\alpha\beta}.$$

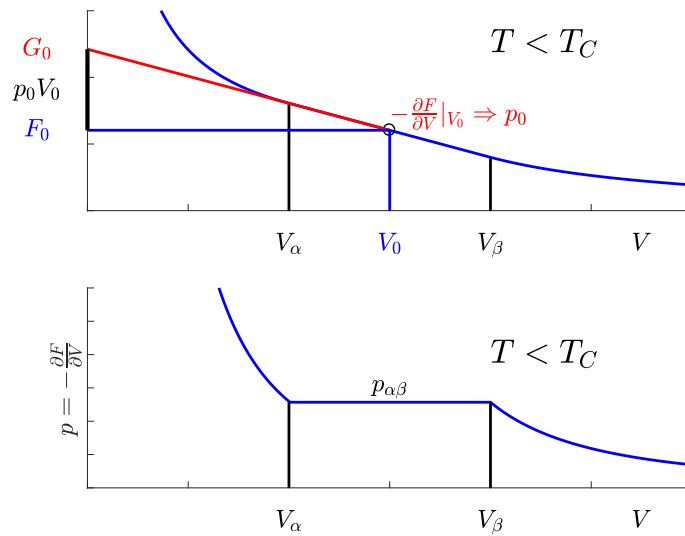Figure 3.3: **Schematic plot of free energy for** $T > T_c$**.**

Figure 3.4: **Schematic plot of free energy for** $T < T_c$**.**

3.2.2 F and G as function of T

As function of temperature, both F and G behave similarly, since

$$-S = \left.\frac{\partial G}{\partial T}\right|_p = \left.\frac{\partial V}{\partial T}\right|_V .$$

At a first order phase transition the entropy S shows a finite jump at T_c, which is then associated with

---

LATENT HEAT

$$\Delta Q = T_{\alpha\beta}\Delta S . \tag{3.57}$$

ΔQ is, however not a material constant, it also depends on the state variables. E.g. for the liquid-gas system, ΔQ depends on pressure. On approaching the critical point, ΔD vanishes. The definition of the order of the phase transition has to refined

3.2.3   Ehrenfest classification

N-TH ORDER PHASE TRANSITION

$$\left.\frac{\partial^m G_\alpha}{\partial T^m}\right|_p = \left.\frac{\partial^m G_\beta}{\partial T^m}\right|_p \qquad \forall m = 1,\ldots n-1 , \tag{3.58a}$$

$$\left.\frac{\partial^m G_\alpha}{\partial p^m}\right|_T = \left.\frac{\partial^m G_\beta}{\partial p^m}\right|_T \qquad \forall m = 1,\ldots n-1 . \tag{3.58b}$$

But

$$\left.\frac{\partial^n G_\alpha}{\partial T^n}\right|_p \neq \left.\frac{\partial^n G_\beta}{\partial T^n}\right|_p \tag{3.58c}$$

$$\left.\frac{\partial^n G_\alpha}{\partial p^n}\right|_T \neq \left.\frac{\partial^n G_\beta}{\partial p^n}\right|_T . \tag{3.58d}$$

Of practical importance are first and second order phase transitions. First order phase transitions have already been discussed in detail. In the case of a second order phase transition, we have

---
SECOND ORDER PHASE TRANSITION

$$G(T, p) \qquad \text{continuous} \qquad (3.59a)$$

$$\left.\frac{\partial G}{\partial T}\right|_p, \left.\frac{\partial G}{\partial p}\right|_T, (\text{i.e. } S(T, p), V(T, p)) \qquad \text{continuous} \qquad (3.59b)$$

$$C_p = -T\left.\frac{\partial^2 G}{\partial T^2}\right|_p \quad \kappa_T = -\frac{1}{V}\left.\frac{\partial^2 G}{\partial p^2}\right|_T \qquad \text{discontinous} \qquad (3.59c)$$

3.3 Critical exponents

Second order phase transitions are of particular interest, as they exhibit universal behaviour close to the phase transition. Completely different systems with second order phase transition show a very similar power law behaviour, which shall be discussed in this section. We define

$$\varepsilon = \frac{T - T_C}{T_C}$$

Very often it is observed that in a close vicinity of T_c, typically $|\varepsilon| < 10^{-2}$, physical observables $f(T)$ show the following behaviour

$$f(\varepsilon) = a\varepsilon^\varphi \left(1 + b\varepsilon^\psi + \ldots\right) \psi > 0 \,,$$

here φ and ψ are real valued exponents. This behaviour is abbreviated as

$$f(\varepsilon) \simeq \varepsilon^\varphi \,, \tag{3.60}$$

One says: f behaves like ε^φ and φ is called the *critical exponent*. The critical exponent is more generally defined by

$$\varphi = \lim_{\varepsilon \to 0} \frac{\ln |f(\varepsilon)|}{\ln |\varepsilon|} \tag{3.61}$$

In general, the critical exponent depends on whether we compute it below or above T_c. For the order parameter it actually makes only sense below T_c, as the order parameter by definition is zero above T_c.

Of course, different observables may have different critical exponents. The critical observable for one observable, however, is almost universal, it only depends on

- spatial dimension

- range of the interaction

- spin dimensionality.

This is the so-called *universality hypothesis* of Griffiths. Te range of the particle interaction is grouped into three classes:

- short-range, if the interaction decreases like

$$r^{-(d+2+\alpha)} \; ; \quad 0 < \alpha \, .$$

   Where the details of the interaction are unimportant. One finds a really universal behaviour.

- long-range, if

$$r^{-(d+2+\alpha)} \; ; \quad \alpha < \frac{d}{2} - 2 \quad \text{(always negative)}.$$

   In this case, the *classical theories* apply (Landau Theory, van der Waals model, Weißferromagnet). In this case, however, the critical exponents are independent of the spatial dimension.

- Intermediate range, if

$$r^{-(d+2+\alpha)} \; ; \quad \frac{d}{2} - 2 < \alpha < 0 \, .$$

   The critical exponents depend on α

Magnetic systems are typically discussed as interacting spin-systems. As spin-dimension (n) we understand the relevant components of the spin vector. Ising model /Potts model has $n = 1$ and is considered as one-dimensional vector, the $x - y$-model has $n = 2$ and the vectors are two-dimensional, and finally the Heisenberg model $n = 3$ is three-dimensional. The critical exponents.

Possible behaviour:

Power law decay $f(\varepsilon) \simeq \varepsilon^\varphi$ with $\varphi > 0$

Power law divergence $f(\varepsilon) \simeq \varepsilon^\varphi$ with $\varphi < 0$

Logarithmic divergence $f(\varepsilon) = a + b\ln(|\varepsilon|)$ we obtain by the definition of the critical exponent in equation (3.61) [previous page] $\varphi = 0$

In general, the critical exponent for $\varepsilon > 0$ (denoted by φ) can differ from that for $\varepsilon < 0$ (denoted by φ')

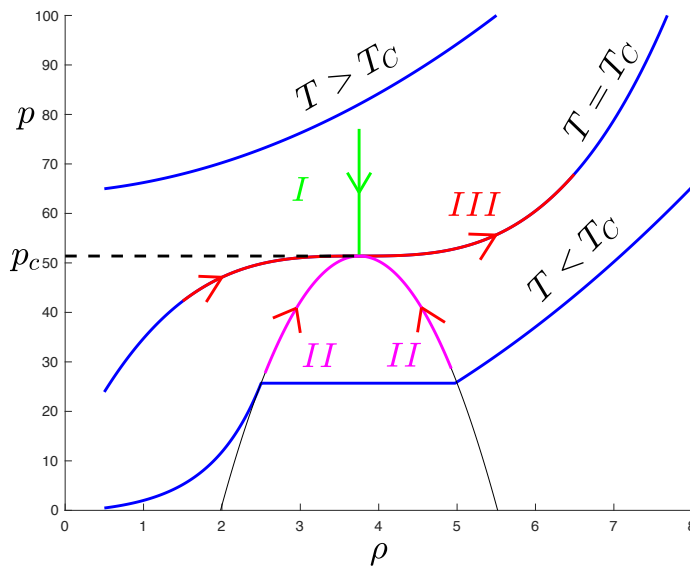### 3.3.1 Important critical exponents

Figure 3.5: **Paths for the definition of the critical exponents.**

1. Heat capacity ($\alpha :_\pm$) for real gases

$$C_V \simeq A_\pm |\varepsilon|^{-\alpha_\pm} : \qquad \begin{cases} - & \text{for path II, i.e. } T \nearrow T_c, \text{with } \rho = \rho_{g,fl} \\ + & \text{for path I, i.e. } T \searrow T_c, \text{with } \rho = \rho_c \end{cases}.$$

$$(3.62)$$

Heat capacity (α', α) for magnets

$$C_B \simeq A_\pm |\varepsilon|^{-\alpha_\pm} : \qquad \begin{cases} - & T \nearrow T_c, \text{with } B = 0 \\ + & \text{for path I, i.e. } T \searrow T_c, \text{with } B = 0 \end{cases} . \tag{3.63}$$

The experiment yields $\alpha_\pm \approx 0$. Ising 2D, exact solution, logarithmic divergence, i.e. $\alpha_\pm = 0$. Classic theories (i.e. Weißferrro-magnet, vdW gas) yield discontinuity, which is equivalent to $\alpha_\pm = 0$.

