# Statistical Physics (Part II)

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## Contents

# I. REAL SYSTEMS: SYSTEMS WITH INTERACTIONS

## A. Classical limit

Consider a gas of $N$ interacting classical indistinguishable particles. The Hamilton function reads

$$H = \sum_{i=1}^{N} \left[ \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j) \ . \tag{1}$$

For the partition function we obttain

$$Z = \frac{1}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^3} \int d^{3N}r \, e^{-\beta H(\{\mathbf{p}_i\},\{\mathbf{r}_i\})} \ . \tag{2}$$

We can separate the integrals over momenta from those over coordinates:

$$Z = \frac{1}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^3} e^{-\beta H_{\text{kin}}(\{\mathbf{p}_i\})} \int d^{3N}r \, e^{-\beta H_{\text{pot}}(\{\mathbf{r}_i\})} \, e^{-\beta H_{\text{int}}(\{\mathbf{r}_i\})} \ . \tag{3}$$

The first integral (over momenta) can easily be calculated using

$$\int \frac{dp_x dp_y dp_z}{(2\pi\hbar)^3} \, e^{-\beta \frac{\mathbf{p}^2}{2m}} = \frac{1}{\lambda_{\text{T}}^3} \ , \tag{4}$$

where $\lambda_{\text{T}} = \sqrt{\frac{2\pi\hbar^2}{mk_{\text{B}}T}}$ is the thermal length. We obtain, thus

$$Z = \frac{1}{N!} \frac{1}{\lambda_T^{3N}} \int d^{3N}r \, e^{-\beta H_{\text{pot}}(\{\mathbf{r}_i\})} \, e^{-\beta H_{\text{int}}(\{\mathbf{r}_i\})} \tag{5}$$

The remaining integral over coordinates is very complicated and cannot be evaluated exactly. Thus we have to resort to approximative methods.

## B. Quantum regime

In the quantum case the situation is even worse. The part of the Hamiltonian corresponding to the kinetic energy does not commute with the rest $[H_{\text{kin}}, H_{\text{pot}} + H_{\text{int}}] \neq 0$. Thus $e^{-\beta H} \neq e^{-\beta H_{\text{kin}}} e^{-\beta(H_{\text{pot}} + H_{\text{int}})}$ and

$$Z = \text{Tr} \left[ e^{-\beta H} \right] \neq \text{Tr} \left[ e^{-\beta H_{\text{kin}}} \right] \text{Tr} \left[ e^{-\beta(H_{\text{pot}} + H_{\text{int}})} \right] \ . \tag{6}$$

We have to find proper approximations.

## II. THERMODYNAMIC PERTURBATION THEORY

Assume the Hamilton operator can be split into a relatively simple "zeroth order" part $H_0$ and a perturbation $gV$, i.e., $H = H_0 + gV$. Here $g$ is a small dimensionless coupling constant. We have to calculate the density matrix

$$\rho = \frac{1}{Z}\, e^{-\beta H} \tag{7}$$

as well as the (canonical) partition function

$$Z = \mathrm{Tr}[e^{-\beta H}] \tag{8}$$

and the free energy

$$F = -\frac{1}{\beta}\, \ln(Z)\ . \tag{9}$$

The idea is that these three objects can be expanded in series of powers of $g$. That is

$$\rho = \rho_0 + g\rho_1 + \dots\ , \tag{10}$$

$$Z = Z_0 + gZ_1 + \dots\ , \tag{11}$$

$$F = F_0 + gF_1 + \dots\ . \tag{12}$$

Note that $Z_1$, $Z_2$ etc. have a completely different meaning here as compared to the following section about the virial expansion (Sec. III). The zeroth order is easy to calculate: $\rho_0 = (1/Z_0)e^{-\beta H_0}$, $Z_0 = \mathrm{Tr}[e^{-\beta H_0}]$, $F_0 = -(1/\beta)\ln(Z_0)$. Our task is to calculate the corrections.

We investigate the exponent $e^{-\tau H}$. In particular we are interested in its value for $\tau = \beta$. We observe that $\tau$ can be thought of as an imaginary time, i.e. $e^{-itH} = e^{-\tau H}$ for $t = -i\tau$. We have $e^{-\tau H} = e^{-\tau H_0} S(\tau)$, where

$$S(\tau) \equiv e^{\tau H_0} e^{-\tau H}\ . \tag{13}$$

The operator $S$ satisfies the following differential equation

$$\begin{aligned} \frac{\partial}{\partial\tau} S(\tau) &= e^{\tau H_0}(H_0 - H)e^{-\tau H} = e^{\tau H_0}(H_0 - H)e^{-\tau H_0}e^{\tau H_0}e^{-\tau H} \\ &= e^{\tau H_0}(-gV)e^{-\tau H_0}S(\tau) = -gV_I(\tau)S(\tau)\ , \end{aligned} \tag{14}$$

where $V_I(\tau) \equiv e^{\tau H_0} V e^{-\tau H_0}$. This is nothing but the interaction representation (recall the lecture course QM II). The formal solution (Dyson series) reads

$$S(\tau) = T_\tau\, e^{-g\int_0^\tau d\tau_1\, V_I(\tau_1)}\ , \tag{15}$$

where $T_\tau$ is the "time" ordering operator. Expanding to the first order we get

$$S(\tau) = 1 - g \int_0^\tau d\tau_1 \, V_I(\tau_1) + \dots \ . \tag{16}$$

Thus we obtain

$$\begin{aligned} Z &= \mathrm{Tr}[e^{-\beta H}] = \mathrm{Tr}[e^{-\beta H_0} S(\beta)] = Z_0 - g \int_0^\beta d\tau \mathrm{Tr}[e^{-\beta H_0} e^{\tau H_0} V e^{-\tau H_0}] + \dots \\ &= Z_0 - g \int_0^\beta d\tau \, \mathrm{Tr}[e^{-\beta H_0} V] + \dots = Z_0 - g\beta \mathrm{Tr}[e^{-\beta H_0} V] + \dots \ . \end{aligned} \tag{17}$$

This we have obtained the first order correction to the partition function

$$Z_1 = -\beta \mathrm{Tr}[e^{-\beta H_0} V] \ . \tag{18}$$

It is straightforward to calculate the correction of the first order to the free energy. We have

$$\begin{aligned} F &= -(1/\beta) \ln(Z) = -(1/\beta) \ln(Z_0 + gZ_1 + \dots) \\ &= -(1/\beta) \ln \left[ Z_0 \left( 1 + g\frac{Z_1}{Z_0} + \dots \right) \right] = F_0 - \frac{gZ_1}{\beta Z_0} + \dots = F_0 + g\langle V \rangle_0 + \dots \ . \end{aligned} \tag{19}$$

Here

$$\langle V \rangle_0 = \frac{1}{Z_0} \mathrm{Tr}[e^{-\beta H_0} V] \ . \tag{20}$$

## III. VIRIAL EXPANSION

This method allows to obtain an expansion of the kind

$$PV = Nk_\mathrm{B}T(1 + Bn + Cn^2 + \dots) \ , \tag{21}$$

which modifies the classical equation of state of the ideal gas $PV = Nk_\mathrm{B}T$. It usually works for $n\lambda_T^3 \ll 1$ or equivalently $z \equiv e^{\beta\mu} \ll 1$, that is in the case of diluted gases. The main idea is to use the expansion of the grand canonical partition function $Z_G$ via the canonical ones $Z_N$, where $N$ is the number of particles. This expansion reads

$$Z_G = \sum_{N=0} Z_N e^{N\beta\mu} = 1 + Z_1 e^{\beta\mu} + Z_2 e^{2\beta\mu} + \dots \ . \tag{22}$$

If $z \equiv e^{\beta\mu} \ll 1$ it might be sufficient to retain only the few first terms in the expansion. Then the problem reduces to calculating the canonical partition functions with small numbers of particles, e.g., $Z_1$ and $Z_2$.

We want to calculate the grand canonical potential $\Omega = -k_\mathrm{B} T \ln Z_G$. We use the expansion

$$\ln(1+x) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1} x^n}{n} \ , \tag{23}$$

which leads to

$$\ln Z_G = (Z_1 e^{\beta\mu} + Z_2 e^{2\beta\mu} + \ldots) - \frac{(Z_1 e^{\beta\mu} + Z_2 e^{2\beta\mu} + \ldots)^2}{2} \ . \tag{24}$$

Collecting the powers of the fugacity $z \equiv e^{\beta\mu}$ we get

$$\ln Z_G = Z_1 e^{\beta\mu} + \left( Z_2 - \frac{Z_1^2}{2} \right) e^{2\beta\mu} + \ldots \ . \tag{25}$$

For the grand potential we obtain

$$\Omega = -k_\mathrm{B} T Z_1 e^{\beta\mu} - k_\mathrm{B} T \left( Z_2 - \frac{Z_1^2}{2} \right) e^{2\beta\mu} + \ldots \ . \tag{26}$$

This expression allows us to calculate the particle number:

$$N = -\frac{\partial \Omega}{\partial \mu}\bigg|_{V,T} = Z_1 e^{\beta\mu} + \left(2Z_2 - Z_1^2\right) e^{2\beta\mu} + \ldots \ . \tag{27}$$

From (26) and (27) we obtain

$$PV = -\Omega = k_\mathrm{B} T \left[ N - \left( Z_2 - \frac{Z_1^2}{2} \right) e^{2\beta\mu} + \ldots \right] \ . \tag{28}$$

With $e^{\beta\mu} \approx \frac{N}{Z_1}$ we get

$$PV = -\Omega = k_\mathrm{B} T \left[ N - \left( Z_2 - \frac{Z_1^2}{2} \right) \frac{N^2}{Z_1^2} + \ldots \right] \ . \tag{29}$$

Finally

$$PV = k_\mathrm{B} T N \left[ 1 + Bn + \ldots \right] \ , \tag{30}$$

where

$$B \equiv -V \left( \frac{Z_2}{Z_1^2} - \frac{1}{2} \right) \ . \tag{31}$$

### A. Van der Waals gas

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j) \ . \tag{32}$$

$$\begin{aligned} Z_N &= \frac{1}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^3} \int d^{3N}r \, e^{-\beta H(\{\mathbf{p}_i\},\{\mathbf{r}_i\})} \\ &= \frac{1}{N!} \frac{1}{\lambda_T^{3N}} \int d^{3N}r \, e^{-\beta \frac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j)} \ . \end{aligned} \tag{33}$$

For $N = 1$ this gives

$$Z_1 = \frac{V}{\lambda_T^3} \ . \tag{34}$$

Limiting the virial expansion at $N = 1$ we would obtain

$$\Omega = -k_\mathrm{B} T Z_1 e^{\beta\mu} \ . \tag{35}$$

This would then give

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = Z_1 e^{\beta\mu} = -\frac{\Omega}{k_\mathrm{B} T} = \frac{PV}{k_\mathrm{B} T} \ . \tag{36}$$

Thus we recover the ideal gas relation $PV = N k_\mathrm{B} T$.

For $N = 2$ we obtain

$$Z_2 = \frac{1}{2} \frac{1}{\lambda_T^6} \int d^3r_1 d^3r_2 \, e^{-\beta V(\mathbf{r}_1 - \mathbf{r}_2)} = \frac{1}{2} \frac{V}{\lambda_T^6} \int d^3r \, e^{-\beta V(\mathbf{r})} \ . \tag{37}$$

$$B = -\frac{1}{2} \int d^3r \, \left[e^{-\beta V(\mathbf{r})} - 1\right] \ . \tag{38}$$

We choose the interaction potential as shown in Fig. 1. For $r > 2r_0$ the potential is week, so that $\beta V(r) \ll 1$. Then

$$\begin{aligned} &e^{-\beta V(r)} - 1 \approx -1 \quad \text{for} \quad r < 2r_0 \ , \\ &e^{-\beta V(r)} - 1 \approx -\beta V(r) \quad \text{for} \quad r > 2r_0 \ . \end{aligned} \tag{39}$$

This gives

$$B = \frac{1}{2} \frac{4\pi}{3} (2r_0)^3 + \frac{\beta}{2} \int\limits_{|r| > 2r_0} d^3r \, V(r) = b - a\beta \ , \tag{40}$$

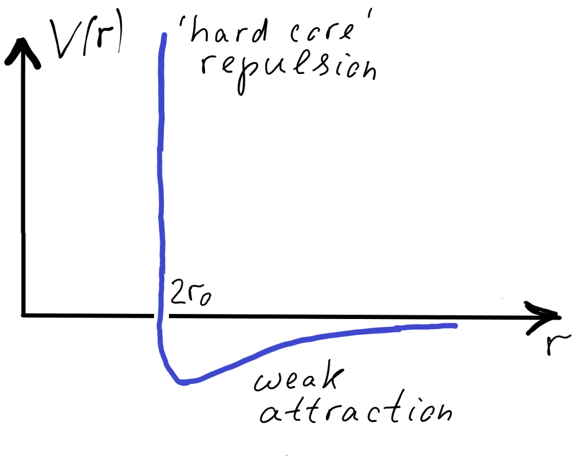

FIG. 1: Interaction potential in VW gas.

where

$$b = \frac{1}{2}\frac{4\pi}{3}(2r_0)^3 > 0 \quad \text{and} \quad a = -\frac{1}{2}\int\limits_{|r|>2r_0} d^3r\, V(r) > 0 \; . \tag{41}$$

Finally, we obtain

$$PV = k_\mathrm{B}TN\left[1 + bn - \frac{an}{k_\mathrm{B}T}\right] \; . \tag{42}$$

This is equivalent to

$$(P + an^2)V = k_\mathrm{B}TN[1 + bn] \; . \tag{43}$$

Since $bn \ll 1$ we can replace $(1+bn) \approx (1-bn)^{-1}$ and we obtain the van der Waals equation of state

$$(P + an^2)(1 - bn)V = (P + an^2)(V - bN) = k_\mathrm{B}TN \; . \tag{44}$$

The physical meaning of the condition $bn \ll 1$ can be understood if we notice that $b$ is roughly the "excluded" volume per particle. It is excluded because particles cannot get closer to each other than $2r_0$. On the other hand $1/n$ is the total volume per particle. Thus $bn \ll 1$ es equivalent to $V_\mathrm{total}/N \gg V_\mathrm{excluded}/N$.

The derivation provided here is limited to the regime of diluted gases ($bn \ll 1$). However, the van der Waals equation turns out to be valid in a wider parameter regime.

### B. Quantum corrections for ideal gases

Consider again the ideal Bose and Fermi gases at high temperatures, such that $n\lambda_T^3 \ll 1$. We can apply the virial expansion in order to clearly see the role of Bose/Fermi statistics. We have

$$Z_1 = \sum_{\mathbf{p},\sigma} e^{-\beta \frac{p^2}{2m}} = (2s+1)\frac{V}{\lambda_T^3} \ , \tag{45}$$

and

$$Z_2 = {\sum}'_{\mathbf{p}_1,\sigma_1,\mathbf{p}_2,\sigma_2} e^{-\beta \frac{p_1^2+p_2^2}{2m}} \ . \tag{46}$$

Here the prime in $\sum'$ means that the quantum (Bose of Fermi) statistics has been taken into account. For Fermions this gives

$$Z_2 = \frac{1}{2}\sum_{\mathbf{p}_1,\sigma_1}\sum_{\mathbf{p}_2,\sigma_2} e^{-\beta \frac{p_1^2+p_2^2}{2m}} - \frac{1}{2}\sum_{\mathbf{p},\sigma} e^{-2\beta\frac{p^2}{2m}} = \frac{1}{2}Z_1^2 - \frac{1}{2}Z_1\Big|_{m\to m/2} \ , \tag{47}$$

where the second term subtracts the contributions of the doubly occupied states. Analogously, for Bosons we get

$$Z_2 = \frac{1}{2}\sum_{\mathbf{p}_1,\sigma_1}\sum_{\mathbf{p}_2,\sigma_2} e^{-\beta \frac{p_1^2+p_2^2}{2m}} + \frac{1}{2}\sum_{\mathbf{p},\sigma} e^{-2\beta\frac{p^2}{2m}} = \frac{1}{2}Z_1^2 + \frac{1}{2}Z_1\Big|_{m\to m/2} \ . \tag{48}$$

Here the second term corrects for the 1/2 factor in the first term for the doubly occupied states. A state here is $\{\mathbf{p},\sigma\}$. Using (45) we obtain

$$Z_2^{B/F} = \frac{1}{2}Z_1^2 \pm \frac{1}{2}Z_1\Big|_{m\to m/2} = \frac{1}{2}\left(Z_1^2 \pm \frac{Z_1}{2^{3/2}}\right) \ . \tag{49}$$

Recall that the virial expansion produces the equation of state $PV = k_\mathrm{B}TN\left[1+Bn\ldots\right]$ with $B = -V\left(\frac{Z_2}{Z_1^2} - \frac{1}{2}\right)$. We obtain

$$B^{B/F} = \mp\frac{V}{2^{5/2}Z_1} = \mp\frac{\lambda_T^3}{2^{5/2}(2s+1)} \ . \tag{50}$$

For Bosons $B^B < 0$. This corresponds to an effective attraction. In contrast, for Fermions, $B^F > 0$, which means effective repulsion.

# IV. MAGNETIC SYSTEMS

## A. Thermodynamics of magnetic systems

We recall the magnetic relations. The magnetic inductance is defined via $\mathbf{B} = \mathrm{rot}\mathbf{A}$, whereas the magnetic field is given by $\mathbf{H} \equiv \mathbf{B} - 4\pi\mathbf{M}$. Here $\mathbf{M}$ is the magnetisation.

$$dU_{\mathrm{Feld}} = \int dV \left( \frac{\mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B}}{4\pi} \right) . \tag{51}$$

A work performed by a magnetic system reads

$$\delta W = -dU_{\mathrm{Feld}} = -\int dV \, \frac{\mathbf{H} \cdot d\mathbf{B}}{4\pi} . \tag{52}$$

Assuming $\mathbf{H}$ is controlled, we have $d\mathbf{H} = 0$ and $d\mathbf{B} = 4\pi d\mathbf{M}$. Thus

$$\delta W = -\int dV \, \mathbf{H} \cdot d\mathbf{M} . \tag{53}$$

We will shorten this as

$$\delta W = -\mathbf{H} \cdot d\mathbf{M} . \tag{54}$$

The first law of thermodynamics reads

$$dU = \delta Q - dW = TdS + \mathbf{H} \cdot d\mathbf{M} . \tag{55}$$

Thus for the inner energy the proper variables are $S$ and $\mathbf{M}$, i.e., $U(S, \mathbf{M})$. The usual Legendre transformation leads to free energy $F = U - TS$. We obtain

$$dF = dU - TdS = -SdT + \mathbf{H} \cdot d\mathbf{M} . \tag{56}$$

Since $\mathbf{M}$ is difficult to control, we prefer to control $\mathbf{H}$. To do so one has to perform another Legendre transformation leading to the free enthalpy: $G = F - \mathbf{H} \cdot \mathbf{M}$. We obtain

$$dG = -SdT - \mathbf{M} \cdot d\mathbf{H} . \tag{57}$$

The proper variables of $G$ are $G(T, \mathbf{H})$ and

$$\mathbf{M} = -\left( \frac{\partial G}{\partial \mathbf{H}} \right)_T . \tag{58}$$

Usually the full field $\mathbf{H}$ is not controlled either. It is only the externally applied field that is controlled. The other part of $\mathbf{H}$, the so called demagnetising field (or the field created by $\mathbf{M}$) is not controlled. Here we neglect the demagnetising effects and approximate $\mathbf{H} \approx \mathbf{H}_{ext} = \mathbf{B}_{ext}$.

The Hamiltonian of the magnetic systems usually contains the term $-\mathbf{H} \cdot \mathbf{M}$. That is, usually, $H = H_U - \mathbf{H}_{ext} \cdot \mathbf{M}$, where $H_U$ can be associated with the inner energy of the system. Thus $H$ corresponds to enthalpy rather than to inner energy. That's why we have

$$G = -k_B T \ln Z \ , \tag{59}$$

where $Z$ has been calculated with the full Hamiltonian, $Z = Tr\left[\exp\left(-\beta H\right)\right]$.

### B. Exchange interaction

Consider two sites $a$ and $b$. If an electron is at site $a$ it has a wave function $\psi_a(r)$. Accordingly, at cite $b$ the wave function is $\psi_b(r)$. (The other levels at sites $a$ and $b$ have very high energy and are disregarded.) We consider two interacting electrons in an external potential $V^{(1)}(r)$, i.e., the Hamiltonian reads

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V^{(1)}(r_1) + V^{(1)}(r_2) + V^{(2)}(r_1, r_2) \ . \tag{60}$$

For example $V^{(2)}$ can be the Coulomb repulsion, i.e., $V^{(2)}(r_1, r_2) = e^2/|r_1 - r_2|$, whereas $V^{(1)}$ has two minima at sites $r_a$ and $r_b$.

The wave function of two electrons must be antisymmetric. That is, if we exchange both the coordinates and the spins, the wave function should get a minus sign:

$$\psi(r_1, s_1, r_2, s_2) = -\psi(r_2, s_2, r_1, s_1) \ . \tag{61}$$

We can achieve in two ways. Either the spatial part is symmetric and the spin part is anti-symmetric, or vice versa. The symmetric/anti-symmetric spatial wave functions are

$$\psi_S(r_1, r_2) = \frac{1}{\sqrt{2}} \left(\psi_a(r_1)\psi_b(r_2)) + \psi_b(r_1)\psi_a(r_2)\right) \ , \tag{62}$$

$$\psi_T(r_1, r_2) = \frac{1}{\sqrt{2}} \left(\psi_a(r_1)\psi_b(r_2)) - \psi_b(r_1)\psi_a(r_2)\right) \ . \tag{63}$$

The indexes $S$ and $T$ will become clear below. There are four possible spin states. One is anti-symmetric, it corresponds to the total spin 0 and is called singlet:

$$\chi_S(s_1, s_2) = \frac{1}{\sqrt{2}} \left(|s_1 =\uparrow\rangle\, |s_2 =\downarrow\rangle - |s_1 =\downarrow\rangle\, |s_2 =\uparrow\rangle\right) = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle\, |\downarrow\rangle - |\downarrow\rangle\, |\uparrow\rangle\right) \ . \tag{64}$$

The other three are symmetric, correspond to the total spin 1 and are called triplet states:

$$\begin{aligned}
\chi_T^{s_z=1}(s_1,s_2) &= |{\uparrow}\rangle\,|{\uparrow}\rangle \ , \\
\chi_T^{s_z=0}(s_1,s_2) &= \frac{1}{\sqrt{2}}\left(|{\uparrow}\rangle\,|{\downarrow}\rangle + |{\downarrow}\rangle\,|{\uparrow}\rangle\right) \ , \\
\chi_T^{s_z=-1}(s_1,s_2) &= |{\downarrow}\rangle\,|{\downarrow}\rangle \ . \qquad (65)
\end{aligned}$$

Thus, the relevant Hilbert space consists of four states:

$$\psi_S(r_1,r_2)\chi_S \quad , \quad \psi_T(r_1,r_2)\chi_T^{s_z=-1,0,1} \ . \qquad (66)$$

The expectation value of the energy takes two values, since the Hamiltonian is spin-independent. For the singlet state it reads

$$\begin{aligned}
E_S &= \langle\psi_S|\,H\,|\psi_S\rangle \\
&= \frac{1}{2}\int dr_1dr_2\,[\psi_a^*(r_1)\psi_b^*(r_2)+\psi_a^*(r_2)\psi_b^*(r_1)]\ H\ [\psi_a(r_1)\psi_b(r_2)+\psi_a(r_2)\psi_b(r_1)] \ . \qquad (67)
\end{aligned}$$

For the triplet states it is

$$\begin{aligned}
E_T &= \langle\psi_T|\,H\,|\psi_T\rangle \\
&= \frac{1}{2}\int dr_1dr_2\,[\psi_a^*(r_1)\psi_b^*(r_2)-\psi_a^*(r_2)\psi_b^*(r_1)]\ H\ [\psi_a(r_1)\psi_b(r_2)-\psi_a(r_2)\psi_b(r_1)] \ . \qquad (68)
\end{aligned}$$

We obtain

$$E_S - E_T = 2\int dr_1dr_2\ [\psi_a^*(r_1)\psi_b^*(r_2)]\ H\ [\psi_a^*(r_2)\psi_b^*(r_1)] \ . \qquad (69)$$

The effective Hamiltonian can be written as

$$H_{eff} = \frac{1}{4}(E_S+3E_T) - \frac{(E_S-E_T)}{\hbar^2}\,\mathbf{S}_1\cdot\mathbf{S}_2 \ . \qquad (70)$$

Indeed, using

$$\mathbf{S}_1\cdot\mathbf{S}_2 = \frac{1}{2}\ \left((\mathbf{S}_1+\mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2\right) \ , \qquad (71)$$

we conclude that in the singlet state

$$\langle\chi_S|\,\mathbf{S}_1\cdot\mathbf{S}_2\,|\chi_S\rangle = -\frac{3}{4}\,\hbar^2 \ , \qquad (72)$$

whereas in the triplet states

$$\langle\chi_T^{s_z}|\,\mathbf{S}_1\cdot\mathbf{S}_2\,|\chi_T^{s_z}\rangle = \frac{1}{4}\,\hbar^2 \ . \qquad (73)$$

Disregarding the unimportant constant we obtain the effective Hamiltonian of the exchange interaction

$$H_{exch} = -J\,\mathbf{S}_1 \cdot \mathbf{S}_2 \ , \tag{74}$$

where

$$J \equiv \frac{(E_S - E_T)}{\hbar^2} \ . \tag{75}$$

## C. Ising model in 1D, exact solution

### 1. *Evaluating partition function*

The Hamiltonian of the model reads

$$H = -J \sum_{n=1}^{N} S_n^z S_{n+1}^z - \gamma B \sum_n S_n^z \ , \tag{76}$$

where $\gamma \equiv g_L e/2mc$ is the gyromagnetic ratio ($g_L$ is the Lande factor), $B = H_{ext}^z$ is the applied external magnetic field. For the spin operators we have $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$. Thus, we can rewrite

$$\beta H = -g \sum_{n=1}^{N} \sigma_n^z \sigma_{n+1}^z - h \sum_n \sigma_n^z \ , \tag{77}$$

where $g \equiv \frac{J\hbar^2}{4k_BT}$ and $h \equiv \frac{\gamma\hbar B}{2k_BT}$. Since only the $\sigma^z$ operators are involved, the model is classical. For brevity we use $\sigma_n \equiv \sigma_n^z$.

We assume periodic boundary conditions, $\sigma_{N+1} = \sigma_1$, meaning that the spins are placed on a ring. For the partition function we get

$$Z(T,B,N) = \sum_{\{\sigma_n\}} e^{-\beta H} = \sum_{\{\sigma_n\}} \prod_{n=1}^{N} e^{\left[g\sigma_n\sigma_{n+1} + \frac{1}{2}(\sigma_n + \sigma_{n+1})\right]} \ . \tag{78}$$

We have written the contribution of the external field in a symmetric fashion: $\frac{1}{2}(\sigma_n + \sigma_{n+1})$. We obtain

$$Z(T,B,N) = \sum_{\sigma_1,\sigma_2,\ldots\sigma_N} T(\sigma_1,\sigma_2)T(\sigma_2,\sigma_3)\ldots T(\sigma_{N-1},\sigma_N)T(\sigma_N,\sigma_1) \ , \tag{79}$$

where

$$T(\sigma,\sigma') \equiv \exp\left[g\sigma\sigma' + \frac{1}{2}(\sigma + \sigma')\right] \ . \tag{80}$$

Since both $\sigma$ and $\sigma'$ can assume two values $\sigma = \pm 1$, $\sigma' = \pm 1$, the function $T$ can be represented as a matrix

$$T_{\sigma,\sigma'} = \begin{pmatrix} e^{g+h} & e^{-g} \\ e^{-g} & e^{g-h} \end{pmatrix} , \tag{81}$$

and it is easy to see that

$$Z = \mathrm{Tr}\left[T^N\right] . \tag{82}$$

The matrix $T$ can be diagonalised, i.e., there exists an (orthogonal) matrix $U$, such that

$$UTU^{-1} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} . \tag{83}$$

Thus

$$Z = \lambda_1^N + \lambda_2^N . \tag{84}$$

The eigenvalues $\lambda_1$ and $\lambda_2$ are obtained from $\det(T - \lambda\hat{1}) = 0$. This gives

$$(e^{g+h} - \lambda)(e^{g-h} - \lambda) - e^{-2g} = 0 , \tag{85}$$

$$\lambda^2 - 2e^g \cosh(h)\lambda + 2\sinh(2g) = 0 , \tag{86}$$

$$\lambda_{1/2} = e^g \cosh(h) \pm \sqrt{e^{2g}\cosh^2(h) - 2\sinh(2g)} , \tag{87}$$

$$\lambda_{1/2} = e^g \left[\cosh(h) \pm \sqrt{\sinh^2(h) + e^{-4g}}\right] . \tag{88}$$

We observe $\lambda_1 > \lambda_2$, thus for $N \to \infty$ we have $\lambda_1^N \gg \lambda_2^N$ and we can approximate

$$Z \approx \lambda_1^N . \tag{89}$$

### 2. *Thermodynamic results*

We can now calculate the free enthalpie

$$G(T, B, N) = -k_B T \ln Z = -k_B T N \ln \lambda_1 . \tag{90}$$

For the magnetisation this gives

$$M = -\left(\frac{\partial G}{\partial B}\right)_{T,N} = \gamma N \frac{\sinh(h)}{\sqrt{\sinh^2(h) + e^{-4g}}} . \tag{91}$$

Two very different cases: ferromagnetic $g > 0$ and antiferromagnetic $g < 0$. See Fig. 2.

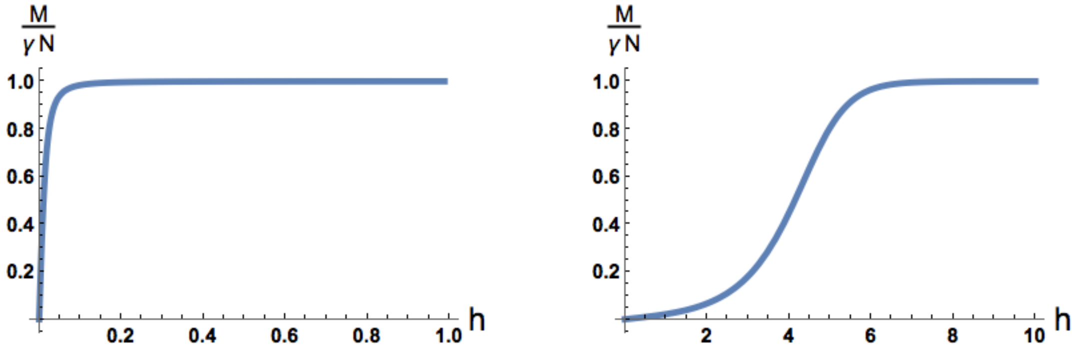

FIG. 2: Magnetisation in 1D Ising model. **Left figure:** Ferromagnetic case, $g = 2$. **Right figure:** Antiferromagnetic case, $g = -2$.

For the linear susceptibility we obtain

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{B=0} = \frac{\gamma^2 N}{k_B T}\, e^{2g} = \frac{\gamma^2 N}{k_B T}\, \exp\left[\frac{2\tilde{J}}{k_B T}\right] \,, \tag{92}$$

where $\tilde{J} \equiv J\hbar^2/4$. In the ferromagnetic case ($\tilde{J} > 0$) we get an exponentially high susceptibility for $T \to 0$. On the other hand, for $k_B T \gg \tilde{J}$ we recover the Curie law: $\chi \to \frac{\gamma^2 N}{k_B T}$.

For the entropy we get

$$S = -\left(\frac{\partial G}{\partial T}\right)_{B,N} = k_B N \ln \lambda_1 + k_B T N \frac{1}{\lambda_1}\frac{\partial \lambda_1}{\partial T} \,. \tag{93}$$

At at $B = 0$ ($h = 0$) we get $\lambda_1 = e^g\left[1 + e^{-2g}\right] = 2\cosh(g)$. Thus

$$\begin{aligned} S &= k_B N \ln[2\cosh(g)] + k_B T N \tanh(g) \frac{\partial g}{\partial T} \\ &= k_B N \left[\ln\left[2\cosh\left(\frac{\tilde{J}}{k_B T}\right)\right] - \left(\frac{\tilde{J}}{k_B T}\right)\tanh\left(\frac{\tilde{J}}{k_B T}\right)\right] \,. \end{aligned} \tag{94}$$

In particular, for $T \to \infty$ we obtain $S \to k_B N \ln 2$, i.e., the entropy of $N$ free spins-1/2. See Fig. 3(left). For the specific heat we get

$$C = T\frac{\partial S}{\partial T} = k_B N \left[\left(\frac{\tilde{J}}{k_B T}\right)\frac{1}{\cosh\left(\frac{\tilde{J}}{k_B T}\right)}\right]^2 \,. \tag{95}$$

See Fig. 3(right).

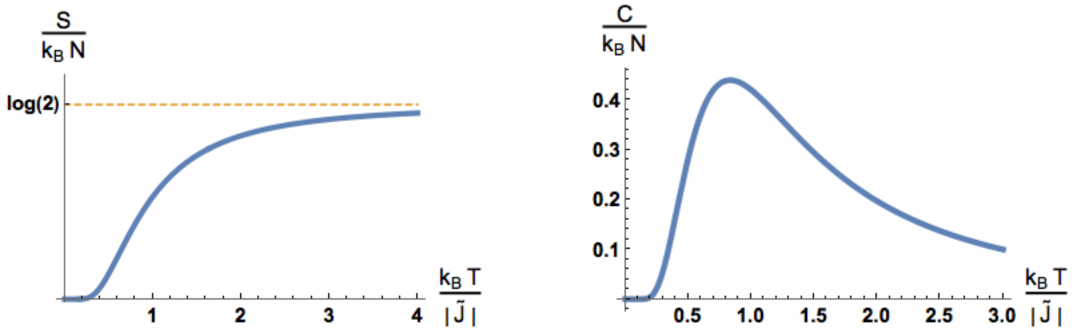

FIG. 3: Left figure: Entropie of the 1D Ising model. Right figure: Heat capacitance.