2. Order parameter (β [not inverse temperature!]). A variable that exists only below T_c and which characterises the order of the system. E.g. magnetization M or the for real gases the density difference $\Delta\rho = \rho_{fl} - \rho_g$, or rather $\Delta\rho = \rho_{fl,g} - \rho_c$, in the two-phase region

$$\frac{\Delta\rho(T)}{2\rho_c} \simeq B|\varepsilon|^\beta \text{ , along path II} \tag{3.64}$$

$$\frac{M(T)}{M(0)} \simeq B|\varepsilon|^\beta \text{ , for } B = 0 . \tag{3.65}$$

The normalizations are introduced to make sure that B is $O(1)$. In principle, β should be β', as we are below T_c, but since the order parameter is only defined below T_c, it is common to use β. Typical experimental values are 0.35 ± 0.02. classical theories yield $\beta = 1/2$. 2D Ising exact, $\beta = 1/8$. For the 3D Ising model one finds $\beta = 0.325 \pm 0.001$. While 3D Heisenberg gives $\beta = 0.3445 \pm 0.002$.

3. Compressibilities and susceptibilities ($\gamma_\pm$)

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T = \frac{1}{\rho}\frac{\partial \rho}{\partial p}\bigg|_T ,$$

$$\chi_T = \frac{\partial M}{\partial B}\bigg|_T$$

$$\frac{\kappa_T}{\kappa_{T_c}^0} \simeq C_\pm |\varepsilon|^{\gamma_\pm} : \qquad \begin{cases} - & \text{for path II, i.e. } T \nearrow T_c, \text{with } \rho = \rho_{g,fl} \\ + & \text{for path I, i.e. } T \searrow T_c, \text{with } \rho = \rho_c \end{cases} . \tag{3.66}$$

Here κ_c^0 is the compressibility of the ideal gas at $T = T_c$, which follows (due to $\rho = \frac{p}{k_B T}$) from

$$\kappa = \frac{1}{\rho}\frac{1}{k_B T} = \frac{1}{p} .$$

Similarly, one uses for the normalization in the magnetic case, the result of an ideal paramagnet

$$M = \frac{C^*}{T} \, ,$$

with C^* being the Curie constant.

$$\frac{\chi_T}{\chi_{T_c}^0} \simeq C_\pm |\varepsilon|^{-\gamma_\pm} : \qquad \begin{cases} - & \text{for path II, i.e. } T \nearrow T_c, \text{with } H = 0 \\ + & \text{for path I, i.e. } T \searrow T_c, \text{with } H = 0 \end{cases} \, .$$

$$(3.67)$$

Typical experimental values differ somewhat about $\gamma \approx \gamma' \approx 1.3$. Model calculations all yield $\gamma = \gamma'$. Classical models $\gamma = 1$, 2D Ising exact, $\gamma = 7/4$, 3D Ising $\gamma \approx 1.24$, 3d Heisenberg $\gamma = 1.39$.

4. Critical isotherm (δ) We define the critical pressure of the ideal gase as the pressure of the ideal gas at T_c and ρ_c via the ideal gas law

$$p_c^{(0)} = k_B T_c \rho_c$$

which clearly differs from the relation of the vdW model (see equation (3.35) [p. 102]). For the real gas we define the isothermal critical exponent as

$$\frac{p - p_c}{p_c^0} \simeq D \left| \frac{\rho - \rho_c}{\rho_c} \right|^\delta \text{sign}(\rho - \rho_c) \, ; \quad (\text{along the path III, } T = T_c) \, .$$

$$(3.68)$$

If we define

$$B_C^{(0)} = \frac{k_B T_c}{\mu_0 m} \, m$$

with m being the magnetic moment per particle, then the corresponding relation for magnets reads

$$\frac{B}{B_C^{(0)}} \simeq D \left| \frac{M(T = T_c, B)}{M(T = 0, B = 0)} \right|^\delta \text{sign}(M) \, .$$

Experimental values are in the range $\delta \in (4, 5)$. The 2D Ising model yields $\delta = 15$, which far off. The 3D Ising and Heisenberg model yields $\delta = 4.9$ (much better). Classical theories yield $\delta = 3$.

5. Correlation lengths (ν, ν', η)

   We define a pair-correlation function, e.g. density-density or spn-spin,

   $$g(\mathbf{r}, \mathbf{r}') = \langle \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}') \rangle \qquad (3.69)$$

   $$g_{ij} = \langle \Delta\mathbf{S}_i\Delta\mathbf{S}_j \rangle \; . \qquad (3.70)$$

   In the critical regions they behave approximately like

ORNSTEIN-ZERNIKE FUNCTION

$$g(\mathbf{r}, \mathbf{r}') = c_0 \, \frac{e^{-\frac{|\mathbf{r}-\mathbf{r}'|}{\xi(T)}}}{|\mathbf{r} - \mathbf{r}'|} \qquad (3.71)$$

$$g_{ij} = g(\mathbf{r}_i, \mathbf{r}_j) \, , \qquad (3.72)$$

---

with $\xi(T)$ is the correlation length. It diverges on approaching the critical point. For real gases one defines

$$\xi \simeq D_\pm |\varepsilon|^{-\nu_\pm} : \qquad \begin{cases} - & \text{on path II} , \\ + & \text{on path I} . \end{cases} \qquad (3.73)$$

For magnets

$$\xi \simeq D_\pm |\varepsilon|^{-\nu_\pm} : \qquad \begin{cases} - & \text{for } T \nearrow T > T_C, B = 0 , \\ + & \text{for } T \searrow T > T_C, B = 0 . \end{cases} \qquad (3.74)$$

Finally, we also introduce the pair-correlation function at the critical temperature $T = T_c$. According to the Ornstein-Zernike formula in equation (3.71) , at $T = T_c$ the correlation length is infinite and, therefore, the pair-correlation would decrease like $1/|\mathbf{r} - \mathbf{r}'|$. This is, however, not the case for real systems. The behaviour is slightly different and expressed by

$$g(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-(d-2+\eta)} \begin{cases} p = p_C & \text{, real gases ,} \\ B = 0, \text{ magnets .} \end{cases}$$

The Ornstein-Zernike formula would imply $\eta = 3 - d$. For the other critical exponents ν, ν' the deviation from the $1/r$ dependence is negligible, as the the correlation length is obtained from the slope of a fit of

$$\ln(g(r)) = c_0 - \frac{r}{\xi(T)} - (d - 2 + \eta)\ln(r)$$

versus r. Here the last term enters only logarithmically in r.

3.3.2 Scaling laws

Generalized homogeneous functions $f(x, y, \ldots)$ in several variables have the following property for arbitrary real λ

$$f(\lambda^{a_x}x, \lambda^{a_y}y, \ldots) = \lambda f(x, y, \ldots), \tag{3.75}$$

where $a_x, a_x, \ldots$ can be any real numbers. An example would be

$$f(x, y) = 4x^3 + 7y^8,$$

with $a_x = 1/3$ and $a_y = 1/8$, while

$$f(x, y) = x + 6x^2 + xy + y^5$$

is no generalized homogeneous function. Next we will define the scaling hypothesis in the case of the free energy $F(T, B)$ of a magnetic system. We are only interested in the non-analytic parts of F near T_C which we denote by $F(\varepsilon, B)$.

SCALING HYPOTHESIS

$$F(\lambda^{a_\varepsilon}\varepsilon, \lambda^{a_B}B) = \lambda F(\varepsilon, B). \tag{3.76}$$

This is not yet strictly proven in general, but there are many important cases where the scaling hypothesis is fulfilled.