### *3. Correlation function*

We are interested to calculate

$$\langle \sigma_i \sigma_j \rangle \equiv \frac{1}{Z} \sum_{\{\sigma_n\}} \sigma_i \sigma_j \, e^{-\beta H} \ . \tag{96}$$

This can be again done using the transfer matrix method. We use again

$$e^{-\beta H} = T(\sigma_1, \sigma_2) T(\sigma_2, \sigma_3) \ldots T(\sigma_{N-1}, \sigma_N) T(\sigma_N, \sigma_1) \ . \tag{97}$$

Thus (assuming $i < j$)

$$\begin{aligned} \sigma_i \sigma_j \, e^{-\beta H} &= T(\sigma_1, \sigma_2) \ldots T(\sigma_{i-1}, \sigma_i) \sigma_i T(\sigma_i, \sigma_{i+1}) \\ &\ldots \ T(\sigma_{j-1}, \sigma_j) \sigma_j T(\sigma_j, \sigma_{j+1}) \ldots T(\sigma_{N-1}, \sigma_N) T(\sigma_N, \sigma_1) \ . \end{aligned} \tag{98}$$

As a result we obtain (for $i < j$)

$$\langle \sigma_i \sigma_j \rangle = \frac{1}{Z} \operatorname{Tr} \left[ T^{i-1} \, \sigma^z \, T^{j-i} \, \sigma^z \, T^{N-j+1} \right] = \frac{\operatorname{Tr} \left[ T^{i-1} \, \sigma^z \, T^{j-i} \, \sigma^z \, T^{N-j+1} \right]}{\operatorname{Tr} \left[ T^N \right]} \ . \tag{99}$$

We introduce the eigenvectors of $T$:

$$T \, |l\rangle = \lambda_l \, |l\rangle \ \ , \tag{100}$$

where $l = 1, 2$ and the eigenvalues have been calculated above. Then

$$\langle \sigma_i \sigma_j \rangle = \sum_{l,m} \frac{\operatorname{Tr} \left[ T^{i-1} \ |l\rangle \langle l| \ \sigma^z \ |m\rangle \langle m| \ T^{j-i} \ |m\rangle \langle m| \ \sigma^z \ |l\rangle \langle l| \ T^{N-j+1} \right]}{\operatorname{Tr} \left[ T^N \right]} \ . \tag{101}$$

This gives

$$\langle \sigma_i \sigma_j \rangle = \sum_{l,m} | \, \langle l| \, \sigma^z \, |m\rangle \, |^2 \, \frac{\lambda_m^{|i-j|} \, \lambda_l^{N-|i-j|}}{\lambda_1^N + \lambda_2^N} \ . \tag{102}$$

For $N \to \infty$ we must take $l = 1$. Thus we get

$$\langle \sigma_i \sigma_j \rangle = \sum_m |\, \langle 1 |\, \sigma^z \,| m \rangle \,|^2 \, \frac{\lambda_m^{|i-j|}}{\lambda_1^{|i-j|}} \ . \tag{103}$$

In particular for $B = 0$ we obtain

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad , \quad |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \ , \tag{104}$$

and

$$\langle \sigma_i \sigma_j \rangle = \frac{\lambda_2^{|i-j|}}{\lambda_1^{|i-j|}} = [\tanh(g)]^{|i-j|} \ . \tag{105}$$

This can be written as

$$\langle \sigma_i \sigma_j \rangle = e^{|i-j| \ln[\tanh(g)]} \ . \tag{106}$$

In the ferromagnetic case ($g > 0$) we obtain

$$\langle \sigma_i \sigma_j \rangle = e^{-\frac{|i-j|}{\xi}} \ , \tag{107}$$

where the inverse correlation length is given by

$$\xi^{-1} = -\ln[\tanh(g)] = \ln\left[\coth\left(\frac{|\tilde{J}|}{k_B T}\right)\right] \ . \tag{108}$$

In the antiferromagnetic case ($g < 0$)

$$\langle \sigma_i \sigma_j \rangle = (-1)^{|i-j|} e^{-\frac{|i-j|}{\xi}} \ . \tag{109}$$

For $T \to 0$ the correlation length diverges, $\xi \to \infty$. This will play an important role later, as we discuss the phase transitions.

### D. Cluster expansion

We consider, e.g., a 2D Ising model with $B = 0$ with nearest neighbours interaction. We obtain

$$Z = \sum_{\{\sigma\}} e^{-\beta H} = \sum \{\sigma\} \prod_{\langle i,j \rangle} e^{g \sigma_i \sigma_j} \ . \tag{110}$$

Here $\langle i, j \rangle$ stands for nearest neighbours pairs. Further

$$e^{g \sigma_i \sigma_j} = \cosh(g) + \sigma_j \sigma_j \sinh(g) = \cosh(g) \left[1 + \sigma_j \sigma_j \tanh(g)\right] \ . \tag{111}$$

This gives

$$Z = (\cosh(g))^P \sum_{\{\sigma\}} \prod_{\langle i,j\rangle} \left[1 + \sigma_j \sigma_j \tanh(g)\right] \ . \tag{112}$$

Here $P$ is the number of pairs of nearest neighbours. For lattices $P \sim Nz/2$, where $z$ is the number of nearest neighbours. For a 2D model on a square lattice $z = 4$. We obtain

$$\begin{aligned} \frac{Z}{(\cosh(g))^P} = \sum_{\{\sigma\}} \Bigg[ & 1 + \tanh(g) \left( \sum_{\langle i,j\rangle} \sigma_j \sigma_j \right) \\ & + \tanh^2(g) \left( \sum_{\langle i,j\rangle \neq \langle k,m\rangle} \sigma_j \sigma_j \sigma_k \sigma_m \right) + \ldots \Bigg] \end{aligned} \tag{113}$$

Combinatoric gives

$$\frac{Z}{(\cosh(g))^P} = 2^N \left[1 + \tanh^4(g) C_4 + \tanh^6(g) C_6 + \ldots \right] \ , \tag{114}$$

where $C_4$ is the number of 4-clusters etc.

### E. Mean field approximation: ferromagnetic Heisenberg model.

Consider the ferromagnetic Heisenberg model in $d$ dimensions. The Hamiltonian reads

$$\hat{\mathcal{H}} = -J \sum_{\langle i,j\rangle} \vec{S}_i \vec{S}_j - \gamma \vec{B} \sum_i \vec{S}_i \ . \tag{115}$$

Here $\gamma = g\mu_B = ge/(2mc)$ is the gyromagnetic ratio and $B = H_{ext}$ is the external field. The ferromagnetic regime means $J > 0$. The operators $\vec{S}_i$ stand for spin-1/2 operators, $\vec{S}_i = (\hbar/2)\vec{\sigma}_i$. The notation $\sum_{\langle i,j\rangle}$ means that each pair of nearest neighbours is counted only once. In terms of the Pauli matrices we obtain

$$\hat{\mathcal{H}} = -\tilde{J} \sum_{\langle i,j\rangle} \vec{\sigma}_i \vec{\sigma}_j - \tilde{\gamma} \vec{B} \sum_i \vec{\sigma}_i \ , \tag{116}$$

where $\tilde{J} = \hbar^2 J/4$ and $\tilde{\gamma} = \hbar\gamma/2$. For brevity we rename $\tilde{J} \to J$, $\tilde{\gamma} \to \gamma$ and the Hamiltonian reads

$$\hat{\mathcal{H}} = -J \sum_{\langle i,j\rangle} \vec{\sigma}_i \vec{\sigma}_j - \gamma \vec{B} \sum_i \vec{\sigma}_i \ . \tag{117}$$

### 1. *Free spins in a magnetic field*

Let us first consider the case $J = 0$, i.e., free spins in the magnetic field $\vec{B}$:

$$\hat{\mathcal{H}} = -\gamma \vec{B} \sum_i \vec{\sigma}_i \ . \tag{118}$$

The partition function is easy to calculate. We denote by $|\uparrow\rangle$ the eigenstate of $\vec{B}\vec{\sigma}$ with the eigenvalue $B \equiv |\vec{B}|$ and by $|\downarrow\rangle$ the eigenvector of $\vec{B}\vec{\sigma}$ with the eigenvalue $-B$. Most convenient is to think that $\vec{B} \parallel \vec{z}$, i.e. $\vec{B} = B\vec{z}$. Then we obtain for one single spin

$$Z_1 = e^{\beta\gamma B} + e^{-\beta\gamma B} = 2\cosh\left(\beta\gamma B\right) \ . \tag{119}$$

The "magnetisation" of one single spin is given by

$$\vec{M}_1 = \gamma\langle\vec{\sigma}\rangle = -\frac{\partial F_1}{\partial \vec{B}} = \frac{1}{\beta}\frac{\partial \ln Z_1}{\partial \vec{B}} = \gamma \tanh(\beta\gamma B)\,\vec{b} \ , \tag{120}$$

where $\vec{b} \equiv \vec{B}/B$. For the expectation value of the spin operator we have

$$\langle\vec{\sigma}\rangle = \tanh(\beta\gamma B)\,\vec{b} \ . \tag{121}$$

For $N$ spins we get

$$Z = (Z_1)^N = \left(2\cosh\left(\beta\gamma B\right)\right)^N \ . \tag{122}$$

Thus

$$\vec{M} = \gamma\sum_i \langle\vec{\sigma}_i\rangle = -\frac{\partial F}{\partial \vec{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \vec{B}} = N\gamma \tanh(\beta\gamma B)\,\vec{b} = N\gamma\langle\vec{\sigma}\rangle \ . \tag{123}$$

Expectation values of all spins are equal, $\langle\vec{\sigma}_i\rangle = \langle\vec{\sigma}\rangle$.

### 2. *Mean field approximation (intuitive way)*

The idea of the mean field approximation is in the fact that every spin, e.g., spin $\vec{\sigma}_i$, "sees" the effective magnetic field created by all its nearest neighbors:

$$\gamma\vec{B}_{\text{eff,i}} = \gamma\vec{B} + \sum_{j\in\langle i,j\rangle} J\vec{\sigma}_j \ . \tag{124}$$

This is however an operator which cannot be reduced to a simple vector. The approximation is thus to replace it by

$$\gamma\vec{B}_{\text{eff,i}} = \gamma\vec{B} + \sum_{j\in\langle i,j\rangle} J\langle\vec{\sigma}_j\rangle \ . \tag{125}$$

Here $\langle\vec{\sigma}_j\rangle$ is the expectation (average) value of spin $j$. In turn, the expectation value $\langle\vec{\sigma}_j\rangle$ is found easily because spin $j$ "sees" the field $\gamma\vec{B}_{\text{eff,j}}$. It is obvious that all spins are polarised in the direction of $\vec{b}$. Moreover all spins have the same expectation value and thus all spins "see" the same effective field. Thus we remove the vector notation and get

$$\langle\sigma\rangle = \tanh(\beta\gamma B_{\text{eff}}) \ . \tag{126}$$

On the other hand

$$\gamma B_{\text{eff}} = \gamma B + Jz\langle\sigma\rangle \ . \tag{127}$$

Here $z$ is the coordination number, i.e., the number of nearest neighbours. Finally, we get the self-consistency (Curie-Weiss) equation

$$\langle\sigma\rangle = \tanh\left[\beta\gamma B + \beta Jz\langle\sigma\rangle\right] \ . \tag{128}$$

### *3. Mean field approximation (formal way)*

The more formal way is to write $\vec{\sigma}_i = \langle\vec{\sigma}_i\rangle + \delta\vec{\sigma}_i$, where $\delta\vec{\sigma}_i \equiv \vec{\sigma}_i - \langle\vec{\sigma}_i\rangle$. Then

$$\vec{\sigma}_i\vec{\sigma}_j = \langle\vec{\sigma}_i\rangle\langle\vec{\sigma}_j\rangle + \langle\vec{\sigma}_i\rangle\,\delta\vec{\sigma}_j + \delta\vec{\sigma}_i\,\langle\vec{\sigma}_j\rangle + \delta\vec{\sigma}_i\,\delta\vec{\sigma}_j \ . \tag{129}$$

One assumes the fluctuations $\delta\vec{\sigma}_i$ to be is some sense small. Therefore one drops the last term, as it represents a product of two small quantities (fluctuations). Thus

$$\begin{aligned} \vec{\sigma}_i\vec{\sigma}_j &\approx \langle\vec{\sigma}_i\rangle\langle\vec{\sigma}_j\rangle + \langle\vec{\sigma}_i\rangle\,\delta\vec{\sigma}_j + \delta\vec{\sigma}_i\,\langle\vec{\sigma}_j\rangle \\ &= \langle\vec{\sigma}_i\rangle\vec{\sigma}_j + \langle\vec{\sigma}_j\rangle\vec{\sigma}_i - \langle\vec{\sigma}_i\rangle\langle\vec{\sigma}_j\rangle \ . \end{aligned} \tag{130}$$

Assuming all spins are polarised equally $\langle\vec{\sigma}_i\rangle = \langle\vec{\sigma}\rangle$ we obtain the mean-field Hamiltonain

$$\hat{\mathcal{H}}_{MF} = -\left[\gamma\vec{B} + zJ\langle\vec{\sigma}\rangle\right]\sum_i\vec{\sigma}_i + \sum_{\langle i,j\rangle} J\,\langle\vec{\sigma}\rangle^2 = -\gamma\vec{B}_{\text{eff}}\sum_i\vec{\sigma}_i + \frac{JzN}{2}\,\langle\vec{\sigma}\rangle^2 \ , \tag{131}$$

where again $\gamma\vec{B}_{\text{eff}} = \gamma\vec{B} + Jz\langle\vec{\sigma}\rangle$. This model is that of free spins in a magnetic field and we obtain (we drop the vectors as all spins are polarised in the direction of $\vec{b}$)

$$Z = \sum_{\{\sigma_i\}} e^{-\beta\hat{\mathcal{H}}_{MF}} = e^{-\frac{\beta JzN}{2}\langle\vec{\sigma}\rangle^2}\,2^N\cosh^N(\beta\gamma B_{\text{eff}}) = e^{-\frac{\beta JzN}{2}\langle\vec{\sigma}\rangle^2}\,2^N\cosh^N(\beta\gamma B + Jz\langle\sigma\rangle) \ . \tag{132}$$

The free enthalpie reads

$$
\begin{aligned}
G(T,B) = -(1/\beta)\ln Z &= \frac{JzN}{2}\,\langle\vec{\sigma}\rangle^2 - (N/\beta)\ln\left[2\cosh(\beta\gamma B_{\text{eff}})\right] \\
&= \frac{JzN}{2}\,\langle\vec{\sigma}\rangle^2 - (N/\beta)\ln\left[2\cosh(\beta\gamma B + \beta Jz\langle\sigma\rangle)\right] \ . \qquad (133)
\end{aligned}
$$

For the magnetisation we obtain

$$
M = -\left(\frac{\partial G}{\partial B_{eff}}\right)_T = N\gamma\tanh(\beta\gamma B_{\text{eff}}) \ . \qquad (134)
$$

(This is not yet the true thermodynamic relation as we do not know $\langle\sigma\rangle$, which is also a function of $B$. However, differentiating with respect to $B$ assuming $\langle\sigma\rangle(B)$ being some function of $B$ gives the same.) On the other hand $M = N\gamma\langle\sigma\rangle$ and we obtain the self-consistency equation

$$
\langle\sigma\rangle = \tanh\left[\beta\gamma B + \beta Jz\langle\sigma\rangle\right] \ . \qquad (135)
$$

From now on we denote $m \equiv \langle\sigma\rangle$ (later we will call this quantity the order parameter). Assuming this self-consistency equation is solved, we can further investigate the free enthalpy given by Eq. (133). We get

$$
\cosh\left[\beta\gamma B + \beta Jzm\right] = \frac{1}{\sqrt{1-\tanh^2\left[\beta\gamma B + \beta Jzm\right]}} = \frac{1}{\sqrt{1-m^2}} \ . \qquad (136)
$$

This gives ($B = H$)

$$
G(T,H) = Nk_BT\left[-\ln 2 + \frac{1}{2}\,\ln\left[1-m^2\right]\right] + \frac{N}{2}\,Jz\,m^2 \ . \qquad (137)
$$

Here we should consider $m = m(H,T)$, which is obtained from the self-consistency equation

$$
m = \tanh\left[\beta\gamma H + \beta Jzm\right] \ . \qquad (138)
$$

We can also calculate the free energy $F(T,M) = G(T,H) + MH$, where the magnetisation reads $M = N\gamma\langle\sigma\rangle = N\gamma m$. In this case we should eliminate the field $H$ using the self-consistency equation. This gives

$$
\beta\gamma H = \text{arctanh}[m] - \beta Jzm = \frac{1}{2}\ln\left(\frac{1+m}{1-m}\right) - \beta Jzm \ . \qquad (139)
$$

For the free energy this gives

$$
F(T,M) = Nk_BT\left[-\ln 2 + \frac{1}{2}\,\ln\left[1-m^2\right] + \frac{m}{2}\,\ln\left(\frac{1+m}{1-m}\right)\right] - \frac{N}{2}\,Jz\,m^2 \ , \qquad (140)
$$

and $m = M/(\gamma N)$. We will discuss, both $G(T,H)$ and $F(T,M)$ below.

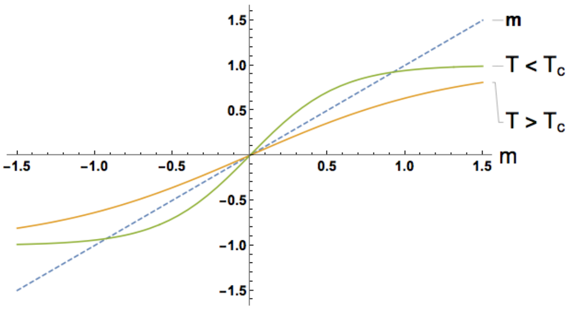

FIG. 4: Graphic solution of the self-consistency equation.

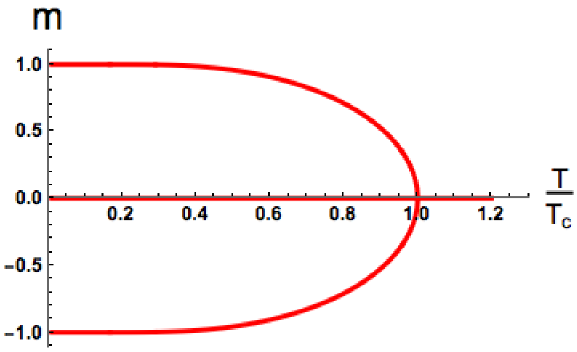

FIG. 5: Solutions of the self-consistency equation.

### *4. Solution of the self-consistency equation*

We denote $m \equiv \langle\sigma\rangle$ (later we will call this quantity the order parameter) and attempt a graphical solution of the self-consistency equation. We start at $B = 0$. Then the self-consistency equation reads

$$m = \tanh\left[\beta J z m\right] \ . \tag{141}$$

This equation can be easily solved graphically (see Fig. 4). For $\beta J z < 1$ there is only one solution $m = 0$. For $\beta J z > 1$ there are three solutions. Thus there is a critical temperature, determined by the condition $\beta z J = 1$, that is $k_B T_c = zJ$. For $T > T_c$ we have only the trivial solution $m = 0$. For $T < T_c$ there are also non-trivial solutions with $|m| \neq 0$ (see Fig. 5).

We consider the vicinity of the critical point $T = T_c$. The self-consistency equation can be rewritten as

$$m = \tanh\left[\frac{\gamma B}{k_B T} + \frac{T_c}{T} m\right] \ . \tag{142}$$

1) $B = 0$, $T < T_c$, $(T_c - T)/T_c \ll 1$. We have

$$m = \tanh\left[\frac{T_c}{T} m\right] \ . \tag{143}$$

The order parameter should be small, $m \ll 1$. Therefore we can expand the RHS using $\tanh(x) = x - x^3/3 + \ldots$. We get

$$m = \frac{T_c}{T} m - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 m^3 \ . \tag{144}$$

Further

$$\frac{T_c - T}{T} m = \frac{1}{3}\left(\frac{T_c}{T}\right)^3 m^3 \approx \frac{1}{3} m^3 \ . \tag{145}$$

Finally

$$m \approx \left(3\,\frac{T_c - T}{T_c}\right)^{1/2} \propto (T_c - T)^{1/2} \ . \tag{146}$$

2) $T = T_c$, $B \neq 0$, $\gamma B \ll k_B T$.

$$m = \tanh\left[m + \frac{\gamma B}{k_B T}\right] \approx m + \frac{\gamma B}{k_B T} - \frac{1}{3}\left(m + \frac{\gamma B}{k_B T}\right)^3 \ . \tag{147}$$

We see that

$$m \approx \left(\frac{3\gamma B}{k_B T}\right)^{1/3} \propto B^{1/3} \ . \tag{148}$$

3) $T > T_c$, $(T - T_c)/T_c \ll 1$, $B \to 0$.

$$m = \tanh\left[\frac{T_c}{T} m + \frac{\gamma B}{k_B T}\right] \approx \frac{T_c}{T} m + \frac{\gamma B}{k_B T} + \ldots \ . \tag{149}$$

$$m \approx \frac{\gamma B}{k_B (T - T_c)} \tag{150}$$

Therefore, for magnetic susceptibility, using $M = N\gamma m$ and $H = B$, we obtain

$$\chi = \left(\frac{\partial M}{\partial H}\right)_{T,H=0} \approx \frac{\gamma^2 N}{k_B (T - T_c)} \propto \frac{1}{(T - T_c)} \ . \tag{151}$$

4) Specific heat. Having defined $T_c$ we can rewrite Eqs. (137) and (138) as follows

$$G(T, H) = N k_B T \left[-\ln 2 + \frac{1}{2}\ln\left[1 - m^2\right]\right] + \frac{N k_B T_c}{2} m^2 \ , \tag{152}$$

where $m = m(H,T)$ is obtained from the self-consistency equation

$$m = \tanh\left[\beta\gamma H + \frac{T_c}{T}\,m\right] \ . \tag{153}$$

For the specific heat we obtain

$$C_H = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_H \ . \tag{154}$$

For $T > T_c$ we have $m = 0$ and

$$G(T, H = 0) = -Nk_BT\ln(2) \ , \tag{155}$$

and for $T < T_c$ we get

$$G(T, H = 0) = \frac{k_BT_cN}{2}\,m^2 + \frac{1}{2}\,Nk_BT\ln(1-m^2) - Nk_BT\ln(2) \ . \tag{156}$$

We substitute

$$m^2 \approx \left(3\,\frac{T_c - T}{T_c}\right) \tag{157}$$

and obtain for $T < T_c$ and $T_c - T \ll T_c$ (the term $\ln(1-m^2)$ should be expanded up to the second order in $m^2$, i.e., up to $m^4$)

$$G(T, H = 0) \approx -Nk_BT\ln(2) - \frac{3k_BN}{4T_c}\,(T - T_c)^2 \ . \tag{158}$$

Thus, $C_H(T = T_c - 0) = (3/2)k_BN$, whereas $C_H(T = T_c + 0) = 0$ and we obtain a jump in the specific heat.

### 6. *$G(T,H)$ vs. $F(T,M)$ above and below the transition.*

Thermodynamic stability. In equilibrium the free energy is minimal for given $T$ and $M$. Thus, the stability requires $d^{(2)}F > 0$. We know that $dF = -SdT + HdM$. Thus, upon variation of $M$ we have

$$d^{(2)}F = \frac{1}{2}\left(\frac{\partial^2 F}{\partial M^2}\right)_T dM^2 = \frac{1}{2}\left(\frac{\partial H}{\partial M}\right)_T dM^2 \ . \tag{159}$$

Thus, stability requires $(\partial H/\partial M)_T > 0$. Note that the stability conditions are obtained upon variations of extensive variables, e.g., $U$ or $M$ but not of the intensive ones, e.g., $T$ or $H$. That's why we use $F(T,M)$ and not $G(T,H)$.

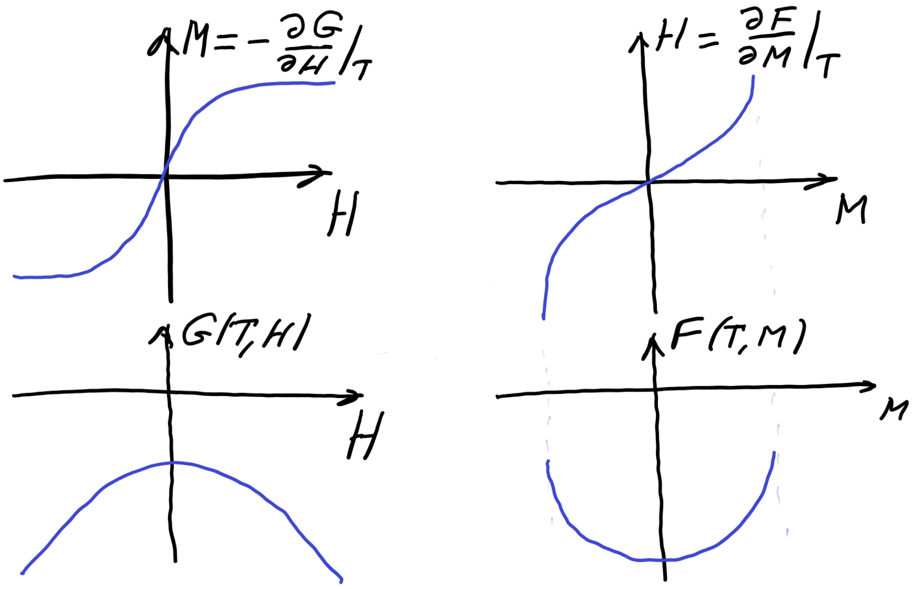

FIG. 6: $G(T,H)$ and $F(T,M)$ obtained by graphical integration at $T > T_c$.

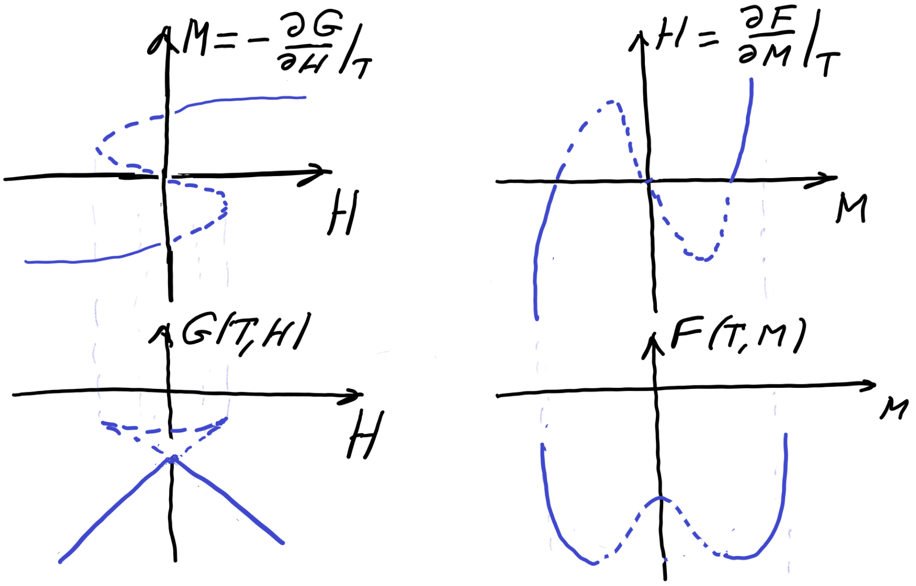

FIG. 7: $G(T,H)$ and $F(T,M)$ obtained by graphical integration at $T < T_c$.

The thermodynamic potentials $G(T,H)$ and $F(T,M)$ can be obtained by a "graphical integration" of the $M(H)$ and $H(M)$ curves. For $T > T_c$ this is shown in Fig. 6. In this case the solutions $M(H)$ and $H(M)$ are unique and the functions $G(T,H)$ and $F(T,M)$ are continuous and smooth.

The situation changes drastically at $T < T_c$ (Fig. 7). For small enough values of $H$ there are three possible values of $M$. One corresponds to an unstable solution ($\partial M/\partial H < 0$). The two others are locally stable. Among this two the one with smaller $G$ should be chosen. This causes a kink in the function $G(T,H)$ at $H=0$. For $F(T,M)$ a double-well potential is obtained. Here a Maxwell construction becomes necessary. Namely, at $T<T_c$ we have a first order transition once $H=0$ is crossed. We will discuss this below.

## V. LANDAU THEORY OF 2-ND ORDER PHASE TRANSITIONS.

The theory developed by Landau in 1937 and further expanded by Ginzburg and Landau in 1950. This is a phenomenological theory.

### A. General considerations

The most important new concept is that of order parameter $m(\vec{r})$ (it can be a scalar or a vector).

$$Z = \text{tr}\left[e^{-\beta H}\right] = \int D[m(\vec{r})]\,\text{tr}'\left[e^{-\beta H}\right]\Big|_{m(\vec{r})} \;. \tag{160}$$

Here tr$'$ means a trace over all (other) degrees of freedom by a given configuration $m(\vec{r})$, whereas $\int D[m]$ means a summation (functional integration) over all configurations $m(\vec{r})$. For example $\vec{m}(\vec{r})$ can be a coarse-grained magnetisation density.

For every configuration $m(\vec{r})$ there is a number of microscopic states in which $m(\vec{r})$ is realised $N[m(\vec{r})] \equiv \exp[S[m(\vec{r})]/k_B]$. Here $S[m(\vec{r})]$ can be interpreted as entropy of the configuration $m(\vec{r})$. Thus

$$\text{tr}'\left[e^{-\beta H}\right]\Big|_{m(\vec{r})} = e^{S[m(\vec{r})]/k_B}\, e^{-\beta U[m(\vec{r}),h(\vec{r})]} \;, \tag{161}$$

where $h$ is the conjugate to $m$ field, e.g., the magnetic field, and $U\left[m(\vec{r}),h(\vec{r})\right]$ is the (properly averaged) energy of the configuration $m(\vec{r})$ in the field $h(\vec{r})$. We introduce the free energy functional (Landau functional)

$$\mathcal{F}[m,h] = U[m,h] - TS[m] \;, \tag{162}$$

so that

$$\text{tr}'\left[e^{-\beta H}\right]\Big|_{m(\vec{r})} = e^{-\beta\mathcal{F}[m(\vec{r}),h(\vec{r})]} \;, \tag{163}$$

and

$$Z = \mathrm{tr}\left[e^{-\beta H}\right] = \int D[m(\vec{r})]\, e^{-\beta\mathcal{F}[m(\vec{r}),h(\vec{r})]} \ . \tag{164}$$

Assuming the external field is constant $h(\vec{r}) = h$ we have, by definition, $Z = e^{-\beta G(T,h)}$. Thus $G(T,h)$ is the true thermodynamic potential (enthalpy), whereas $\mathcal{F}[m(\vec{r}),h]$ is not.

In this phenomenological theory $\mathcal{F}$ is chosen on the basis of very general considerations. These are:

i) symmetries: a) translations and rotations of the space; b) internal symmetries: $SO(3)$ rotations of $\vec{m}$ for Heisenberg model or $m \to -m$ for Ising model.

ii) Locality:

$$\mathcal{F} = \int d^d r f[m(r), \nabla m(r), \ldots, h(r)] \ . \tag{165}$$

iii) The theory holds only in the vicinity of the phase transition, thus $m$ is small.

### B. Landau-Ginzburg functional

After all these discussions we write down the Landau-Ginzburg functional

$$\mathcal{F} = \int d^d r \left[\frac{1}{2} t\, m^2(\vec{r}) + \frac{1}{4} b\, m^4(\vec{r}) + \frac{1}{2} K \left[\vec{\nabla} m(\vec{r})\right]^2 - h\, m(\vec{r})\right] \ . \tag{166}$$

The coefficient $t$ is chosen as $t = a(T - T_c)$ with $a > 0$, whereas $b > 0$ and $K > 0$.

One has now to perform the functional integration

$$Z = \int D[m(\vec{r})]\, e^{-\beta\mathcal{F}[m(\vec{r}),h(\vec{r}),T]} \ . \tag{167}$$

The mean-field approximation consists in approximating $Z$ as follows

$$Z \approx e^{-\beta\mathcal{F}_{min}(T,h)} \ , \tag{168}$$

where $\mathcal{F}_{\min}(T,h) = \min_{m(\vec{r})} \mathcal{F}[m,h,T] = G(T,h)$.

We look for a homogeneous solution providing the minimum of $\mathcal{F}[m,h,T]$. Then we use

$$f(m,T,h) = \frac{\mathcal{F}}{V} = \frac{t}{2} m^2 + \frac{b}{4} m^4 - hm \ . \tag{169}$$

The variation gives an equation for the mean-field solution $m_0$:

$$t m_0 + b m_0^3 - h = 0 \ . \tag{170}$$

At $h = 0$ we obtain

$$m_0 = \begin{cases} 0 & \text{for } T > T_c \ , \\ \pm\sqrt{\frac{|t|}{b}} = \pm\sqrt{\frac{a(T_c - T)}{b}} & \text{for } T < T_c \ . \end{cases} \tag{171}$$

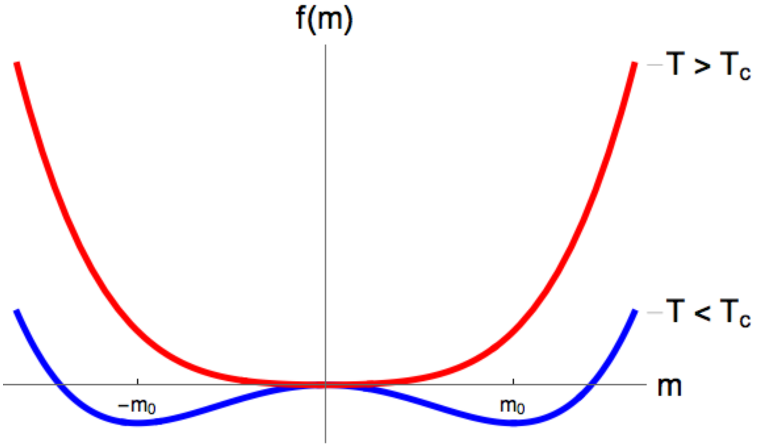

FIG. 8: Landau functional at $T > T_c$ and $T < T_c$.

### C. Phase transition at $T = T_c$. Critical exponents.

The Landau functional both at $T > T_c$ and $T < T_c$ is shown in Fig. 8. Below the critical temperature two minima at $m = \pm|m_0|$ appear. We investigate the critical behaviour:

- For the order parameter we have

$$m_0 \propto (T_c - T)^{\beta} \ , \tag{172}$$

where the Landau theory predicts the critical exponent $\beta$ to be given by $\beta = 1/2$.

- For the magnetisation at $T = T_c$, i.e., $t = 0$ we obtain

$$m_0 = \left(\frac{h}{b}\right)^{1/3} \propto h^{1/\delta} \ . \tag{173}$$

Thus $\delta = 3$ in the Landau theory.

- To calculate the susceptibility at $T \neq T_c$ we differentiate Eq. (170) with respect to $h$. This gives

$$(t + 3bm_0^2)\,\frac{\partial m_0}{\partial h} - 1 = 0 \ . \tag{174}$$

Thus, for $T > T_c$ and $m_0(h = 0) = 0$ we obtain

$$\chi = \frac{\partial m_0}{\partial h} = \frac{1}{t} = \frac{1}{a(T - T_c)} \ . \tag{175}$$

For $T < T_c$ we have $m_0(h = 0) = \sqrt{|t|/b}$. Thus

$$\chi = \frac{\partial m_0}{\partial h} = \frac{1}{t + 3bm_0^2} = \frac{1}{t + 3|t|} = \frac{1}{(-2t)} = \frac{1}{2a(T_c - T)} \ . \tag{176}$$

The critical behaviour is characterised by $\chi \propto |T-T_c|^{-\gamma}$ with $\gamma = 1$.

- Heat capacitance for $h = 0$: $C \propto |T-T_c|^{-\alpha}$. In Landau theory $\alpha = 0$. To show that we notice that the thermodynamic potential (free enthalpy) is given in the saddle-point approximation by

$$G(T, h=0) = \mathcal{F}_{min}[m] = V\left(\frac{1}{2}tm_0^2 + \frac{1}{4}bm_0^4\right) = \begin{cases} 0 \quad \text{for} \quad T > T_c \\ -\frac{V|t|^2}{4b} = -\frac{Va^2(T-T_c)^2}{4b} \quad \text{for} \quad T < T_c \end{cases} . \tag{177}$$

This gives

$$C_h = -T\,\frac{\partial^2 G}{\partial T^2} = \begin{cases} 0 \quad \text{for} \quad T > T_c \\ \frac{Va^2T}{2b} \quad \text{for} \quad T < T_c \end{cases} . \tag{178}$$

Thus the heat capacitance "jumps", but there is no divergency and $C_h \propto |T-T_c|^{-\alpha}$ with $\alpha = 0$.