Now we can use the scaling hypothesis to express the critical exponents in terms of the scaling parameters a_ε and a_B. Differentiation w.r.t. B yields

$$\lambda^{a_B}\frac{\partial}{\partial \lambda^{a_B}B}F(\lambda^{a_\varepsilon}\varepsilon, \lambda^{a_B}B) = \lambda\frac{\partial}{\partial B}F(\varepsilon, B).$$

Now we have

$$M = -\frac{\partial F}{\partial B}$$

and therefore we have

$$\lambda^{a_B} M(\lambda^{a_\varepsilon} \varepsilon, \lambda^{a_B} B) = \lambda M(\varepsilon, B) \ . \tag{3.77}$$

1. Exponent β. We use $B = 0$ and obtain

$$M(\lambda^{a_\varepsilon} \varepsilon, 0) = \lambda M(\varepsilon, 0) \ ,$$

   which is valid for any λ, also for

$$\lambda = (-\varepsilon)^{-1/a_\varepsilon} \ ,$$

   resulting in

$$M(\varepsilon, 0) = (-\varepsilon)^{\frac{1-a_B}{a_\varepsilon}} M(-1, 0) \simeq (-\varepsilon)^{\frac{1-a_B}{a_\varepsilon}} \ .$$

   Hence,

$$\beta = \frac{1 - a_B}{a_\varepsilon} \ .$$

2. Exponent δ (critical isotherm) Next we use $\varepsilon = 0$ and have

$$M(0, B) = \lambda^{a_B - 1} M(0, \lambda^{a_B} B) \ .$$

   Here we choose $\lambda = B^{-1/a_B}$ and obtain

$$M(0, B) \simeq B^{\frac{1-a_B}{a_B}}$$
$$B \simeq M^{\frac{a_B}{1-a_B}} \ ,$$

   and hence $\delta = \frac{a_B}{1-a_B}$. In summar, we have

$$a_B = \frac{\delta}{1 + \delta} \tag{3.78}$$

$$a_\varepsilon = \frac{1}{\beta} \frac{1}{1 + \delta} \tag{3.79}$$

$$\tag{3.80}$$

We can express further critical exponents in terms of the scaling parameters, which then in turn allows to find relations among the critical exponents: From the scaling laws one finds

$$\alpha = \alpha' \; ; \quad \gamma = \gamma' \; ; \quad \nu = \nu' \; . \tag{3.81}$$

and also

$$\alpha + 2\beta + \gamma = 2 \tag{3.82}$$
$$\alpha + \beta(1 + \delta) = 2 \tag{3.83}$$
$$\beta = \frac{\gamma}{\delta - 1} \tag{3.84}$$
$$\nu = \frac{\gamma}{2 - \eta} \; . \tag{3.85}$$

3.3.3 Pottsmodel

It can be considered as generalisation of the Ising model, where the spin can take on more than just two values. Usually they are enumerated $s \in \{1, 2, \ldots, q\}$. It is called the *q-state Potts model*. The Hamiltonian of the Potts model reads

---

POTTSMODEL
(*q states*)

$$H_P = -J \sum_{ij} \delta_{s_i s_j} \; , \tag{3.86}$$

---

i.e. when spins on neighbouring sites are equal, they experience a lower energy ($E = -J$) than when the have different spin values ($E = 0$). The Potts model is used to study the behaviour of ferromagnets and other phenomena of solid-state physics.

Apart from statistical physics it is also used in computer science (signal processing) and biology (neural networks).

The strength of the Potts model is not so much that it models these physical systems well; it is rather that the one-dimensional case is exactly solvable, and that it has interesting physical properties. For $d \geq 2$ it shows a phase transition. It is second order for $q \leq 4$ and first order for $q > 4$.

3.3.4   Maxwell Relations

We know

$$dU(S, V, N) = TdS - pdV + \mu dN$$

Hence

$$\left.\frac{\partial U(S, V, N)}{\partial S}\right|_{V,N} = T(S, V, N)$$

$$\left.\frac{\partial U(S, V, N)}{\partial V}\right|_{S,N} = -p(S, V, N) \, .$$

From this we obtain

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = \frac{\partial}{\partial V}\left(\left.\frac{\partial U}{\partial S}\right|_{V,N}\right)\Bigg|_{S,N} = \frac{\partial}{\partial S}\left(\left.\frac{\partial U}{\partial V}\right|_{S,N}\right)\Bigg|_{V,N} = -\left.\frac{\partial p}{\partial S}\right|_{V,N}$$

In the following we use the convention

$$\frac{\partial^2 f(x, y, z)}{\partial x \partial y} = \frac{\partial}{\partial y}\left(\left.\frac{\partial f}{\partial x}\right|_{y,z}\right)\Bigg|_{x,z} \, .$$

and we can simplify the former equation to

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial p}{\partial S}\right|_{V,N} = \frac{\partial^2 U(S, V, N)}{\partial S \partial V} \, .$$

Similarly we find with

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

$$\left.\frac{\partial F(T, V, N)}{\partial V}\right|_{S,N} = -p(T, V, N) \, .$$

the relation

$$\left.\frac{\partial S(T, V, N)}{\partial V}\right|_{T,N} = \left.\frac{\partial p(T, V, N)}{\partial T}\right|_{V,N} = -\frac{\partial^2 F(T, V, N)}{\partial V \partial T}$$

Based on the free enthalpy $G(T, p, N)$ we obtain with

$$\left.\frac{\partial G(T, p, N)}{\partial T}\right|_{p,N} = -S(T, p, N)$$

$$\left.\frac{\partial G(T, p, N)}{\partial p}\right|_{S,N} = V(T, p, N) \, .$$

the relation

$$-\frac{\partial S(T,p,N)}{\partial p}\bigg|_{T,N} = \frac{\partial V(T,p,N)}{\partial T}\bigg|_{p,N} = \frac{\partial^2 G(T,p,N)}{\partial p \partial T}$$

Finally, we introduce the *enthalpy* $H(S,p,N)$ via the Legendre transformation of $U(S,V,N)$ with respect to V, i.e.

$$H(S,p,N) = U(S,V,N) + pV \,,$$

for which we have

$$\frac{\partial H(S,p,N)}{\partial S}\bigg|_{p,N} = T(S,p,N)$$

$$\frac{\partial H(S,p,N)}{\partial p}\bigg|_{S,N} = V(S,p,N) \,.$$

Then we find

$$\frac{\partial T(S,p,N)}{\partial p}\bigg|_{S,N} = \frac{\partial V(S,p,N)}{\partial S}\bigg|_{p,N} = \frac{\partial^2 H(S,p,N)}{\partial p \partial S}$$

We summaries these results

<div style="border:1px solid">

<center>MAXWELLRELATIONS</center>

$$\frac{\partial T(S,V,N)}{\partial V}\bigg|_{S,N} = -\frac{\partial p(S,V,N)}{\partial S}\bigg|_{V,N} = \frac{\partial^2 U(S,V,N)}{\partial S \partial V} \qquad (3.87a)$$

$$\frac{\partial S(T,V,N)}{\partial V}\bigg|_{T,N} = \frac{\partial p(T,V,N)}{\partial T}\bigg|_{V,N} = -\frac{\partial^2 F(T,V,N)}{\partial V \partial T} \qquad (3.87b)$$

$$-\frac{\partial S(T,p,N)}{\partial p}\bigg|_{T,N} = \frac{\partial V(T,p,N)}{\partial T}\bigg|_{p,N} = \frac{\partial^2 G(T,p,N)}{\partial p \partial T} \qquad (3.87c)$$

$$\frac{\partial T(S,p,N)}{\partial p}\bigg|_{S,N} = \frac{\partial V(S,p,N)}{\partial S}\bigg|_{p,N} = \frac{\partial^2 H(S,p,N)}{\partial p \partial S} \,. \qquad (3.87d)$$

</div>

3.3.5 Ehrenfest equations

Next we derive the analogue of Clausius-Clapeyron for second order phase transitions. In this case, S and V are continuous when crossing the phase boundary. Along a phase boundary between phase α and β we therefore have in the Gibbs ensemble (T, p, N) fixed

$$
\begin{aligned}
S_\alpha(T, p, N) &= S_\beta(T, p, N) \\
V_\alpha(T, p, N) &= V_\beta(T, p, N) \,,
\end{aligned}
$$

and also

$$
\begin{aligned}
dS_\alpha &= dS_\beta \\
dV_\alpha &= dV_\beta \,.
\end{aligned}
$$

We can use these equations, to obtain dp/dT along the phase boundary. We combine these equation as

$$
dX_\alpha(T, p, N) = dX_\beta(T, p, N) \,,
$$

where X stands either for S or V. Since N is fixed, it will not vary along the phase boundary. We therefore have

$$
\left.\frac{\partial X_\alpha}{\partial T}\right|_{p,N} dT + \left.\frac{\partial X_\alpha}{\partial p}\right|_{T,N} dp = \left.\frac{\partial X_\beta}{\partial T}\right|_{p,N} dT + \left.\frac{\partial X_\beta}{\partial p}\right|_{T,N} dp \,,
$$

from which we obtain

$$
\left(\left.\frac{\partial X_\beta}{\partial T}\right|_{p,N} - \left.\frac{\partial X_\alpha}{\partial T}\right|_{p,N}\right) dT = -\left(\left.\frac{\partial X_\beta}{\partial p}\right|_{T,N} - \left.\frac{\partial X_\alpha}{\partial p}\right|_{T,N}\right) dp
$$

$$
\frac{dp}{dT} = -\frac{\left.\frac{\partial X_\beta}{\partial T}\right|_{p,N} - \left.\frac{\partial X_\alpha}{\partial T}\right|_{p,N}}{\left.\frac{\partial X_\beta}{\partial p}\right|_{T,N} - \left.\frac{\partial X_\alpha}{\partial p}\right|_{T,N}} := -\frac{\left.\Delta\frac{\partial X_\beta}{\partial T}\right|_{p,N}}{\left.\frac{\partial \Delta X_\beta}{\partial p}\right|_{T,N}}
$$