### D. Correlations and fluctuations

We aim at finding the order parameter $m(r)$ for an imhomogeneous weak external field $h(r)$. We have to minimise $\mathcal{F} = \int d^d r\, f$, where

$$f \equiv \left[\frac{1}{2}t\, m^2(\vec{r}) + \frac{1}{4}b\, m^4(\vec{r}) + \frac{1}{2}K\left[\vec{\nabla}m(\vec{r})\right]^2 - h\, m(\vec{r})\right] . \tag{179}$$

For this one has to solve the Euler-Lagrange equation

$$\frac{\partial f}{\partial m} - \vec{\nabla}\frac{\partial f}{\partial(\vec{\nabla}m)} = 0 . \tag{180}$$

This gives

$$t\, m(r) + b\, m^3(r) - K\vec{\nabla}^2 m(r) = h(r) . \tag{181}$$

We assume $m = m_0 + \delta m$ and linearise. This gives

$$\begin{aligned} m_0^2 &= \frac{|t|}{b} \quad \text{for} \quad T < T_c , \\ m_0 &= 0 \quad \text{for} \quad T > T_c , \end{aligned} \tag{182}$$

and

$$(t + 3bm_0^2)\delta m(r) - K\vec{\nabla}^2\delta m(r) = h(r) . \tag{183}$$

Applying the Fourier transform we obtain

$$(t + 3bm_0^2)\delta m(q) + Kq^2\delta m(q) = h(q) , \tag{184}$$

where e.g., $h(q) = \int d^d r\, h(r)\, e^{-iqr}$ and, respectively, $h(r) = (2\pi)^{-d}\int d^d q\, h(q)\, e^{iqr}$.

### 1. *Susceptibility*

Thus

$$\chi(q) = \frac{\partial m(q)}{\partial h(q)} = \frac{1}{t + 3bm_0^2 + Kq^2} \ . \tag{185}$$

We get

$$\chi(q) = \begin{cases} \frac{1}{a(T-T_c)+Kq^2} & \text{for} \quad T > T_c \\ \frac{1}{2a(T_c-T)+Kq^2} & \text{for} \quad T < T_c \end{cases} \ . \tag{186}$$

This result can be rewritten as

$$\chi(q) = \frac{\chi_0}{1+\xi^2 q^2} = \frac{1}{K}\frac{1}{q^2+\xi^{-2}} \ , \tag{187}$$

where

$$\chi_0 = \begin{cases} \frac{1}{a(T-T_c)} & \text{for} \quad T > T_c \\ \frac{1}{2a(T_c-T)} & \text{for} \quad T < T_c \end{cases} \ , \tag{188}$$

as obtained above, and

$$\xi = \begin{cases} \sqrt{\frac{K}{a(T-T_c)}} & \text{for} \quad T > T_c \\ \sqrt{\frac{K}{2a(T_c-T)}} & \text{for} \quad T < T_c \end{cases} \ . \tag{189}$$

The length $\xi$ is called the correlation length (will be explained below) and shows the critical behaviour $\xi \propto |T - T_c|^{-\nu}$, where $\nu = 1/2$.

The physical meaning of the correlation length $\xi$ is easier to understand in the $r$ space. The linear response relation $\delta m(q) = \chi(q)h(q)$ becomes upon the Fourier transform

$$\delta m(r) = \int d^d r' \, \chi(r - r')h(r') \ , \tag{190}$$

where

$$\chi(\vec{r}) = \int \frac{d^d q}{(2\pi)^d} \frac{e^{i\vec{q}\vec{r}}}{K} \frac{1}{q^2+\xi^{-2}} \ . \tag{191}$$

The function $\chi(\vec{r})$ describes the response to point-like perturbation. Indeed for $h(\vec{r}) = \lambda\delta(\vec{r} - \vec{0})$ (a delta-like field centered in the origin) we obtain $\delta m(\vec{r}) = \lambda\chi(\vec{r})$. Introducing a dimensionless wave vector $\vec{s} \equiv \xi\vec{q}$ we get

$$\begin{aligned} \chi(\vec{r}) &= \frac{1}{K\xi^{d-2}} \int \frac{d^d s}{(2\pi)^d} \frac{e^{i\vec{s}(\vec{r}/\xi)}}{1+s^2} = \frac{1}{Kr^{d-2}} \left(\frac{r}{\xi}\right)^{d-2} \int \frac{d^d s}{(2\pi)^d} \frac{e^{i\vec{s}(\vec{r}/\xi)}}{1+s^2} \\ &= \frac{1}{Kr^{d-2}} Y(r/\xi) \ , \end{aligned} \tag{192}$$

where

$$Y(r/\xi) = \left(\frac{r}{\xi}\right)^{d-2} \int \frac{d^d s}{(2\pi)^d} \frac{e^{i\vec{s}(\vec{r}/\xi)}}{K} \frac{1}{1+s^2} \ . \tag{193}$$

The behaviour of $Y(x)$ is well known

$$Y(x) \sim \begin{cases} 1 \quad \text{for} \quad x \ll 1 \\ x^{\frac{d-3}{2}} e^{-x} \quad \text{for} \quad x \gg 1 \end{cases} . \tag{194}$$

Thus, for $r \ll \xi$ the susceptibility shows a power low dependence $\chi(r) \sim r^{-(d-2)}$, whereas for $r \gg \xi$ it crosses over to the exponential decay $\chi(r) \sim e^{-r/\xi}$. Thus, $\xi$ is the spacial extent of the domain in which the system responds to a delta-like field.

At the critical point, $T = T_c$, we have $\xi = \infty$ and for arbitrary large $r$ we obtain $\chi(r) \sim r^{-(d-2)}$, which corresponds to $\chi(q) \sim q^{-2}$. The general form is $\chi(r) \sim r^{-(d-2+\eta)}$ or $\chi(q) \sim q^{-(2-\eta)}$. In Landau theory the critical exponent $\eta$ vanishes, $\eta = 0$.

### *2. Correlation function.*

Next we calculate the correlation function of fluctuations, i.e.,

$$C(r - r') \equiv \langle m(r)m(r')\rangle - \langle m(r)\rangle \langle m(r')\rangle = \langle \delta m(r)\delta m(r')\rangle \ . \tag{195}$$

Per definition

$$\langle m(r)\rangle = \frac{1}{Z}\int [Dm]\, m(r) e^{-\beta \mathcal{F}[m]} \ , \tag{196}$$

and

$$\langle m(r)m(r')\rangle = \frac{1}{Z}\int [Dm]\, m(r)m(r') e^{-\beta \mathcal{F}[m]} \ . \tag{197}$$

Here the partition function is given by

$$Z = \int [Dm]\, e^{-\beta \mathcal{F}[m]} \ . \tag{198}$$

In our case

$$\mathcal{F} = \int d^d r \left[\frac{1}{2} t\, m^2(\vec{r}) + \frac{1}{4} b\, m^4(\vec{r}) + \frac{1}{2} K \left[\vec{\nabla} m(\vec{r})\right]^2 - h\, m(\vec{r})\right] \ . \tag{199}$$

The only thing important to us now is the linear coupling to the external field $h(r)$. The rest of $\mathcal{F}$ can be arbitrary. We thus obtain

$$\langle m(r)\rangle = \frac{1}{\beta Z}\frac{\delta Z}{\delta h(r)} = \frac{1}{\beta}\frac{\delta \ln Z}{\delta h(r)} \ , \tag{200}$$

and

$$\langle m(r)m(r')\rangle = \frac{1}{\beta^2 Z}\frac{\delta^2 Z}{\delta h(r')\delta h(r)} \ , \tag{201}$$

**Here we use the variational derivative which is defined as follows: assume there is a functional $A[\eta(r)]$ with the function/argument $\eta(r)$. Then**

$$\frac{\delta A}{\delta \eta(r')} \equiv \lim_{\epsilon \to 0} \frac{A[\eta(r) + \epsilon \delta(r - r')] - A[\eta(r)]}{\epsilon} \ . \tag{202}$$

Let us calculate the nonlocal susceptibility:

$$\chi(r, r') = \frac{\delta \langle m(r) \rangle}{\delta h(r')} = \frac{\delta}{\delta h(r')} \frac{1}{\beta} \frac{\delta \ln Z}{\delta h(r)} = \frac{1}{\beta} \frac{\delta^2 \ln Z}{\delta h(r') \delta h(r)} \ . \tag{203}$$

Further

$$\chi(r, r') = \frac{1}{\beta} \frac{\delta}{\delta h(r')} \left[ \frac{1}{Z} \frac{\delta Z}{\delta h(r)} \right] = \frac{1}{\beta Z} \frac{\delta^2 Z}{\delta h(r') \delta h(r)} - \frac{1}{\beta Z^2} \left[ \frac{\delta Z}{\delta h(r)} \right] \left[ \frac{\delta Z}{\delta h(r')} \right] \ . \tag{204}$$

This, finally, gives

$$\chi(r, r') = \beta \left\langle \delta m(r) \delta m(r') \right\rangle = \beta C(r, r') \ . \tag{205}$$

This relation is a special case of the Fluctuation-Dissipation-Theorem (FDT). Thus knowing the susceptibility $\chi(r, r')$ we also know the correlation function $C = \chi / \beta$. Of course one can also calculate $C(r, r')$ directly (exercise).

## E. Validity of the mean-field approximation, Ginzburg criterion.

### 1. *Relative strength of fluctuations*

We define the fluctuations in the correlation volume

$$\delta m_\xi \equiv \frac{1}{V_\xi} \int_{V_\xi} d^d r \, \delta m(r) \ . \tag{206}$$

Here $V_\xi = \xi^d$. We are interested in the strength of fluctuations

$$\begin{aligned} \langle \delta m_\xi^2 \rangle &= \frac{1}{V_\xi^2} \int_{V_\xi} d^d r_1 \int_{V_\xi} d^d r_2 \ \langle \delta m(r_1) \delta m(r_2) \rangle \\ &= \frac{1}{V_\xi^2} \int_{V_\xi} d^d r_1 \int_{V_\xi} d^d r_2 \ C(r_1 - r_2) \ . \end{aligned} \tag{207}$$

Up to coefficients of order unity we get

$$\langle \delta m_\xi^2 \rangle \approx \frac{1}{V_\xi} \int_{V_\xi} d^d r \ C(r) = \frac{1}{\beta V_\xi} \int_{V_\xi} d^d r \ \chi(r) \ . \tag{208}$$

Using (192) and (194) we obtain

$$\langle \delta m_\xi^2 \rangle \approx \frac{1}{K\beta\xi^d}\int_{V_\xi} d^d r\; r^{2-d} \approx \frac{\xi^{2-d}}{K\beta} \ . \tag{209}$$

We now compare $\langle \delta m_\xi^2 \rangle$ with $m_0^2$. We obtain

$$\frac{\langle \delta m_\xi^2 \rangle}{m_0^2} \approx \frac{\xi^{2-d}\, b}{K\beta|t|} \ . \tag{210}$$

Substituting $|t| = a|T-T_c|$ and $\xi \sim \sqrt{K/|t|}$ we obtain

$$\frac{\langle \delta m_\xi^2 \rangle}{m_0^2} = \frac{b}{K^{d/2}\beta|t|^{\frac{4-d}{2}}} \approx \left|\frac{T-T_c}{T_c}\right|^{\frac{d-4}{2}} \frac{(aT_c)^{\frac{d-4}{2}}\, b}{K^{d/2}\beta} \ . \tag{211}$$

Finally, we can replace $\beta$ by $1/(k_B T_c)$, since we investigate the vicinity of $T_c$:

$$\frac{\langle \delta m_\xi^2 \rangle}{m_0^2} = \frac{b}{K^{d/2}\beta|t|^{\frac{4-d}{2}}} \approx \left|\frac{T-T_c}{T_c}\right|^{\frac{d-4}{2}} \frac{(aT_c)^{\frac{d-4}{2}}\, b\, k_B T_c}{K^{d/2}} = \left|\frac{T-T_c}{T_c}\right|^{\frac{d-4}{2}} \tau_G^{\frac{4-d}{2}} \ , \tag{212}$$

where we have introduced the dimensionless Ginzburg parameter $\tau_G$ given by

$$\tau_G = \left[\frac{(aT_c)^{\frac{d-4}{2}}\, b\, k_B T_c}{K^{d/2}}\right]^{\frac{2}{4-d}} \ . \tag{213}$$

We see that for $d > 4$ the mean field theory works well and $\frac{\langle \delta m_\xi^2 \rangle}{m_0^2} \to 0$ as $T \to T_c$. For $d < 4$ the situation is more involved. The mean field theory works well as long as $|T-T_c|/T_c > \tau_G$. Closer to the critical point, that is for $|T-T_c|/T_c < \tau_G$ the mean field theory does not work. Fortunately, in some materials like, e.g., the superconducting aluminum, the Ginzburg parameter is very small ($\sim 10^{-16}$). This makes the mean field theory applicable almost everywhere. In other systems (e.g., ferromagnets) it is not so and one has to take into account fluctuations.

### 2. *Fluctuation correction to the heat capacitance*

We can obtain Ginzburg criterion differently. We consider fluctuations around the mean field solution at $h = 0$. That is we write

$$\mathcal{F} = \mathcal{F}_0 + \delta\mathcal{F} \ , \tag{214}$$

where

$$\mathcal{F} = \int d^d r \left[\frac{1}{2} t\, m^2(\vec{r}) + \frac{1}{4} b\, m^4(\vec{r}) + \frac{1}{2} K \left[\vec{\nabla} m(\vec{r})\right]^2\right] \ . \tag{215}$$

$$\mathcal{F}_0 = \mathcal{F}[m_0] \ , \quad \text{where} \quad m_0^2 = |t|/b \ . \tag{216}$$

We assume $m(r) = m_0 + \delta m(r)$ and keep only the second order in $\delta m$ terms (the first order vanishes because $m_0$ is the saddle-point. We obtain

$$\begin{aligned} \delta\mathcal{F} &= \int d^d r \left[\frac{1}{2} t\, \delta m^2(\vec{r}) + \frac{3}{2} b\, m_0^2 \delta m^2(\vec{r}) + \frac{1}{2} K \left[\vec{\nabla}\delta m(\vec{r})\right]^2\right] \\ &= \frac{1}{2}\int d^d r \left[A \delta m^2(\vec{r}) + K \left[\vec{\nabla}\delta m(\vec{r})\right]^2\right] \ , \end{aligned} \tag{217}$$

where $A \equiv t + 3bm_0^2$. In Fourier space this gives

$$\delta\mathcal{F} = \frac{1}{2}\int \frac{d^d q}{(2\pi)^d} \left[A + Kq^2\right] \delta m_q \delta m_{-q} \ . \tag{218}$$

For the partition function this gives

$$Z = \int [Dm] e^{-\beta\mathcal{F}} = e^{-\beta\mathcal{F}_0} \int [Dm] e^{-\beta\delta\mathcal{F}} \ . \tag{219}$$

We get

$$\int [Dm] e^{-\beta\delta\mathcal{F}} = \prod_q \int (C_q dm_q)\, e^{-\frac{(\Delta q)^d}{(2\pi)^d}\frac{\beta}{2}[A+Kq^2]\delta m_q \delta m_{-q}} \ . \tag{220}$$

The integration measure $C_q$ is impossible to guess now. From the exercise about the derivation of the Landau functional from the Ising model we know that $C_q \propto \sqrt{\beta}$, whereas the rest of the constants are not important. This gives

$$\int [Dm] e^{-\beta\delta\mathcal{F}} = \mathcal{N} \prod_q \frac{1}{\sqrt{A + Kq^2}} \ , \tag{221}$$

where $\mathcal{N}$ contains all the constants (independent of $\beta$). The constant $\mathcal{N}$ as well as the product after it are dimensionful. Before calculating the logarithm it is convenient to make both dimensionless. We extract a dimensionful constant as follows $A = aT_c A_0$, where

$$A_0 \equiv \frac{T - T_c}{T_c} + \frac{3bm_0^2}{aT_c} = \begin{cases} \frac{|T-T_c|}{T_c} & \text{for} \quad T > T_c \\ \frac{2|T-T_c|}{T_c} & \text{for} \quad T < T_c \end{cases} \ . \tag{222}$$

Analogously $K = aT_c\xi_0^2$, where $\xi_0^2 \equiv K/(aT_c)$. Then we obtain

$$\int [Dm] e^{-\beta\delta\mathcal{F}} = \mathcal{N}' \prod_q \frac{1}{\sqrt{A_0 + \xi_0 q^2}} \ , \tag{223}$$

where $\mathcal{N}'$ is the new dimensionless constant, which is independent of temperature. For the partition function we thus get

$$Z = e^{-\beta\mathcal{F}_0} \mathcal{N}' \prod_q \frac{1}{\sqrt{A_0 + \xi_0 q^2}} \ , \tag{224}$$

and for the thermodynamic potential (free enthalpie)

$$G(T,h=0) = -\frac{1}{\beta}\ln Z = \mathcal{F}_0 + \frac{k_B T}{2}\sum_q \ln\left(A_0+\xi_0^2 q^2\right) - k_B T \ln \mathcal{N}' \ . \tag{225}$$