If we insert S for X we find

$$
\frac{dp}{dT} = -\frac{\left.\Delta\frac{\partial S}{\partial T}\right|_{p,N}}{\left.\frac{\partial \Delta S}{\partial p}\right|_{T,N}} \,. \tag{3.88}
$$

We use

$$\frac{\partial S}{\partial T}\bigg|_{p,N} = \frac{1}{T}C_p \ ,$$

and from the Maxwell relations we use

$$\frac{\partial S}{\partial p}\bigg|_{T,N} = -\frac{\partial V}{\partial T}\bigg|_{p,N} \ .$$

The change in volume w.r.t. temperature is related to the α

COEFFICIENT OF THERMAL EXPANSION
(*for constant pressure*)

$$\alpha_p := \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_{p,N} \qquad (3.89)$$

With these response functions, we find

$$\frac{dp}{dT}\bigg|_{\text{ph.b.}} = \frac{1}{VT}\frac{\Delta C_p}{\Delta \alpha_p} \ . \qquad (3.90)$$

Alternatively, if we use V as X, we have

$$\frac{dp}{dT} = -\frac{\Delta \frac{\partial V}{\partial T}\big|_{p,N}}{\frac{\partial \Delta V}{\partial p}\big|_{T,N}} \ . \qquad (3.91)$$

Here we employ the relations

$$\alpha_p = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_{p,N}$$

$$\kappa_p = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_{T,N} \ ,$$

and find

$$\frac{dp}{dT}\bigg|_{\text{ph.b.}} = \frac{\Delta \alpha_p}{\Delta \kappa_p} \ . \qquad (3.92)$$

In summary we have the

ЕHRENFEST EQUATIONS

$$\left.\frac{dp}{dT}\right|_{\text{ph.b.}} = \frac{\Delta\alpha_p}{\Delta\kappa_p} = \frac{1}{VT}\frac{\Delta C_p}{\Delta\alpha_p}. \tag{3.93}$$

3.4   Ising again

$$s := \sinh(2K)$$

$$f = \frac{F}{JN} = -K\left[\frac{\ln(2)}{2} + \frac{1}{4\pi}\int_0^{2\pi}\log\left(1 + s^4 + \sqrt{1 + s^4 - 2s^2\cos(x)}\right)dx\right]$$

T_c from

$$s_c = \sinh(2K_c) = 1$$
$$K_c = J\beta_c = 0.440687$$
$$\frac{k_B T_c}{J} = 2.26919\,.$$

$$u = \frac{U}{JN} = -\coth(2K)\left[1 + \frac{2(2\tanh^2(2K) - 1)}{\pi}\int_0^{\pi/2}\frac{1}{\sqrt{1 - \frac{4k}{(1+k)^2}\sin^2(x)}}\right]$$

For $T \leq T_c$

$$M(T) = \left[1 - \left(\sinh^{-4}(2K)\right)\right]^{1/8}.$$

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial F}{\partial \beta}\frac{d\beta}{dT} = \frac{J}{k_B T^2}\frac{\partial F}{\partial J\beta}$$

$$= \frac{K}{T}\frac{\partial F}{\partial K} = \frac{KJN}{T}\frac{\partial f}{\partial K}$$

$$\frac{S}{N} = k_B\frac{KJ}{k_B T}\frac{\partial f}{\partial K}$$

$$s = \frac{S}{k_B N} = K^2\frac{\partial f}{\partial K}$$

$$U = F + TS = fJN + Tsk_B N$$

$$= JN\left(f + \frac{Tk_B}{J}s\right)$$

$$u = f + \frac{s}{K}$$

$$s = Kf - K^3\frac{d}{dK}\frac{1}{4\pi}\int_0^{2\pi}\log\left(1 + s^2 + \sqrt{1 + s^4 - 2s^2\cos(x)}\right)dx$$

$$= Kf - K^3\left(\frac{d}{ds}\frac{1}{4\pi}\int_0^{2\pi}\log\left(1 + s^2 + \sqrt{1 + s^4 - 2s^2\cos(x)}\right)dx\right)\frac{d}{dK}\sinh(2K)$$

$$= K\left(f - K^2\left(\frac{d}{ds}\frac{1}{4\pi}\int_0^{2\pi}\log\left(1 + s^2 + \sqrt{1 + s^4 - 2s^2\cos(x)}\right)dx\right)! \, 2\sqrt{1 + s^2}\right).$$

$$u = f + \frac{s}{K}$$

Chapter 4

Appendix

4.1 Sommerfeld expansion

We are interested in integrals of the form

$$I = \int_0^\infty f(\varepsilon) n_F(\varepsilon | \mu, T) \, d\varepsilon$$

for low temperatures. The function $f(\varepsilon)$ is assumed to be independent of T and regular at $\varepsilon = \mu$. First we split the integral as follows

$$I = \int_0^\mu f(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \, d\varepsilon + \int_\mu^\infty f(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \, d\varepsilon \, ,$$

and modify the first term using $1/(e^x + 1) = 1 - 1/(e^{-x} + 1)$

$$I = \underbrace{\int_0^\mu f(\varepsilon) \, d\varepsilon}_{=I_1} - \underbrace{\int_0^\mu f(\varepsilon) \frac{1}{e^{-\beta(\varepsilon - \mu)} + 1} \, d\varepsilon}_{=I_2} + \underbrace{\int_\mu^\infty f(\varepsilon) \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \, d\varepsilon}_{=I_3}$$

In I_2 we use the transformation

$$x = -\beta(\varepsilon - \mu) \, ,$$
$$\varepsilon = \mu - k_B T \, x \, ,$$
$$d\varepsilon = -k_B T dx \, ,$$

and find

$$I_2 = -k_B T \int_0^{\beta\mu} \frac{f(\mu - k_B T x)}{e^x + 1} \, .$$

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The kernel $1/(e^x - 1)$ decreases rapidly with x and for small values of T the upper integration limit $\beta\mu$ is much greater than 1, so we can as well extend the integral all the way up to infinity

$$I_2 = -k_B T \int_0^\infty \frac{f(\mu - k_B T x)}{e^x + 1} \ .$$

For I_3 we introduce the substitution

$$x = \beta(\varepsilon - \mu) \ ,$$
$$\varepsilon = \mu + k_B T \, x \ ,$$
$$d\varepsilon = k_B T dx \ ,$$

and obtain

$$I_3 = k_B T \int_0^\infty \frac{f(\mu + k_B T x)}{e^x + 1} \ .$$

Since $1/(e^x + 1)$ decreases rapidly, x is essentially restricted to $x \lesssim 1$. Hence $k_B T x \lesssim k_B T$. So if $k_B T / \mu$ is small, then we can use a Taylor expansion

$$f(\mu + \sigma k_B T x) = \sum_{n=1}^\infty (\sigma)^{n+1} \frac{(k_B T x)^{n-1}}{\Gamma(n)} f^{(n-1)}(\mu) \ .$$

We need

$$I_3 - I_2 = k_B T \int_0^\infty dx \left(f(\mu + k_B T x) - f(\mu + k_B T x) \right) \frac{1}{e^x + 1}$$

$$= 2 \sum_{n=1}^{\text{odd}} (k_B T)^{n+1} \frac{1}{n!} f^{(n)}(\mu) \int_0^\infty dx \frac{x^n}{e^x + 1}$$

$$= 2 \sum_{n=1}^{\text{odd}} (k_B T)^{n+1} \frac{1}{n!} f^{(n)}(\mu) \left(1 - \frac{1}{2^n} \right) \Gamma(n+1) \zeta(n+1)$$

$$= 2 \sum_{n=1}^{\text{odd}} \left(1 - \frac{1}{2^n} \right) \zeta(n+1) (k_B T)^{n+1} f^{(n)}(\mu)$$

The final result reads

SOMMERFELD EXPANSION

$$\int_0^\infty f(\varepsilon) n_F(\varepsilon|\mu, T) d\varepsilon = \int_0^\mu f(\mu) + 2 \sum_{n=1}^{\text{odd}} \left(1 - \frac{1}{2^n}\right) \zeta(n+1) \left(k_B T\right)^{n+1} f^{(n)}(\mu)$$

(4.1)

So the leading order terms in the Sommerfeld expansion are

$$I = \int_0^\mu f(\varepsilon) d\varepsilon + \frac{\pi^2}{6} \left(k_B T\right)^2 f'(\mu) + \mathcal{O}\left(\left(\frac{k_B T}{\mu}\right)^4\right)$$

4.2   Euler Mac-Laurin formula

We are interested in sums of the form $\sum_{n=0}^\infty f(n + \frac{1}{2})$. We begin with the integral over $f(x)$, which shall be differentiable at least twice and the integral over $(0, \infty)$ shall exist. Then

$$\int_0^\infty f(x) dx = \sum_{n=0}^\infty \int_n^{n+1} f(x) dx = \sum_{n=0}^\infty \int_{-\frac{1}{2}}^{\frac{1}{2}} f(n + \tfrac{1}{2} + \xi) d\xi$$

$$= \sum_{n=0}^\infty \int_{-\frac{1}{2}}^{\frac{1}{2}} \left(f(n + \tfrac{1}{2}) + f'(n + \tfrac{1}{2})\xi + f''(n + \tfrac{1}{2})\frac{\xi^2}{2} + \dots \right) d\xi$$

$$= \sum_{n=0}^\infty \left(f(n + \tfrac{1}{2}) \int_{-\frac{1}{2}}^{\frac{1}{2}} d\xi + f'(n + \tfrac{1}{2}) \int_{-\frac{1}{2}}^{\frac{1}{2}} \xi d\xi + \frac{f''(n + \tfrac{1}{2})}{2} \int_{-\frac{1}{2}}^{\frac{1}{2}} \xi^2 d\xi + \dots \right) d\xi$$

$$= \sum_{n=0}^\infty \left(f(n + \tfrac{1}{2}) + f''(n + \tfrac{1}{2})\frac{2}{2 \cdot 3 \cdot 2^3} + \dots \right) d\xi .$$

The leading order terms are

$$\sum_{n=0}^\infty f(n + \tfrac{1}{2}) = \int_0^\infty f(x) dx - \frac{1}{24} \sum_{n=0}^\infty f''(n + \tfrac{1}{2}) + \dots$$

We can use this formula again to express the sum on the rhs also by an integral, resulting in

$$\sum_{n=0}^\infty f(n + \tfrac{1}{2}) = \int_0^\infty f(x) dx - \frac{1}{24} \left(\int_0^\infty f''(x) dx - \frac{1}{24} \sum_{n=0}^\infty f^{(iv)}(n + \tfrac{1}{2}) \right) + \dots ,$$

and we obtain

EULER-MACLAURIN FORMULA
(leading order)

$$\sum_{n=0}^{\infty} f(n + \tfrac{1}{2}) = \int_0^{\infty} f(x)dx + \frac{1}{24}f'(0) - \frac{1}{24}f'(\infty) + \dots \qquad (4.2)$$

These are actually the first terms of the *Euler MacLaurin formula* formula.

4.3 One-particle density of states

The one-particle density of states in D spatial dimensions is

$$
\begin{aligned}
\rho^{(D)}(\varepsilon) &= \sum_{\mathbf{k}} \delta(\varepsilon - \frac{\hbar^2 \mathbf{k}^2}{2m}) \\
&= \frac{V^{(D)}}{(2\pi)^D} \int d^D\mathbf{k}\, \delta\left(\varepsilon - \left(\frac{\hbar \mathbf{k}}{\sqrt{2m}}\right)^2\right) \\
&= \frac{V^{(D)}}{(2\pi)^D} \left(\frac{\sqrt{2m}}{\hbar}\right)^D \int d^D\mathbf{x}\, \delta(\varepsilon - \mathbf{x}^2) \\
&= \frac{V^{(D)}(2m)^{D/2}}{(2\pi)^D \hbar^D} \Omega_D \int_0^{\infty} dx\, x^{D-1}\delta(\varepsilon - x^2) \\
&= \frac{V^{(D)}(2m)^{D/2}}{(2\pi)^D \hbar^D} \Omega_D\, \theta(\varepsilon \geq 0) \int_0^{\infty} dx\, x^{D-1}\frac{\delta(x - \sqrt{\varepsilon})}{2x} \\
&= \frac{V^{(D)}(2m)^{D/2}}{(2\pi)^D \hbar^D} \frac{\Omega_D}{2}\, \varepsilon^{\frac{D-2}{2}}\, \theta(\varepsilon \geq 0)
\end{aligned}
$$

In appendix C of the statistics I script we have derived the surface Ω_D of a a D-dimensional hypersphere of unit radius

$$\Omega_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}.$$

The D-dimensional dos of the free electron gas is therefore

DENSITY OF STATES
(D-dimensional free electron gas)

$$\rho^{(D)}(\varepsilon) = \frac{V^{(D)} m^{\frac{D}{2}}}{\hbar^D (2\pi)^{\frac{D}{2}} \Gamma\left(\frac{D}{2}\right)} \; \varepsilon^{\frac{D-2}{2}} \; \theta(\varepsilon \geq 0) \, . \tag{4.3a}$$

$$\rho^{(1)}(\varepsilon) = \frac{L\sqrt{m}}{\hbar\sqrt{2\pi}} \; \frac{1}{\sqrt{\varepsilon}} \; \theta(\varepsilon \geq 0) \, . \tag{4.3b}$$

$$\rho^{(2)}(\varepsilon) = \frac{V^{(2)} m}{\hbar^2 \, 2 \, \pi} \; \theta(\varepsilon \geq 0) \, , \tag{4.3c}$$

$$\rho^{(3)}(\varepsilon) = \frac{V m^{\frac{3}{2}}}{\hbar^3 \sqrt{2\pi^2}} \; \sqrt{\varepsilon} \; \theta(\varepsilon \geq 0) \, . \tag{4.3d}$$

4.4   Eigenvalues of the free electron gas in a homogeneous magnetic field

Here we determine the one-particle eigenvalues of the free electron gas in a homogeneous magnetic field. Since the electron do not interact with each other, it suffices to consider the hamiltonian of single electron, which reads

$$H = \frac{\left(\hat{\mathbf{p}} + e\hat{\mathbf{A}}\right)^2}{2m} + \mu_B g_e \mathbf{B}\hat{\mathbf{S}} \, ,$$

where $\mathbf{S}$ is the vector operator of the electronic spin. The direction of the magnetic field field defines the z-direction. Since there is no spin-orbit coupling, the eigenvector is a tensor product of the orbital and spin degrees of freedom. For the letter the vector is the eigenvector of the operator S_z, i.e.

$$|\psi\rangle = |\Phi\rangle \otimes |\sigma\rangle$$

The eigenvalue problem turns into

$$H|\psi\rangle = |\sigma\rangle \otimes \left(\frac{\left(\hat{\mathbf{p}} + e\hat{\mathbf{A}}\right)^2}{2m} + \underbrace{\frac{\mu_B \hbar g_e}{2} \sigma}_{=b}\right)|\Phi\rangle = \varepsilon|\sigma\rangle \otimes |\Phi\rangle$$

The orbital part of the eigenvalue problem reads

$$\frac{\left(\hat{\mathbf{p}} + e\hat{\mathbf{A}}\right)^2}{2m}|\Phi\rangle = \varepsilon'|\Phi\rangle$$

and the the eigenvalues of the entire hamitonian are

$$\varepsilon = \varepsilon' + b\sigma \ .$$

The vector potential for the homogeneous magnetic field in z-direction can be chosen (Landau gauge) as

$$\mathbf{A} = B(0, x, 0) \ .$$

We readily see that it gives the correct **B** field

$$\mathbf{B} = \nabla \times \mathbf{A}$$
$$= \begin{pmatrix} \partial_y A_z - \partial_z A_y \\ \partial_z A_x - \partial_x A_z \\ \partial_x A_y - \partial_y A_x \end{pmatrix}$$
$$= B \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \ .$$

Inserting **A** into the orbital eigenvalue problem gives

$$\frac{\hat{p}_x^2 + (\hat{p}_y + eB\hat{x})^2 + \hat{p}_z^2}{2m}|\Phi\rangle = \varepsilon'|\Phi\rangle$$

The y and z coordinate only enters via the momenta, therefore, the eigenvector is a tensor product of the form

$$|\Phi\rangle = |\Phi_x\rangle \otimes |p_y\rangle \otimes |p_z\rangle \ ,$$

where $|k_x\rangle$ ($|k_x\rangle$) is an eigenvector of the momentum operator p_x (p_y) with the corresponding eigenvalue. Then

$$\frac{\hat{p}_x^2 + (\hat{p}_y + eB\hat{x})^2 + \hat{p}_z^2}{2m}|\Phi\rangle = |p_y\rangle \otimes |p_z\rangle \otimes \frac{\hat{p}_x^2 + (p_y + eB\hat{x})^2 + p_z^2}{2m}|\Phi_x\rangle$$
$$= |p_y\rangle \otimes |p_z\rangle \otimes \left(\varepsilon'|\Phi_x\rangle\right)$$