For the heat capacity this gives

$$C_{h=0} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{h=0} = C_0 - k_B T\left(\frac{\partial A_0}{\partial T}\right)\sum_q \frac{1}{A_0+\xi_0^2 q^2} + \frac{k_B T^2}{2}\left(\frac{\partial A_0}{\partial T}\right)^2 \sum_q \frac{1}{(A_0+\xi_0^2 q^2)^2} \ , \tag{226}$$

where

$$C_0 = -T\left(\frac{\partial^2 \mathcal{F}_0}{\partial T^2}\right)_{h=0} = \begin{cases} 0 & \text{for} \quad T > T_c \\ \frac{Va^2T}{2b} & \text{for} \quad T < T_c \end{cases} \ . \tag{227}$$

is the mean-field contribution and we have used the fact that $\partial^2 A_0/\partial T^2 = 0$. Making sums into integrals we obtain

$$\begin{aligned} C_{h=0} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{h=0} = C_0 \ &- \ k_B T\left(\frac{\partial A_0}{\partial T}\right) V\int \frac{d^d q}{(2\pi)^d}\frac{1}{A_0+\xi_0^2 q^2} \\ &+ \ \frac{k_B T^2}{2}\left(\frac{\partial A_0}{\partial T}\right)^2 V\int \frac{d^d q}{(2\pi)^d}\frac{1}{(A_0+\xi_0^2 q^2)^2} \ . \end{aligned} \tag{228}$$

We consider the vicinity of the phase transitions, $A_0 \approx 0$. In this limit both integrals diverge either at $q \to \infty$ (ultra-violet divergency) or at $q \to 0$ (infra-red divergency) or in both limits logarithmically. The ultra-violet divergency is unrelated to the phase transition and might be an artefact of us using the long wave length theory (GL theory) for all $q$. Thus we will disregard the ultra-violet divergency and focus on the infra-red one. This divergency is cut-off at $q \sim \xi^{-1} = \sqrt{A_0}/\xi_0$, where $\xi$ is the correlation length introduced earlier. Here the second integral is more dangerous. Indeed

$$\int \frac{d^d q}{(2\pi)^d}\frac{1}{(A_0+\xi_0^2 q^2)^2} = \frac{\Omega_d}{\xi_0^4}\int_0^\infty \frac{q^{d-1}dq}{(2\pi)^d}\frac{1}{(\xi^{-2}+q^2)^2} \ . \tag{229}$$

This integral has an infra-red divergency for $d < 4$ and is given in this case

$$\frac{\Omega_d}{\xi_0^4}\int_0^\infty \frac{q^{d-1}dq}{(2\pi)^d}\frac{1}{(\xi^{-2}+q^2)^2} \sim \frac{\Omega_d}{(2\pi)^d\,\xi_0^4}\int_{\xi^{-1}}^\infty dq\, q^{d-5} \sim \frac{\Omega_d \xi^{4-d}}{(2\pi)^d\,(4-d)\xi_0^4} \ . \tag{230}$$

The first integral has an infra-red divergency for $d < 2$ and, even in that case, would diverge "weaker" than the second one. Thus it can be neglected.

Taking into account $(\partial A_0/\partial T)^2 \sim T_c^{-2}$ we obtain the contribution of fluctuations for $d < 4$:

$$C_{fluc} \sim \frac{k_B V T^2}{T_c^2}\frac{\xi^{4-d}}{\xi_0^4} \sim \frac{k_B V T^2}{\xi_0^d T_c^2} A_0^{\frac{d-4}{2}} \sim \frac{k_B V T^2}{\xi_0^d T_c^2}\left|\frac{T-T_c}{T_c}\right|^{\frac{d-4}{2}} \quad . \tag{231}$$

Thus $C_{fluc}$ diverges at $T \to T_c$ as $C_{fluc} \sim |T - T_c|^{\frac{d-4}{2}}$ and becomes bigger than $C_0$ close enough to $T_c$. Comparing with $C_0$ at $T < T_c$ ($C_0 \sim V a^2 T/b$) we see that the contribution of fluctuation dominates at

$$\left|\frac{T-T_c}{T_c}\right|^{\frac{d-4}{2}} \gg \frac{a^2 \xi_0^d T_c}{k_B b} = \frac{a^2 K^{d/2} T_c}{k_B b (a T_c)^{d/2}} = \frac{K^{d/2}}{k_B T_c b (a T_c)^{(d-4)/2}} \; . \tag{232}$$

Thus we recover again Ginzburg's criterion.

### *3. Lower and upper critical dimensions*

As we have seen for $d > 4$ the MF theory is correct whereas for $d < 4$ it is not and one has to take into account fluctuations around the mean field value of the order parameter. Thus $d_u = 4$ is the upper critical dimension of this theory.

There is also a lower critical dimension. It turns out that the phase transition becomes impossible at $T > 0$ (the fluctuations are too strong) if the dimension is low. For the Ising model the lower critical dimension is $d_l = 1$. Indeed as we have seen the one-dimensional Ising model does not have a transition at any finite temperature (actually strictly $T_c = 0$). For the Heisenberg model $d_l = 2$.

## F. Classification of phase transitions.

1) Analyse again $G(T, H)$ and $F(T, M)$ (see Figs. 6,7) for Ising model or, equivalently, for Landau theory. Introduce 1-st order and 2-nd order transitions and the critical point, where the 1-st order line terminates by a 2-nd order point.

Explain coexistence domain around the line of the 1-st order transition. The Landau $\mathcal{F}(t, m, h)$ functional has two local minima as a function of $m$ in this case.

Maxwell construction for $F(T, M)$. Assume the system separates into tow phases with magnetisation pro volume (or per spin) $m_1$ and volume $V_1$ and magnetisation per spin $m_2$ and volume $V_2$. We have

$$V = V_1 + V_2 \quad , \quad m = \frac{M}{V} = \frac{m_1 V_1 + m_2 V_2}{V} \; . \tag{233}$$

Clearly $m$ is between $m_1$ and $m_2$. We can extract $V_1$ (and $V_2$) as a function of $m$:

$$V_1 = \frac{m - m_2}{m_1 - m_2} V \quad , \quad V_2 = \frac{m_1 - m}{m_1 - m_2} V \ . \tag{234}$$

The free energy of the mixture is then given by

$$F_{mix}(T, M) = V_1 f(T, m_1) + V_2 f(T, m_2) \ , \tag{235}$$

where $f = F/V$ is the free energy density of a pure phase. We obtain

$$\begin{aligned} F_{mix}(T, M)/V &= \frac{m - m_2}{m_1 - m_2} f(T, m_1) + \frac{m_1 - m}{m_1 - m_2} f(T, m_2) \\ &= m \, \frac{f(T, m_1) - f(T, m_2)}{m_1 - m_2} + \frac{m_1 \, f(T, m_2) - m_2 \, f(T, m_1)}{m_1 - m_2} \ . \end{aligned} \tag{236}$$

Thus, $F_{mix}$ is a linear function of $M$. Maxwell construction.

2) The same for van der Waals gas. From the van der Waals equation of state

$$(P + an^2)(V - bN) = k_{\mathrm{B}} T N \tag{237}$$

we get

$$\frac{P}{k_B T} = \frac{n}{1 - bn} - \frac{an^2}{k_B T} \ . \tag{238}$$

At $T < T_c$ there are three possible values of $n$ for a given $P$. Maxwell construction for $F(T, V)$ (equivalently for $F(T, n = N/V)$.

Latent heat: it appears if the entropies (entropy densities) of the two phases are different. Then

$$\delta Q = T_c (S_1 - S_2) = T_c \left[ S(T_c + \epsilon) - S(T_c - \epsilon) \right] \ . \tag{239}$$

Recall that $G(T, p, N) = U + pV - TS$ (or in magnetic case $G(T, H) = U - MH - TS$). At the phase transition $G$ is continuous and so is $pV$. Therefore a discontinuity in $S$ means discontinuity in $U$. There is latent heat in the case of van der Waals gas/liquid. There is no latent heat in the case of the 1-st order ferromagnetic transition driven by $H$. This is because of the symmetry $H \to -H$. The 1-st order transition line is parallel to the $T$ axis. Thus, no entropy difference in two phases.

3) Superconductivity.

There exist two classifications:

1) The most popular is the classification according to the behaviour of the order parameter. In phase transitions of the 1-st order the order parameter jumps discontinuously, whereas in the phase transitions of the 2-nd order the order parameter is continuous.

2) Another classification is due to P. Ehrenfest. Here one looks and the behaviour of the thermodynamic potential at the transition point. The phase transitions are labeled by the lowest derivative of the free energy that is discontinuous at the transition.

$C_V(T)$ for transitions of 1-st, 2-nd and 3-d order transitions. Latent heat from the delta function in $C_V(T)$.

The Ehrenfest classification should be generalised if fluctuations around mean field are taken into account, and, e.g., $\alpha \neq 0$. We remind $C \sim |t|^{-\alpha}$. Thus a more appropriate Ehrenfest criterion would be that $n$-th derivative of the thermodynamic potential has a singularity of some kind, whereas lower order derivatives are continuous. For example, if $\alpha = 1/2$ (like in our calculation above) then $G \sim |t|^{2-\alpha}$ is continuous, $S \sim \partial G/\partial t \sim |t|^{1-\alpha}$ is continuous, but $C \sim \partial^2 G/\partial t^2$ is singular and the transition is of the 2-nd order.

Interestingly, the Bose-Einstein condensation of the ideal Bose gas is a transition of the 3-d order. To understand this consider the free energy $F(T, N, V)$ as the function of $T$ and $N$ (and $V$ constant and large). Indeed, as we have seen $C_V = -T\left(\partial^2 F/\partial T^2\right)_N$ is continuous but has a kink, i.e., $\left(\partial^3 F/\partial T^3\right)_N$ is discontinuous. Analogously, $\mu = -\left(\partial F/\partial N\right)_T$ has a discontinuity in the second derivative, i.e. in $\partial^2 \mu/\partial T^2$.

### G. Critical exponents, universality classes

Thus far we have introduced several critical exponents characterising a 2-nd order phase transition and calculated them in the mean field (MF) approximation. Systems with $d_l < d < d_u$ can be characterised by completely different critical exponents. There families of systems (models) having the same set of exponents. These are called universality classes. In the following table the critical exponents are shown for MF theory as well as for the 3D Ising class.

| Exponent | Controlled quantity | Scaling | Conditions | MF value | 3D Ising |
|---|---|---|---|---|---|
| $\alpha$ | Heat capacity | $C_h \propto \|t\|^{-\alpha}$ | $\|t\| \to 0,\ h = 0$ | 0 | 0.11 |
| $\beta$ | Order parameter | $m \propto \|t\|^{\beta}$ | $t \to 0 - \epsilon,\ h = 0$ | 1/2 | 0.33 |
| $\gamma$ | Susceptibility | $\chi \propto \|t\|^{-\gamma}$ | $\|t\| \to 0,\ h = 0$ | 1 | 1.24 |
| $\delta$ | Order parameter | $m \propto \|h\|^{1/\delta}$ | $\|t\| = 0,\ h \to 0$ | 3 | 4.8 |
| $\nu$ | Correlation length | $\xi \propto \|t\|^{-\nu}$ | $\|t\| \to 0,\ h = 0$ | 1/2 | 0.63 |
| $\eta$ | Correlation function | $C(r) \propto \|r\|^{-d+2-\eta}$ | $\|t\| = 0,\ h = 0$ | 0 | 0.04 |

As we will see below the critical exponents are not independent.

### H. Scaling hypothesis. Relations between critical exponents.

#### 1. *Scaling in the mean field theory*

The thermodynamic potential $G(T,H)$ can be written in the vicinity of the phase transition as $G = G(t,h)$, where $t \propto (T - T_c)$ and $h \propto H$. In the mean field (Landau) theory we have

$$\frac{G_{MF}(t,h)}{V} = \min_m \left[\frac{t}{2}m^2 + \frac{b}{4}m^4 - hm\right] . \tag{240}$$

The optimal value $m(t,h)$ is found by solving the equation

$$tm + bm^3 = h . \tag{241}$$

In this equation we can rescale $t \to t' = s^x t$ and $h \to h' = s^y h$ and look for $m'$ which satisfies $t'm' + bm'^3 = h'$ ($b$ is not rescaled). Choosing $m' = s^z m$ we obtain $x + z = 3z = y$. Choosing $x = 1$ we get $z = 1/2$ and $y = 3/2$. Thus we obtain

$$m(t',h') = s^{1/2}m(t,h) \quad \text{or} \quad m(t,h) = s^{-1/2}m(st, s^{3/2}h) . \tag{242}$$

This gives

$$G_{MF}(t,h) = V\left\{\frac{t}{2}[m(t,h)]^2 + \frac{b}{4}[m(t,h)]^4 - hm[t,h]\right\} = s^{-2}G_{MF}(st, s^{3/2}h) . \tag{243}$$

Since $s$ is arbitrary, we can choose $s = 1/|t|$, which then gives

$$\frac{G_{MF}(t,h)}{V} = |t|^2 g_\pm\left(\frac{h}{|t|^{3/2}}\right) . \tag{244}$$

Here $g_\pm(x) \equiv G_{MF}(\pm 1, x)/V$.

#### 2. *Scaling hypothesis (Widom, 1966)*

Near the critical point there is a scaling relation

$$\frac{G(t,h)}{V} = |t|^{2-\alpha} g_\pm\left(\frac{h}{|t|^\Delta}\right) . \tag{245}$$

Equivalently

$$G(t,h) = s^{\alpha-2}G(st, s^\Delta h) . \tag{246}$$

This scaling relation can be used to derive the critical exponents. So, for the order parameter at $h = 0$ we obtain

$$m = -\frac{1}{V}\left(\frac{\partial G}{\partial h}\right)_t = -|t|^{2-\alpha-\Delta} g'_\pm\left(\frac{h}{|t|^\Delta}\right) \ . \tag{247}$$

Since at $h = 0$ and $t \neq 0$ the function $G$ is regular, we have $g'_\pm(x \to 0) \to const.$. We obtain, thus, the first critical exponent

$$\beta = 2 - \alpha - \Delta \ . \tag{248}$$

For $t = 0$ we can use directly (246). The function $G(t, h)$ is finite at $t = 0$. Thus we have

$$G(0, h) = s^{\alpha-2} G(0, s^\Delta h) \ . \tag{249}$$

We can choose $s = h^{-1/\Delta}$. Then

$$G(0, h) = h^{\frac{2-\alpha}{\Delta}} G(0, 1) \ . \tag{250}$$

Differentiating we obtain

$$m \sim h^{\frac{2-\alpha-\Delta}{\Delta}} \ , \tag{251}$$

and we obtain the second critical exponent

$$\delta = \frac{\Delta}{2 - \alpha - \Delta} = \frac{\Delta}{\beta} \ . \tag{252}$$

Finally, for the heat capacitance at $h = 0$ we have

$$G(t, 0) = s^{\alpha-2} G(st, 0) \ . \tag{253}$$

Choosing $s = 1/|t|$ we get $G(t, 0) \sim |t|^{2-\alpha}$ and

$$C \sim -T\left(\frac{\partial^2 G}{\partial T^2}\right) \sim |t|^{-\alpha} \ . \tag{254}$$

Thus, the notation $\alpha$ was chosen properly.

We see that all critical exponents can be expressed as functions of only two, i.e., $\alpha$ and $\Delta$. Thus, they are not independent. For example, from $\Delta = \beta\delta$ we obtain $\beta = 2 - \alpha - \beta\delta$ or

$$\beta = \frac{2 - \alpha}{1 + \delta} \ . \tag{255}$$

The scaling hypothesis was justified using the renormalisation group (RG) technique (Wilson 1971). The RG also allows to calculate the critical exponents.

## VI. ELEMENTS OF PHYSICAL KINETICS

### A. Langevin Equation

The Brownian motion is usually described by the Langevin equation:

$$M\ddot{X} + M\gamma\dot{X} + \frac{\partial U(X)}{\partial X} = \xi(t)\ . \tag{256}$$

Here $U(x)$ is the potential energy. The stochastic force $\xi$ is zero on average $\langle\xi(t)\rangle = 0$ and is delta correlated $\langle\xi(t_1)\xi(t_2)\rangle = q\delta(t_1 - t_2)$. Moreover $\xi(t)$ is assumed to be a Gaussian distributed random function:

$$\rho(\{\xi(t)\}) \propto e^{-\frac{q}{2}\int dt[\xi(t)^2]}\ . \tag{257}$$

We solve for $U(X) = 0$. Introducing the velocity, $V = \dot{X}$, we obtain

$$M\dot{V} + M\gamma V = \xi(t)\ . \tag{258}$$

The homogeneous equation has a solution $V(t) = V_0 e^{-\gamma t}$, thus we look for a particular solution of the inhomogeneous equation in the form $V(t) = C(t)e^{-\gamma t}$. Substituting we get

$$M\dot{C}(t)e^{-\gamma t} = \xi(t)\ , \tag{259}$$

and

$$C(t) = C_0 + (1/M)\int\limits_0^t dt'\xi(t')e^{\gamma t'}\ . \tag{260}$$

The general solution reads (constant $C_0$ included in $V_0$)

$$V(t) = V_0 e^{-\gamma t} + (1/M)\int\limits_0^t dt'\xi(t')e^{-\gamma(t-t')} \tag{261}$$

For the average velocity this gives

$$\langle V(t)\rangle = V_0 e^{-\gamma t}\ . \tag{262}$$

For the correlation function we obtain

$$\langle V(t_1)V(t_2)\rangle = V_0^2 e^{-\gamma(t_1+t_2)} + \frac{1}{M^2}\int\limits_0^{t_1} dt_1'\int\limits_0^{t_2} dt_2'\langle\xi(t_1')\xi(t_2')\rangle\, e^{-\gamma(t_1-t_1')}\, e^{-\gamma(t_2-t_2')}\ . \tag{263}$$

Using $\langle \xi(t_1')\xi(t_2')\rangle = q\delta(t_1'-t_2')$ we obtain

$$\begin{aligned}
\langle V(t_1)V(t_2)\rangle &= V_0^2 e^{-\gamma(t_1+t_2)} + \frac{q}{M^2}\int\limits_0^{\min(t_1,t_2)} dt'\, e^{-\gamma(t_1-t')}\, e^{-\gamma(t_2-t')} \\
&= V_0^2 e^{-\gamma(t_1+t_2)} + \frac{q}{M^2} e^{-\gamma(t_1+t_2)} \int\limits_0^{\min(t_1,t_2)} dt'\, e^{2\gamma t'} \\
&= V_0^2 e^{-\gamma(t_1+t_2)} + \frac{q}{2\gamma M^2} e^{-\gamma(t_1+t_2)} \left[e^{2\gamma \min(t_1,t_2)} - 1\right] \\
&= V_0^2 e^{-\gamma(t_1+t_2)} + \frac{q}{2\gamma M^2} \left[e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}\right] \ . \qquad (264)
\end{aligned}$$

For $t_1, t_2 \gg 1/\gamma$ we obtain the stationary (depending only on $t_1 - t_2$) correlation function

$$\langle V(t_1)V(t_2)\rangle = \frac{q}{2\gamma M^2}\, e^{-\gamma|t_1-t_2|} \ . \qquad (265)$$

In particular

$$\langle V^2(t)\rangle = \frac{q}{2\gamma M^2} \ . \qquad (266)$$

In equilibrium the equipartition means

$$\langle E_{kin}\rangle = \frac{M\langle V^2\rangle}{2} = \frac{1}{2}\, k_B T \ . \qquad (267)$$

Thus

$$q = 2M\gamma k_B T \ . \qquad (268)$$

This is again the classical case of the fluctuation-dissipation theorem (FDT).