The remaining 1D problem reads

$$\frac{\hat{p}_x^2 + (p_y + eB\hat{x})^2 + p_z^2}{2m}|\Phi_x\rangle = \varepsilon'|\Phi_x\rangle$$

The electron gas is confined to a box of size $L_x \times L_y \times L_y$. The momentum eigenvalues are therefore quantized as

$$p_y = \hbar \frac{2\pi}{L_y} n_y \, , \qquad \text{with } n_y \in \mathbf{N} \tag{4.4}$$

$$p_z = \hbar \frac{2\pi}{L_z} n_z \, , \qquad \text{with } n_z \in \mathbf{N} \tag{4.5}$$

$$\tag{4.6}$$

The 1D hamiltonian can be rewritten in the form

$$\left(\frac{1}{2m} \hat{p}_x^2 + \frac{eB}{2m} (\hat{x} + \underbrace{\frac{p_y}{eB}}_{:=-x_0})^2 + \frac{p_z^2}{2m} \right) |\Phi_x\rangle = \varepsilon' |\Phi_x\rangle$$

This is the hamiltonian of a harmonic oscillator shifted by x_0. The prefactor of the x^2 term corresponds to $\omega_c/2$, hence $\omega_c = eB/m$. The eigenvalues of the harmonic oscillator yield

$$\varepsilon' = \frac{p_z^2}{2m} + \hbar \omega_c \left(n + \tfrac{1}{2} \right) \, .$$

These eigenvalues are independent of p_y and, therefore, degenerate. p_y defines the center x_0 of the harmonic oscillator, which has to be within $(0, L_x)$, resulting in the condition

$$0 \leq \frac{p_y}{eB} \leq L_x$$

$$0 \leq \frac{\hbar 2\pi}{L_y eB} n_y \leq L_x$$

$$0 \leq n_y \leq \frac{L_x L_y eB}{2\pi\hbar} \, .$$

The number of allowed p_y values defines the degeneracy

$$N_{\text{deg}} = \left\lfloor \frac{L_x L_y eB}{2\pi\hbar} \right\rfloor + 1.$$

This number will be much greater than 1 and we can, therefore, ignore the fact that it has to be an integer and we simply use

$$N_{\text{deg}} = \frac{L_x L_y eB}{2\pi\hbar} \, . \tag{4.7}$$

4.5 Langevin Diamagnetismus

Now we consider the entire free-electron gas model. The single electron energies are now

$$\varepsilon_{n,\sigma}(k_z) = \varepsilon(k_z) + \hbar\omega_c(n + \tfrac{1}{2}) + \sigma b$$

$$\varepsilon(k_z) = \frac{\hbar^2 k_z^2}{2m}$$

with $b = \frac{\mu_B g_e}{2}$ and the cyclotron frequency $\omega_c = \frac{eB}{m}$, and $\mu_B = \frac{e\hbar}{2m}$. The degeneracy of these levels is

$$N_{\text{deg}} = \frac{L_x L_y e B}{2\pi\hbar} = B C_{deg} .$$

We use again the formula for the grand canonical partition function of non-interacting particles

$$\ln(Z) = \sum_\nu \ln\left(1 + {}^{-\beta(\varepsilon_\nu - \mu)}\right)$$

Inserting the one particle energies results in

$$\ln(Z) = B C_{deg} \sum_\sigma \sum_{n=0}^{\infty} \underbrace{\int d\varepsilon \rho^{(1d)}(\varepsilon) \ln\left(1 + e^{-\beta(\varepsilon + \hbar\omega_c(n+\frac{1}{2}) + b\sigma - \mu)}\right)}_{:=F(\mu - \hbar\omega_c(n + \frac{1}{2}) - b\sigma)} . \quad (4.8)$$

$$\underbrace{\phantom{F(\mu - \hbar\omega_c(n + \tfrac{1}{2}) - b\sigma)}}_{:=f(n+\frac{1}{2})}$$

Now we invoke the leading Euler-Mac-Laurin formula in equation (4.2) to leading order and use $f'(\infty) = 0$.

$$\sum_{n=0}^{\infty} f(n + \tfrac{1}{2}) = \int_0^\infty f(x)dx + \frac{1}{24}f'(0) + \dots$$

$$= \int_0^\infty F(\mu - \hbar\omega_c x - b\sigma)dx + \frac{1}{24}\frac{\partial}{\partial x}F(\mu - \hbar\omega_c x - b\sigma)\Big|x = 0 + \dots$$

$$= \frac{1}{\hbar\omega_c}\int_0^\infty F(\mu - y - b\sigma)dy - \frac{\hbar\omega_c}{24}\frac{\partial}{\partial\mu}F(\mu - b\sigma) + \dots .$$

Next we expand this expression in terms of B, or rather b, up to second order. We also include already the sum over the electronic spin, which

allows to omit term proportional to σ^m for odd m.

$$\sum_{\sigma}\sum_{n}f(n+\tfrac{1}{2}) = \sum_{\sigma}\frac{1}{\hbar\omega_c}\left(\int_0^{\infty}F(\mu-y)dy - \cancel{b}\int_0^{\infty}\frac{\partial}{\partial\mu}F(\mu-y)dy+\right.$$

$$\left. +\frac{b^2}{2}\int_0^{\infty}\frac{\partial^2}{\partial\mu^2}F(\mu-y)dy - \frac{(\hbar\omega_c)^2}{24}\frac{\partial}{\partial\mu}F(\mu) + \mathcal{O}(B^4)\right)$$

$$=\frac{2}{\hbar\omega_c}\left(\int_{-\infty}^{\mu}F(z)dz+\right.$$

$$\left. +\frac{b^2}{2}\int_0^{\infty}\frac{\partial^2}{\partial y^2}F(\mu-y)dy - \frac{(\hbar\omega_c)^2}{24}\frac{\partial}{\partial\mu}F(\mu) + \mathcal{O}(B^4)\right)$$

$$=\frac{2}{\hbar\omega_c}\left(\int_{-\infty}^{\mu}F(z)dz+\right.$$

$$\left. +\frac{b^2}{2}\left(\frac{\partial}{\partial\mu}F(\mu-y)\right)\Big|_{y=0}^{y=\infty} - \frac{(\hbar\omega_c)^2}{24}\frac{\partial}{\partial\mu}F(\mu) + \mathcal{O}(B^4)\right)$$

$$=\frac{2}{\hbar\omega_c}\left(\int_{-\infty}^{\mu}F(z)dz+\frac{1}{2}\left(b^2 - \frac{(\hbar\omega_c)^2}{12}\right)\frac{\partial}{\partial\mu}F(\mu) + \mathcal{O}(B^4)\right).$$

Inserting the definition of ω_c and b yields

$$b^2 - \frac{(\hbar\omega_c)^2}{12} = B^2\left(\mu_B^2\left(\frac{g_e}{2}\right)^2 - \frac{1}{12}\left(\frac{\hbar e}{m}\right)^2\right)$$

$$= B^2\mu_B^2\left(\left(\frac{g_e}{2}\right)^2 - \frac{4}{12}\right)$$

The grand potential up to order B^2 reads

$$\Omega = -k_B T\ln(Z)$$

$$= \underbrace{-\frac{2k_B T C_{deg} B}{\hbar\omega_c}}_{=D}\left(\int_0^{\infty}F(\mu-y)dy + \frac{\mu_B^2 B^2}{2}\left(\left(\frac{g_e}{2}\right)^2 - \frac{4}{12}\right)\frac{\partial}{\partial\mu}F(\mu)\right)$$

$$= D\int_0^{\infty}F(\mu-y)dy + \frac{1}{2}\left(\left(\frac{g_e}{2}\right)^2 - \frac{4}{12}\right)D\frac{\partial}{\partial\mu}F(\mu).$$

For $B = 0$ we obtain

$$\Omega(T,\mu,B=0) = D\int_0^{\infty}F(\mu-y)dy$$

We can exploit

$$\frac{\partial}{\partial \mu} \int_{-\infty}^{\mu} F(z)dz = F(\mu)$$

$$\Rightarrow \qquad \frac{\partial}{\partial \mu} F(\mu) = \frac{\partial^2}{\partial \mu 2} \int_{-\infty}^{\mu} F(z)dz$$

to rewrite the grand potential as

$$\Omega(T, \mu, B) = \Omega(T, \mu, B = 0) + \frac{\mu_B^2 B^2}{2}\left(\left(\frac{g_e}{2}\right)^2 - \frac{1}{3}\right)\frac{\partial^2}{\partial \mu^2}\Omega(T, \mu, B = 0) .$$

The susceptibility is defined as

$$\chi = -\left.\frac{\partial \Omega}{\partial B^2}\right|_{\mu,T} = -\mu_B^2\left(\left(\frac{g_e}{2}\right)^2 - \frac{1}{3}\right)\frac{\partial^2}{\partial \mu^2}\Omega(T, \mu, B = 0) ,$$

Finally, we exploit the equation $\left.\frac{\partial \Omega}{\partial \mu}\right|_{T,B} = N(T, \mu, B)$ resulting in

$$\chi = -\left.\frac{\partial \Omega}{\partial B^2}\right|_{\mu,T} = \left(1 - \frac{1}{3}\left(\frac{2}{g_e}\right)^2\right)\left(\mu_B^2\left(\frac{g_e}{2}\right)^2\frac{\partial}{\partial \mu}N(T, \mu, B = 0)\right) ,$$

According to equation (2.38) [p. 73] the last bracket is equal to the Pauli-spin susceptibility, i.e.

$$\chi = \chi_P - \frac{1}{3}\left(\frac{2}{g_e}\right)^2\chi_P$$

The additional term is called *Landau Diamagnetism* and for $g_e \approx 2$ is is

$$\chi_L = -\frac{1}{3}\chi_P$$

The total susceptibility is still positive

$$\chi \approx \frac{2}{3}\chi_P .$$

4.6 Bogoliubov inequality

Here we will prove the Bogoliubov inequality. To this end we will exploit the Schwarz inequality

$$|(A|B)|^2 \leq (A|A)(B|B) , \tag{4.9}$$

where $(X|Y)$ are scalar products between any vectors A and B. To be able to use this relation, we have to introduce a suitable scalar product, that involves the operators A and B

$$\left(A|B\right) := \sum_{n,m}^{E_m \neq E_n} \langle m|A^\dagger|n\rangle\langle n|B|m\rangle \frac{\rho_m - \rho_n}{E_n - E_m}$$

with

$$\rho_m = \frac{e^{-\beta E_m}}{\mathrm{tr}\left\{e^{-\mathrm{fiH}}\right\}} .$$

This product fulfils the four defining properties of a scalar product

- $(A|B) = (B|A)^*$ This is obviously the case

$$\begin{aligned}
\left(B|A\right)^* &= \sum_{n,m}^{E_m \neq E_n} \left(\langle m|B^\dagger|n\rangle\langle n|A|m\rangle\right)^* \frac{\rho_m - \rho_n}{E_n - E_m} \\
&= \sum_{n,m}^{E_m \neq E_n} \langle n|A|m\rangle^*\langle m|B^\dagger|n\rangle^* \frac{\rho_m - \rho_n}{E_n - E_m} \\
&= \sum_{n,m}^{E_m \neq E_n} \langle m|A^\dagger|n\rangle\langle n|B|m\rangle \frac{\rho_m - \rho_n}{E_n - E_m} , \qquad \checkmark
\end{aligned}$$

- Linearity $\left(A|\alpha B_1 + \beta B_2\right) = \alpha\left(A|B_1\right) + \beta\left(A|B_2\right)$, which follows from the linearity of the matrix elements $\bar{n}B|n\rangle$.

- $(A|A) \geq 0$, since

$$\left(A|A\right) = \sum_{n,m}^{E_m \neq E_n} \underbrace{|\langle n|A^\dagger|m\rangle)|^2}_{\geq 0} \underbrace{\frac{\rho_m - \rho_n}{E_n - E_m}}_{\geq 0} .$$

- From $A = 0$ follows clearly $(A|A) = 0$, but not conversly

So we can conclude that $(A|B)$ is a semi-definite scalar product, for which the Schwarz inequality applies. In addition, the product has the special feature

$$\left(H|A\right) = 0 , \qquad \forall\text{operators } A . \tag{4.10}$$

This is easily seen, since $\bar{m}|H^\dagger|n\rangle = E_n\delta_{mn}$; but $m = n$ is excluded from he sum.

Next we exploit it for the prove of the Bogoliubov inequality. To this end, we first use $B = [C^\dagger, H]$ in the Schwarz relation. For the lhs we need $(A|B)$

$$
\begin{aligned}
(A|B) &= \left(A \middle| [C^\dagger, H]\right) \\
&= \sum_{mn}^{E_m \neq E_n} \langle m|A^\dagger|n\rangle \, \langle n|[C^\dagger, H]|m\rangle \frac{\rho_m - \rho_n}{E_n - E_m} \\
&= \sum_{mn}^{E_m \neq E_n} \langle m|A^\dagger|n\rangle \, \langle n|C^\dagger|m\rangle (E_m - E_n) \frac{\rho_n - \rho_m}{E_m - E_n} \\
&= \sum_{mn}^{E_m \neq E_n} \langle m|A^\dagger|n\rangle \, \langle n|C^\dagger|m\rangle (\rho_n - \rho_m) \\
&= \sum_{mn} \rho_n \langle n|C^\dagger|m\rangle \, \langle m|A^\dagger|n\rangle - \sum_{mn}^{E_m \neq E_n} \rho_m \langle m|A^\dagger|n\rangle \, \langle n|C^\dagger|m\rangle .
\end{aligned}
$$

In the last step we have omitted the restriction in the sum, since $\rho_m - \rho_n = 0$, if $E_m = E_n$. Eventually, we have

$$
(A|B) = \left\langle [C^\dagger, A^\dagger]_- \right\rangle \tag{4.11}
$$

If we also choose $A = B = [C^\dagger, H]_-$ in equation (4.11), we obtain

$$
(B|B) = \left\langle [C^\dagger, [H, C]]_- \right\rangle = \left\langle [[C, H], C^\dagger]_- \right\rangle \geq 0 \tag{4.12}
$$

Finally, we consider for $E_n \neq E_m$

$$
0 < \frac{\rho_m - \rho_n}{E_n - E_m} = \frac{\rho_m + \rho_n}{E_n - E_m} \underbrace{\frac{\rho_m - \rho_n}{\rho_m + \rho_n}}_{=\tanh\left(\frac{\beta}{2}(E_n - E_m)\right)}
$$

$$
0 < \frac{\beta}{2} \left(\rho_m + \rho_n\right) \frac{\tanh\left(\frac{\beta}{2}(E_n - E_m)\right)}{\frac{\beta}{2}(E_n - E_m)} .
$$

Since $\tanh(x)/x < 1$, we find

$$
0 < \frac{\rho_m - \rho_n}{E_n - E_m} < \frac{\beta}{2} \left(\rho_m + \rho_n\right) .
$$

From this relation we obtain

$$
(A|A) = \sum_{mn}^{E_m \neq E_n} \langle n|A^\dagger|m\rangle \langle m|A|n\rangle \frac{\rho_m - \rho_n}{E_n - E_m} < \frac{\beta}{2} \sum_{mn}^{E_m \neq E_n} \langle n|A^\dagger|m\rangle \langle m|A|n\rangle \left(\rho_m + \rho_n\right) .
$$

The omitted terms for $E_n = E_m$ are positive, so including them assures the inequality

$$\left(A|A\right) < \frac{\beta}{2} \sum_{mn} \langle n|A^\dagger|m\rangle \langle m|A|n\rangle \left(\rho_m + \rho_n\right) = \frac{\beta}{2} \langle [A^\dagger, A]_+ \rangle \qquad (4.13)$$

Now return the the Schwarz inequality in equation (4.9) [p. 135]

$$|(A|B)|^2 \leq (A|A)(B|B), \qquad (4.14)$$

and insert piece by piece the relations we just derived for the various terms. Beginning with equation (4.11) [previous page] and equation (4.12) [previous page] we get

$$\langle [C, A] \rangle^2 \leq (A|A) \left\langle [[C, H], C^\dagger]_- \right\rangle,$$

Along with equation (4.13) we finally obtain

$$\langle [C, A] \rangle^2 \leq \frac{\beta}{2} \langle [A^\dagger, A]_+ \rangle \left\langle [[C, H], C^\dagger]_- \right\rangle, \qquad (4.15)$$

which proves the Bogoliubov inequality.