Now let us investigate the coordinate:

$$X(t) = X_0 + \int\limits_0^t dt' V(t') \ . \qquad (269)$$

We get

$$\langle (X(t)-X_0)^2\rangle = \int\limits_0^t dt_1 \int\limits_0^t dt_2 \langle V(t_1)V(t_2)\rangle \ . \qquad (270)$$

Assuming $t \gg 1/\gamma$ we can disregard all the transient terms and substitute (265), which gives

$$\langle (X(t)-X_0)^2\rangle = \frac{q}{2\gamma M^2} \int\limits_0^t dt_1 \int\limits_0^t dt_2\, e^{-\gamma|t_1-t_2|} = \frac{q}{\gamma^2 M^2}\, t \ . \qquad (271)$$

We obtain diffusion, $\langle (X(t)-X_0)^2\rangle = 2Dt$, where for the diffusion coefficient we obtain the Einstein relation

$$D = \frac{q}{2\gamma^2 M^2} = \frac{k_B T}{M\gamma} \ . \tag{272}$$

The quantity $\mu = 1/(M\gamma)$ is called mobility. If an external force $F$ is applied the Langevin equation reads

$$M\dot{V} + M\gamma V = F + \xi(t) \ . \tag{273}$$

Averaging we get

$$\langle V\rangle = \mu F \ . \tag{274}$$

### 1. RCL circuits

Introduce flux in the coil $\Phi$. The voltage is given by $V = \dot{\Phi}$ (Faraday).

$$C\ddot{\Phi} + \frac{\dot{\Phi}}{R} + \frac{\Phi}{L} = \delta I \ . \tag{275}$$

Johnson-Nyquist relation

$$\langle \delta I(t)\delta I(t')\rangle = \frac{2k_B T}{R}\,\delta(t-t') \ . \tag{276}$$

### 2. Caldeira-Leggett model

This is a popular model describing interaction of a "heavy" particle with the bath of oscillators. The "heavy" particle is characterised by the coordinate $X$, momentum $P$, and mass $M$. This model is equivalent to a particle with multiple attached springs. The Hamiltonian reads

$$H = \frac{P^2}{2M} + U(X) + \sum_n \left[\frac{p_n^2}{2m_n} + \frac{m_n\omega_n^2\left(x_n - X\right)^2}{2}\right] \ . \tag{277}$$

We generalize slightly

$$H = \frac{P^2}{2M} + U(X) + \sum_n \left[\frac{p_n^2}{2m_n} + \frac{m_n\omega_n^2\left(x_n - \frac{\lambda_n}{m_n\omega_n^2}X\right)^2}{2}\right] \ . \tag{278}$$

The original model is obtained by choosing $\lambda_n = m_n\omega_n^2$.

Equations of motion:

$$\begin{aligned}
\dot{X} &= \frac{\partial H}{\partial P} = \frac{P}{M} \ , \\
\dot{P} &= -\frac{\partial H}{\partial X} = -\frac{\partial U}{\partial X} + \sum_n \lambda_n \left( x_n - \frac{\lambda_n}{m_n \omega_n^2} X \right) \ , \\
\dot{x}_n &= \frac{\partial H}{\partial p_n} = \frac{p_n}{m_n} \ , \\
\dot{p}_n &= -\frac{\partial H}{\partial x_n} = -m_n \omega_n^2 \left( x_n - \frac{\lambda_n}{m_n \omega_n^2} X \right) \ . \qquad (279)
\end{aligned}$$

This gives

$$\begin{aligned}
&M\ddot{X} = -\frac{\partial U}{\partial X} + \sum_n \lambda_n x_n - X \sum_n \frac{\lambda_n^2}{m_n \omega_n^2} \ , \\
&m_n \ddot{x}_n + m_n \omega_n^2 x_n = \lambda_n X \ . \qquad (280)
\end{aligned}$$

The second equation is solved by the Fourier transform. We obtain

$$x_n(t) = \int dt' \alpha_n(t-t') X(t') + x_n^{(\mathrm{free})}(t), \qquad (281)$$

where

$$\alpha_n(\omega) = \frac{\lambda_n}{m_n(\omega_n^2 - (\omega + i\delta)^2)} \ . \qquad (282)$$

The sign of the $i\delta$ term is chosen to make $\alpha_n$ retarded, i.e., $\alpha_n(\tau < 0) = 0$. We obtain

$$\sum_n \lambda_n x_n(t) = \int dt' \alpha(t-t') X(t') + \xi(t) \ , \qquad (283)$$

where

$$\alpha(\omega) = \sum_n \frac{\lambda_n^2}{m_n(\omega_n^2 - (\omega + i\delta)^2)} \qquad (284)$$

and

$$\xi(t) = \sum_n \lambda_n x_n^{(\mathrm{free})}(t) \ . \qquad (285)$$

We introduce the spectral density

$$J(\nu) \equiv \frac{\pi}{2} \sum_n \frac{\lambda_n^2}{m_n \omega_n} \delta(\nu - \omega_n) \ . \qquad (286)$$

This gives

$$\alpha(\omega) = \frac{2}{\pi} \int d\nu \frac{\nu J(\nu)}{\nu^2 - (\omega + i\delta)^2} \qquad (287)$$

and, finally,

$$\operatorname{Im}\alpha(\omega) = \alpha''(\omega) = \begin{cases} J(\omega) & for \quad \omega > 0 \\ -J(-\omega) & for \quad \omega < 0 \end{cases} . \tag{288}$$

An Ohmic bath is defined by

$$J(\omega) = M\gamma\omega \ , \tag{289}$$

up to some cutoff frequency $\omega_c$. We disregard, first, $\operatorname{Re}\alpha(\omega) = \alpha'(\omega)$ and obtain

$$\alpha''(t-t') = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} iM\gamma\omega = M\gamma \frac{\partial}{\partial t'}\delta(t-t') \ . \tag{290}$$

Thus

$$\int dt' \alpha''(t-t')X(t') = -M\gamma\dot{X}(t) \ . \tag{291}$$

The equation of motion now reads

$$M\ddot{X} = -\frac{\partial U}{\partial X} - M\gamma\dot{X} - X\sum_n \frac{\lambda_n^2}{m_n\omega_n^2} + \int dt'\alpha'(t-t')X(t') + \xi(t) \tag{292}$$

The second term of the RHS is the friction force due to the oscillators (resistor). The third and the fourth terms represent the renormalisation of $U(X)$. Our choice of coupling to the oscillators was such that these two terms mostly cancel each other. Finally, the last term of the RHS is the Langevin random force. We see that this is due to the free motion of the oscillators.

Let us investigate $\xi$ closer. Since

$$\xi(t) = \sum_n \lambda_n x_n^{(\mathrm{free})}(t) \ , \tag{293}$$

it is defined by the behaviour of the bath of free oscillators. Thus we consider such a bath (equivalent to the bath of photons in a cavity) and omit the superscript "free". It is much easier to calculate quantum mechanically. We consider $x_n(t)$ as an operator in the Heisenberg picture. We have

$$x_n = \sqrt{\frac{\hbar}{2m_n\omega_n}}(a_n + a_n^\dagger) \ . \tag{294}$$

Thus in the Heisenberg picture

$$x_n(t) = \sqrt{\frac{\hbar}{2m_n\omega_n}}(a_n\, e^{-i\omega_n t} + a_n^\dagger\, e^{i\omega_n t}) \ . \tag{295}$$

We use the usual equilibrium density matrix of the bath

$$\rho_{\text{bath}} = \frac{1}{Z}\, e^{-\beta H_{\text{bath}}} \ . \tag{296}$$

It is easy to show that $\langle x_n(t)\rangle = \mathrm{Tr}(x_n(t)\rho_{\text{bath}}) = 0$. For the correlation function we get

$$\begin{aligned} C_n(t_1,t_2) = \langle x_n(t_1)x_n(t_2)\rangle &= \frac{\hbar}{2m_n\omega_n}\left[e^{-i\omega_n(t_1+t_2)}\langle (a_n)^2\rangle + e^{i\omega_n(t_1+t_2)}\langle (a_n^\dagger)^2\rangle\right] \\ &+ \frac{\hbar}{2m_n\omega_n}\left[e^{-i\omega_n(t_1-t_2)}\langle a_n a_n^\dagger\rangle + e^{i\omega_n(t_1-t_2)}\langle a_n^\dagger a_n\rangle\right] \\ &= \frac{\hbar}{2m_n\omega_n}\left[e^{-i\omega_n(t_1-t_2)}\,(n_n+1) + e^{i\omega_n(t_1-t_2)}\,n_n\right] \ . \end{aligned} \tag{297}$$

Thus $C_n(t_1,t_2) = C_n(t_1-t_2)$. The occupation numbers are as usual

$$n_n = \frac{1}{e^{\beta\hbar\omega_n}-1} \ . \tag{298}$$

For the Fourier transform we get

$$C_n(\nu) = \frac{\hbar}{2m_n\omega_n}\left[2\pi\delta(\nu-\omega_n)(n_n+1) + 2\pi\delta(\nu+\omega_n)n_n\right] \ . \tag{299}$$

Finally,

$$C(t_1-t_2) \equiv \langle \xi(t_1)\xi(t_2)\rangle = \sum_n \lambda_n^2 C_n(t_1-t_2) \ . \tag{300}$$

For the Fourier transform we obtain

$$\begin{aligned} C(\nu) &= \sum_n \frac{\hbar\lambda_n^2}{2m_n\omega_n}\left[2\pi\delta(\nu-\omega_n)(n_B(\omega_n)+1) + 2\pi\delta(\nu+\omega_n)n_B(\omega_n)\right] \\ &= \sum_n \frac{\hbar\lambda_n^2}{2m_n\omega_n}\left[2\pi\delta(\nu-\omega_n)(n_B(\nu)+1) + 2\pi\delta(\nu+\omega_n)n_B(-\nu)\right] \\ &= \begin{cases} 2\hbar J(\nu)(n_B(\nu)+1) & \text{for} \quad \nu>0 \\ 2\hbar J(|\nu|)(n_B(|\nu|)) & \text{for} \quad \nu<0 \end{cases} \ . \end{aligned} \tag{301}$$

For $\nu \ll k_B T/\hbar$ we get

$$C(\nu) \approx 2M\gamma k_B T \ . \tag{302}$$

Thus $C(t-t') \approx 2M\gamma k_B T\,\delta(t-t')$, as above.

### B. Master equation

Consider a system with $N$ quantum states. In general, the system is described by a density matrix $\rho(n,n')$. Frequently it is sufficient to consider only the diagonal matrix elements $\rho(n) \equiv \rho(n,n)$. Due to a coupling to other degrees of freedom or due to external excitation the system undergoes transitions between the states. In the Markovian limit (will be explained later) the transitions are described by transition rates. So $W(n',n)$ denotes a rate of transition from the state $n'$ to the state $n$. Then the probability to be in the state $n$ satisfies the following differential equation

$$\frac{d}{dt}\,\rho(n) = \sum_{n'} W(n',n)\rho(n') - \sum_{n'} W(n,n')\rho(n) \ . \tag{303}$$

This equation is called "master equation". It is Markovian because $d\rho(t)/dt$ depends only on $\rho(t)$, i.e., it depends on the state of the system at the same time.

If the transition processes are due to the coupling to an equilibrium reservoir (bath) then the stationary solution of the master equation should be the equilibrium density matrix:

$$\rho^{eq} \propto e^{-\beta E_n} \quad \text{and} \quad \frac{d}{dt}\,\rho^{eq} = 0 \ . \tag{304}$$

These conditions are satisfied if, e.g., for each pair of states $(n,n')$ the following relation holds

$$W(n',n)e^{-\beta E_{n'}} = W(n,n')e^{-\beta E_n} \ , \tag{305}$$

or

$$\frac{W(n',n)}{W(n,n')} = e^{-\beta(E_n - E_{n'})} \ . \tag{306}$$

This is a sufficient but not necessary condition. It is called the "detailed balanced condition" (the balance is satisfied for every pair $(n,n')$). If the system is driven by an external excitation it can be in a non-equilibrium stationary state.

### *1. Example: random walk on a 1D lattice*

The states $n$ are in this case the particle being in a lattice cite number $n$. There are only transitions one step to the right or one step to the left. Thus

$$W(n_1,n_2) = \Gamma_L \delta_{n_1,n_2+1} + \Gamma_R \delta_{n_1,n_2-1} \ . \tag{307}$$

Assume that in the beginning the particle is on the lattice cite $n=0$, i.e. $\rho(n,t=0) = \delta_{n,0}$. We write down the master equation

$$\frac{d}{dt}\rho(n,t) = \Gamma_R \rho(n-1,t) + \Gamma_L \rho(n+1,t) - (\Gamma_L + \Gamma_R)\rho(n,t) \ . \tag{308}$$

This equation is very convenient to solve using the Fourier transform. Let us introduce

$$\Phi(k,t) = \sum_n \rho(n,t) e^{-ikn} \ , \tag{309}$$

so that

$$\rho(n,t) = \int_{-\pi}^{\pi} \frac{dk}{2\pi}\, \Phi(k,t)\, e^{ikn} \ . \tag{310}$$

We multiply Eq. (308) with $e^{-ikn}$ and sum over $n$. This gives

$$\frac{d}{dt}\Phi(k,t) = \Gamma_R(e^{-ik}-1)\Phi(k,t) + \Gamma_L(e^{ik}-1)\Phi(k,t) \ . \tag{311}$$

The initial condition reads $\Phi(k,0)=1$. Thus the solution reads

$$\ln \Phi(k,t) = t\left[\Gamma_R(e^{-ik}-1) + \Gamma_L(e^{ik}-1)\right] \tag{312}$$

It is easy to find the moments

$$\langle n^m(t)\rangle = \sum_n n^m \rho(n,t) = i^m \frac{d^m}{dk^m}\Phi(k,t)\Big|_{k=0} \ . \tag{313}$$

In particular

$$\langle n\rangle = (\Gamma_R - \Gamma_L)t \ . \tag{314}$$

$$\langle n^2\rangle - \langle n\rangle^2 = (\Gamma_R + \Gamma_L)t \ . \tag{315}$$

In general

$$\rho(n,t) = \int_{-\pi}^{\pi} \frac{dk}{2\pi}\, e^{\ln\Phi(k,t)}\, e^{ikn} \ . \tag{316}$$

If $t$ is large it is a good approximation to expand $\ln\Phi(k,t)$ around $k=0$. We obtain

$$\ln \Phi(k,t) = t\left[(\Gamma_R-\Gamma_L)(-ik) - \frac{1}{2}(\Gamma_L+\Gamma_R)k^2 + \dots\right] \tag{317}$$

Then the Fourier transform gives

$$\rho(n,t) \approx \frac{1}{\sqrt{2\pi(\Gamma_L+\Gamma_R)t}} \exp\left[-\frac{[n-t(\Gamma_R-\Gamma_L)]^2}{2(\Gamma_R+\Gamma_L)t}\right] \ . \tag{318}$$

We obtain a Gaussian distribution.