4.7   Proof used for the Bogoliubov inequality

Here we prove the relation

$$\left\langle \left[[C, H]_-, C^\dagger \right]_- \right\rangle \leq 4\hbar^2 N \left(|b\mathcal{S}_{\mathbf{Q}}(T, b)| + \mathbf{k}^2 X \right). \qquad (4.16)$$

We recall that

$$C = S_{\mathbf{k}}^+ = \sum_l e^{i\mathbf{k}\mathbf{R}_l} S_l^+ .$$

Hence We begin with $[S_k^+, H]_-$

$$[C, H_H]_- = [S_{\mathbf{k}}^+, H_H]_-$$

$$= -\sum_l e^{i\mathbf{R}_l\mathbf{k}} \sum_{jj'} J_{jj'}\left([S_l^+, S_j^+ S_{j'}^-] + [S_l^+, S_j^z S_{j'}^z] \right)$$

$$= -\sum_l e^{i\mathbf{R}_l\mathbf{k}} \sum_{jj'} J_{jj'}\left(S_j^+ [S_l^+, S_{j'}^-] + S_j^z[S_l^+, S_{j'}^z] + [S_l^+, S_j^z]S_{j'}^z \right)$$

$$= -\hbar\sum_l e^{i\mathbf{R}_l\mathbf{k}} \sum_{jj'} J_{jj'}\left(2S_j^+ \delta_{lj'}S_l^z - S_j^z\delta_{lj'}S_l^+ - \delta_{lj}S_l^+ S_{j'}^z \right)$$

$$= -\hbar\sum_l e^{i\mathbf{R}_l\mathbf{k}} \sum_{j} J_{jl}\left(2S_j^+ S_l^z - S_j^z S_l^+ - S_l^+ S_j^z \right)$$

$$= -2\hbar\sum_l e^{i\mathbf{R}_l\mathbf{k}} \sum_{j} J_{jl}\left(S_j^+ S_l^z - S_l^+ S_j^z \right).$$

We have used the symmetry $J_{jj'} = J_{j'j}$ and $S_j^z S_l^+ = S_l^+ S_j^z + [S_j^z S_l^+]$. The commutator is proportional to δ_{jl} and hence to J_{jj}, which is zero. Meanwhile we have

$$[C, H_H]_- = -2\hbar\sum_{lj} \left(e^{i\mathbf{R}_l\mathbf{k}} - e^{i\mathbf{R}_j\mathbf{k}} \right) J_{jl}\, S_j^+ S_l^z .$$

We continue with the second commutator

$$\left[[C, H_H]_-, C^\dagger\right]_- = -2\hbar\sum_{lj} \left(e^{i\mathbf{R}_l\mathbf{k}} - e^{i\mathbf{R}_j\mathbf{k}} \right) J_{jl} \sum_{l'} e^{-i\mathbf{k}\mathbf{R}_{l'}} \left[S_j^+ S_l^z, S_{l'}^-\right] .$$

With

$$\left[S_j^+ S_l^z, S_{l'}^-\right] = S_j^+ \left[S_l^z, S_{l'}^-\right] + \left[S_j^+, S_{l'}^-\right] S_l^z$$
$$= -\delta_{ll'}\hbar S_j^+ S_l^- + 2\hbar\delta_{l'j} S_j^z S_l^z$$

we obtain

$$\left[[C, H_H]_-, C^\dagger\right]_- = -2\hbar^2\sum_{lj} \left(e^{i\mathbf{R}_l\mathbf{k}} - e^{i\mathbf{R}_j\mathbf{k}} \right) J_{jl}\left(-e^{-i\mathbf{k}\mathbf{R}_l} S_j^+ S_l^- + 2e^{-i\mathbf{k}\mathbf{R}_j} S_j^z S_l^z \right)$$

$$= 2\hbar^2\sum_{lj} J_{jl}\left(\left(1 - e^{i(\mathbf{R}_j-\mathbf{R}_l)\mathbf{k}}\right)S_j^+ S_l^- - 2\left(e^{-i(\mathbf{R}_j-\mathbf{R}_l)\mathbf{k}} - 1\right)S_j^z S_l^z \right)$$

$$= 2\hbar^2\sum_{lj} J_{jl}\left(1 - e^{i(\mathbf{R}_j-\mathbf{R}_l)\mathbf{k}}\right)\left(S_j^+ S_l^- + 2S_j^z S_l^z \right).$$

In the last step we have substituted $j \leftrightarrow l$ and used the symmetry of J_{jl}. Finally, we repeat the calculation for the field term

$$[C, H_b]_- = [S_{\mathbf{k}}^+, H_b]_- = b \sum_{ll'} e^{i\mathbf{R}_l \mathbf{k}} e^{i\mathbf{R}_{l'} \mathbf{Q}} \underbrace{[S_l^+, S_{l'}^z]}_{=-\delta_{ll'} \hbar S_l^+}$$

$$= b\hbar \sum_l e^{i\mathbf{R}_l(\mathbf{k}+\mathbf{Q})} S_l^+ .$$

Then

$$\left[[C, H_b]_-, C^\dagger\right] = b\hbar \sum_l e^{i\mathbf{R}_l(\mathbf{k}+\mathbf{Q})} \sum_{l'} e^{-i\mathbf{k}\mathbf{R}_{l'}} \underbrace{[S_l^+, S_{l'}^-]}_{=\delta_{ll'} 2\hbar S_l^z}$$

$$= 2b\hbar^2 \sum_l e^{i\mathbf{R}_l \mathbf{Q}} S_l^z$$

$$= 2b\hbar^2 S_{\mathbf{Q}}^z$$

$$= 2bN\hbar^2 \mathcal{S}_{\mathbf{Q}}(T, b) .$$

Hence for $C = C_{\mathbf{k}}$ we have

$$\left\langle [[C_{\mathbf{k}}, H]_-, C_{\mathbf{k}}^\dagger] \right\rangle = 2bN\hbar^2 \mathcal{S}_Q(T, b)$$

$$+ \quad 2\hbar^2 \sum_{lj} J_{jl} \left(1 - e^{i(\mathbf{R}_j - \mathbf{R}_l)\mathbf{k}}\right) \left(\underbrace{\langle S_j^+ S_l^- \rangle + \langle S_j^z S_l^z \rangle}_{=\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle} + \langle S_j^z S_l^z \rangle \right)$$

$$= 2bN\hbar^2 \mathcal{S}_Q(T, b)$$

$$+ \quad 2\hbar^2 \sum_{lj} J_{jl} \left(1 - e^{i(\mathbf{R}_j - \mathbf{R}_l)\mathbf{k}}\right) \left(\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle + \left\langle S_j^z S_l^z \right\rangle \right) .$$

From equation (4.12) we know that $\left[[C, H_b]_-, C^\dagger\right]$ originates from the scalar product $(B|B)$. It is therefore a real and non-negative function for all $\mathbf{k}$. Then

$$\left\langle [[C_{\mathbf{k}}, H]_-, C_{\mathbf{k}}^\dagger] \right\rangle \leq \left\langle [[C_{\mathbf{k}}, H]_-, C_{\mathbf{k}}^\dagger] \right\rangle + \left\langle [[C_{-\mathbf{k}}, H]_-, C_{-\mathbf{k}}^\dagger] \right\rangle$$

$$\left\langle [[C_{\mathbf{k}}, H]_-, C_{\mathbf{k}}^\dagger] \right\rangle \leq 4bN\hbar^2 \mathcal{S}_Q(T, b)$$

$$+ \quad 4\hbar^2 \sum_{lj} J_{jl} \left(1 - \cos\left(\mathbf{R}_j - \mathbf{R}_l\right)\mathbf{k}\right) \left(\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle + \left\langle S_j^z S_l^z \right\rangle \right)$$

$$\leq 4N\hbar^2 |b\mathcal{S}_Q(T, b)|$$

$$+ \quad 4\hbar^2 \sum_{lj} |J_{jl}| \underbrace{\left(1 - \cos\left(\mathbf{R}_j - \mathbf{R}_l\right)\mathbf{k}\right)}_{\geq 0} \left(|\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle| + |\left\langle S_j^z S_l^z \right\rangle| \right) .$$

Finally, we can use the Schwarz inequality for the scalar products $\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle$

$$|\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle|^2 \leq \langle \mathbf{S}_j^2 \rangle \langle \mathbf{S}_l^2 \rangle = \left(\hbar^2 S(S+1) \right)^2$$

$$|\langle \mathbf{S}_j \cdot \mathbf{S}_l \rangle| \leq \hbar^2 S(S+1) \ .$$

Moreover, $|\langle S_j^z S_l^z \rangle| \leq |\langle S_j S_l \rangle| \leq \hbar^2 S(S+1)$. In total we have

$$\left\langle [[C,H]_-, C^\dagger] \right\rangle \leq 4N\hbar^2 \left(|b\mathcal{S}_Q(T,b)| + 2S(S+1) \frac{1}{N} \sum_{jl} |J_{jl}| \left(1 - \cos\left(\mathbf{R}_j - \mathbf{R}_l)\mathbf{k} \right) \right) \right)$$

Moreover we use

$$1 - \cos(x) \leq \frac{x^2}{2} \ ,$$

and obtain

$$\left\langle [[C,H]_-, C^\dagger] \right\rangle \leq 4N\hbar^2 \left(|b\mathcal{S}_Q(T,b)| + \underbrace{\mathbf{k}^2 \frac{S(S+1)}{N} \sum_{jl} |J_{jl}| |\mathbf{R}_j - \mathbf{R}_l|^2}_{=X \text{with } 0 \leq X < \infty} \right)$$

Which proves equation (4.16) [p. 138].

Chapter 5

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