The index $n$ is substituted by a continuous index $x$ (e.g., position of a particle). The master equation reads

$$\frac{d}{dt}\,\rho(x) = \int dx'\, W(x',x)\rho(x') - \int dx'\, W(x,x')\rho(x)\ . \tag{319}$$

Introduce $\xi = x - x'$.

$$\frac{d}{dt}\,\rho(x) = \int d\xi\, W(x-\xi,x)\rho(x-\xi) - \int d\xi\, W(x,x-\xi)\rho(x)\ . \tag{320}$$

Introduce new rates $\tilde{W}(x,\xi) \equiv W(x,x+\xi)$. Then

$$\frac{d}{dt}\,\rho(x) = \int d\xi\, \tilde{W}(x-\xi,\xi)\rho(x-\xi) - \int d\xi\, \tilde{W}(x,-\xi)\rho(x)\ . \tag{321}$$

In the second term we can replace under the integral $\xi \to -\xi$. Thus

$$\frac{d}{dt}\,\rho(x) = \int d\xi\, \left[\tilde{W}(x-\xi,\xi)\rho(x-\xi) - \tilde{W}(x,\xi)\rho(x)\right]\ . \tag{322}$$

Assuming the substantial transition rates exist only for small values of $\xi$ we can expand. This gives

$$\frac{d}{dt}\,\rho(x) = -\int d\xi\,\xi\,\frac{\partial}{\partial x}\left[\tilde{W}(x,\xi)\rho(x)\right] + \frac{1}{2}\int d\xi\,\xi^2\,\frac{\partial^2}{\partial x^2}\left[\tilde{W}(x,\xi)\rho(x)\right] + \ldots\ . \tag{323}$$

We define the moments

$$\alpha^{(m)}(x) \equiv \int d\xi\,\xi^m\,\tilde{W}(x,\xi)\ . \tag{324}$$

This gives

$$\frac{d}{dt}\,\rho(x) = -\frac{\partial}{\partial x}\left[\alpha^{(1)}(x)\rho(x)\right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[\alpha^{(2)}(x)\rho(x)\right] + \ldots\ . \tag{325}$$

Generalisation to multiple dimensions

$$\frac{d}{dt}\,\rho(x) = -\frac{\partial}{\partial x_i}\left[\alpha_i^{(1)}(\{x\})\rho(\{x\})\right] + \frac{1}{2}\frac{\partial^2}{\partial x_i \partial x_j}\left[\alpha_{ij}^{(2)}(\{x\})\rho(\{x\})\right] + \ldots\ . \tag{326}$$

The moments $\alpha^{(1)}$ and $\alpha^{(2)}$ can be presented as

$$\alpha^{(1)}(x) = \frac{1}{\Delta t}\,\langle x(t+\Delta t) - x(t)\rangle\Big|_{x(t)=x}\ . \tag{327}$$

$$\alpha^{(2)}(x) = \frac{1}{\Delta t}\,\langle (x(t+\Delta t) - x(t))^2\rangle\Big|_{x(t)=x}\ . \tag{328}$$

If these moments are $x$-independent we obtain the simplest form of the Fokker-Planck equation

$$\frac{d\rho(x)}{dt} = -\bar{v}\frac{\partial\rho(x)}{\partial x} + D\frac{\partial^2\rho(x)}{\partial x^2} \ , \tag{329}$$

where the drift velocity is given by $\bar{v} \equiv \alpha^{(1)}$ and the diffusion constant is $D \equiv (1/2)\alpha^{(2)}$.

For example, in the 1D random walk model we introduce the lattice constant $a$. In one time step $\Delta t$ the particle makes one step right with probability $q$ or one step left with probability $1-q$. Then

$$\alpha^{(1)} = \frac{aq - a(1-q)}{\Delta t} = \frac{a}{\Delta t}(2q-1) = \bar{v} \ . \tag{330}$$

$$\alpha^{(2)} = \frac{a^2 q + a^2(1-q)}{\Delta t} = \frac{a^2}{\Delta t} = 2D \ . \tag{331}$$

The Fokker-Planck equation (329) can be easily solved by Fourier transform.

$$\rho(x) = \int \frac{dk}{2\pi}\, \rho(k) e^{ikx} \ . \tag{332}$$

$$\frac{d\rho(k)}{dt} = -(i\bar{v}k + Dk^2)\rho(k) \ . \tag{333}$$

Thus

$$\rho(k,t) = \rho(k,0) e^{-(i\bar{v}k + Dk^2)t} \ . \tag{334}$$

For the initial condition $\rho(x,0) = \delta(x)$ we have $\rho(k,0) = 1$. Thus

$$\rho(k,t) = e^{-(i\bar{v}k + Dk^2)t} \ . \tag{335}$$

The inverse Fourier transform gives

$$\rho(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left[-\frac{(x-\bar{v}t)^2}{4Dt}\right] \ . \tag{336}$$

### 3. *Master equation for a two-level system coupled to a bath*

We analyse the dissipative processes in two-level systems (qubits). Let us consider a purely transverse coupling between a qubit and a bath

$$H = -\frac{1}{2}\Delta E\, \sigma_z - \frac{1}{2} Y\, \sigma_x + H_{\text{bath}} \ , \tag{337}$$

where $Y$ is a bath operator. For example, for a bath of oscillators, as in Caldeira-Leggett model, $Y = \sum_n \lambda_n x_n$. We denote the ground and excited states of the free qubit by $|0\rangle$ and

$|1\rangle$, respectively. In the weak-noise limit we consider $Y$ as a perturbation and apply Fermi's golden rule to obtain the relaxation rate, $\Gamma_\downarrow = \Gamma_{|1\rangle \to |0\rangle}$, and excitation rate, $\Gamma_\uparrow = \Gamma_{|0\rangle \to |1\rangle}$.

For the relaxation the initial state is actually given by $|1\rangle\,|i\rangle$, where $|i\rangle$ is some state of the environment. This state is not known, but we assume, that the environment is in thermal equilibrium. Thus the probability to have state $|i\rangle$ is given by $\rho_i = Z^{-1} e^{-\beta E_i}$ ($H_{\rm bath}\,|i\rangle = E_i\,|i\rangle$). The final state is given by $|0\rangle\,|f\rangle$, where $|f\rangle$ is the state of the environment after the transition. To obtain the relaxation rate of the qubit we have to sum over all possible $|i\rangle$ states (with probabilities $\rho_i$) and over all $|f\rangle$. Thus, for $\Gamma_\downarrow$ we obtain

$$\begin{aligned}
\Gamma_\downarrow &= \frac{2\pi}{\hbar} \sum_{i,f} \rho_i \, |\, \langle i|\,\langle 1|\, \frac{1}{2} Y \sigma_x \,|0\rangle\,|f\rangle\,|^2 \; \delta(E_i + \Delta E - E_f) \\
&= \frac{2\pi}{\hbar}\,\frac{1}{4} \sum_{i,f} \rho_i \, |\, \langle i|\, Y \,|f\rangle\,|^2 \; \delta(E_i + \Delta E - E_f) \\
&= \frac{2\pi}{\hbar}\,\frac{1}{4} \sum_{i,f} \rho_i \; \langle i|\, Y \,|f\rangle \, \langle f|\, Y \,|i\rangle \; \frac{1}{2\pi\hbar} \int dt \; e^{i \frac{t}{\hbar}\,(E_i + \Delta E - E_f)} \\
&= \frac{1}{4\hbar^2} \int dt \, \sum_i \rho_i \; \langle i|\, Y(t) Y \,|i\rangle \; e^{i \frac{t}{\hbar}\,\Delta E} \\
&= \frac{1}{4\hbar^2}\, C_Y(\omega = \Delta E/\hbar) = \frac{1}{4\hbar^2}\, \langle Y^2_{\omega = \Delta E/\hbar} \rangle \;. \qquad (338)
\end{aligned}$$

Here we have defined the correlation function (correlator) $C_Y(t) = {\rm Tr}(\rho_E Y(t) Y)$ and its Fourier trasform $\langle Y^2_\omega \rangle \equiv C_Y(\omega) = \int dt\, C_Y(t)\, e^{i\omega t}$. Similarly, we obtain

$$\Gamma_\uparrow = \frac{1}{4\hbar^2}\, C_Y(\omega = -\Delta E/\hbar) = \frac{1}{4\hbar^2}\, \langle Y^2_{\omega = -\Delta E/\hbar} \rangle \;. \qquad (339)$$

How is this all related to the relaxation time of the diagonal elements of the density matrix ($T_1$)?. To understand this we write down the master equation for the probabilities $p_0 = \rho_{00}$ and $p_1 = \rho_{11}$:

$$\begin{aligned}
\dot p_0 &= -\Gamma_\uparrow p_0 + \Gamma_\downarrow p_1 \\
\dot p_1 &= -\Gamma_\downarrow p_1 + \Gamma_\uparrow p_0 \;. \qquad (340)
\end{aligned}$$

We observe that the total probability $p_0 + p_1$ is conserved and should be equal 1. Then for $p_0$ we obtain

$$\dot p_0 = -(\Gamma_\uparrow + \Gamma_\downarrow) p_0 + \Gamma_\uparrow \;, \qquad (341)$$

which gives

$$p_0(t) = \frac{\Gamma_\downarrow}{\Gamma_\uparrow + \Gamma_\downarrow} + \left( p_0(0) - \frac{\Gamma_\downarrow}{\Gamma_\uparrow + \Gamma_\downarrow} \right) e^{-(\Gamma_\uparrow + \Gamma_\downarrow) t} \;, \qquad (342)$$

and $p_1(t) = 1 - p_0(t)$.

For the relaxation time we thus find

$$\frac{1}{T_1} = \Gamma_\downarrow + \Gamma_\uparrow = \frac{1}{2\hbar^2}\, S_Y(\omega = \Delta E/\hbar) \ , \tag{343}$$

and for the equilibrium magnetization

$$\langle \sigma_z \rangle_{t=\infty} = p_0(t=\infty) - p_1(t=\infty) = \frac{\Gamma_\downarrow - \Gamma_\uparrow}{\Gamma_\downarrow + \Gamma_\uparrow} = \frac{A_Y(\omega = \Delta E/\hbar)}{S_Y(\omega = \Delta E/\hbar)} \ , \tag{344}$$

where we have introduced symmetrized correlator, $S_Y(\omega) \equiv \frac{1}{2}(C_Y(\omega) + C_Y(-\omega))$, and the the antisymmetrized correlator $A_Y(\omega) \equiv \frac{1}{2}(C_Y(\omega) - C_Y(-\omega))$.

### *4. Fluctuation Dissipation Theorem (FDT)*

Are $C_Y(\omega)$ and $C_Y(-\omega)$ related? In other words, what is the relation between the symmetrized correlation function $S_Y(\omega)$ and the anti-symmetrized one $A_Y(\omega)$? We use the spectral decomposition in the eigenbasis of the Hamiltonian of the environment $H_{\text{bath}} |n\rangle = E_n |n\rangle$:

$$\begin{aligned} C_Y(t) &= \text{Tr}(\rho_E Y(t) Y) = \frac{1}{Z}\sum_n e^{-\beta E_n} \langle n| Y(t) Y |n\rangle \\ &= \frac{1}{Z}\sum_{n,m} e^{-\beta E_n} \langle n| Y(t) |m\rangle \langle m| Y |n\rangle = \frac{1}{Z}\sum_{n,m} e^{-\beta E_n} e^{i(E_n - E_m)t} |\langle m| Y |n\rangle|^2 \end{aligned} \tag{345}$$

Thus

$$C_Y(\omega) = \int dt C_Y(t) e^{i\omega t} = \frac{1}{Z}\sum_{n,m} e^{-\beta E_n} |\langle m| Y |n\rangle|^2\, 2\pi\delta(\omega - (E_m - E_n)) \ . \tag{346}$$

For $C_Y(-\omega)$ we obtain

$$\begin{aligned} C_Y(-\omega) &= \frac{1}{Z}\sum_{n,m} e^{-\beta E_n} |\langle m| Y |n\rangle|^2\, 2\pi\delta(-\omega - (E_m - E_n)) \\ &= \frac{1}{Z}\sum_{n,m} e^{-\beta E_n} |\langle m| Y |n\rangle|^2\, 2\pi\delta(\omega - (E_n - E_m)) \\ &= \frac{1}{Z}\sum_{n,m} e^{-\beta E_m} |\langle m| Y |n\rangle|^2\, 2\pi\delta(\omega - (E_m - E_n)) \\ &= \frac{1}{Z}\sum_{n,m} e^{-\beta (E_n + \omega)} |\langle m| Y |n\rangle|^2\, 2\pi\delta(\omega - (E_m - E_n)) \\ &= e^{-\beta\omega}\, C_Y(\omega) \ . \end{aligned} \tag{347}$$

The relation $C_Y(-\omega) = e^{-\beta\omega} C_Y(\omega)$ is the fully quantum version of the Fluctuation-Dissipation-Theorem. A simple algebra then gives $S_Y(\omega) = \coth\left(\frac{\beta\omega}{2}\right) A_Y(\omega)$. Thus we obtain the detailed balance relation as introduced above (see Eq. 306)

$$\frac{\Gamma_\uparrow}{\Gamma_\downarrow} = e^{-\beta\Delta E} \ . \tag{348}$$

We also observe that the probabilities $p_0(t=\infty) = \frac{1}{e^{-\beta\Delta E}+1}$ and $p_1(t=\infty) = 1 - p_0(t=\infty)$ are the equilibrium ones. Finally,

$$\langle\sigma_z\rangle_{t=\infty} = \frac{A_Y(\omega = \Delta E/\hbar)}{S_Y(\omega = \Delta E/\hbar)} = \tanh\frac{\Delta E}{2k_{\mathrm{B}}T} \ . \tag{349}$$

### C. Linear response theory

Consider a system described by a Hamiltonian $H_0$. The system is perturbed by an external time-dependent force, so that the full Hamiltonian reads $H = H_0 + V(t)$. The perturbation Hamiltonian reads $V(t) = -f(t)B$. Here $f(t)$ is the time-dependent parameter (force) and $B$ is an observable of the system. Clearly $f(t)$ is a real function of time, while $B$ is a Hermitian operator. We want to know how the expectation value of another system's operator $A$ responds to the perturbation. That is we expect that without the perturbation (in equilibrium) $\langle A\rangle = A_0$, whereas with the perturbation $\langle A\rangle = A_0 + \delta A(t)$. Without the perturbation the system is in equilibrium, i.e., it is described by the equilibrium density matrix $\rho_0$ and, thus, $A_0 = \mathrm{Tr}(A\rho_0)$. Due to the perturbation either the density matrix of the system changes (Schrödinger picture) or the operator $A$ acquires an extra time dependence (Heisenberg representation).

$$\langle A\rangle = \mathrm{Tr}(A\rho_S(t)) = \mathrm{Tr}(A_H(t)\rho_0) \ . \tag{350}$$

($A = A_S$ is the operator in the Schrödinger picture). We can now go to the interaction picture, in which

$$\langle A\rangle = \mathrm{Tr}(A_I(t)\rho_I(t)) \ . \tag{351}$$

Here $A_I(t) = e^{iH_0t/\hbar} A e^{-iH_0t/\hbar}$, i.e., the Heisenberg operator with respect to $H_0$. On the other hand

$$\rho_I(t) = U_I(t)\,\rho_0\,U_I^\dagger(t) \ , \tag{352}$$

where

$$U_I(t) = \left[ T e^{-(i/\hbar)\int\limits_0^t d\tau\, V_I(\tau)} \right] \ . \tag{353}$$

Thus we obtain

$$\langle A \rangle = \mathrm{Tr}(A_I(t)\, U_I(t)\, \rho_0\, U_I^\dagger(t)) = \mathrm{Tr}(U_I^\dagger(t)\, A_I(t)\, U_I(t)\, \rho_0) \ . \tag{354}$$

In other words

$$A_H(t) = U_I^\dagger(t)\, A_I(t)\, U_I(t) \ . \tag{355}$$

Expanding up to the first order in the perturbation we obtain

$$\begin{aligned} A_H(t) &= A_I(t) - \frac{i}{\hbar}\int\limits_0^t d\tau\ [A_I(t), V_I(\tau)] \\ &= A_I(t) - \frac{i}{\hbar}\int\limits_0^t d\tau\ [A_I(t), B_I(\tau)]\ f(\tau) \ . \end{aligned} \tag{356}$$

Finally, this gives

$$\langle A \rangle = A_0 + \frac{i}{\hbar}\int\limits_0^t d\tau\, \langle [A_I(t), B_I(\tau)] \rangle_0\, f(\tau) \ , \tag{357}$$

where $\langle \dots \rangle_0 \equiv \mathrm{Tr}(\rho_0 \dots)$. Taking the initial time $t_0 = 0$ to $t_0 = -\infty$ we get

$$\delta A(t) = \int dt' \chi(t,t') f(t') \ , \tag{358}$$

where the linear response susceptibility is defined as

$$\chi(t,t') \equiv \frac{i}{\hbar}\, \langle [A_I(t), B_I(t')] \rangle_0\, \theta(t-t') \ . \tag{359}$$

Since $A_I$ and $B_I$ are essentially the Heisenberg operators with respect to $H_0$, one can write

$$\chi(t,t') \equiv \frac{i}{\hbar}\, \langle [A(t), B(t')] \rangle_0\, \theta(t-t') \ . \tag{360}$$

We see that the linear response is determined exclusively by the equilibrium correlation function $\langle [A(t), B(t')] \rangle_0$.

### 1. *Linear response and FDT*

Frequently one is interested in the case when $A = B$. For example, for magnetic susceptibility $f(t) \propto H(t)$ (magnetic field), whereas $A = B = M$ (magnetisation). The same is for the polarisability (dielectric response). In this case $f(t) \propto \phi(r,r)$ (scalar potential), whereas $A = B = \rho(r,t)$ (electronic density). Thus

$$\chi(t,t') \equiv \frac{i}{\hbar}\,\langle [A(t), A(t')]\rangle_0\, \theta(t-t') \ . \tag{361}$$

This susceptibility is related to the correlation function

$$C_A(t,t') = C_A(t-t') = \langle A(t)A(t')\rangle_0 \ . \tag{362}$$

Once again, $A(t)$ is the Heisenberg operator with respect to $H_0$ and $\langle \dots \rangle_0 \equiv \mathrm{Tr}(\rho_0 \dots)$ is the averaging in the equilibrium state. We obtain

$$\hbar\chi(t,t') = \hbar\chi(t-t') = i\theta(t-t')\,[C_A(t-t') - C_A(t'-t)] \ . \tag{363}$$

Using the notations introduces around Sec. VI B 4 we write

$$\hbar\chi(\tau) = i\theta(\tau)\,[C_A(\tau) - C_A(\tau)] = 2i\theta(\tau)A_A(\tau) \ , \tag{364}$$

where $A_A(\tau)$ is the anti-symmetrised correlator introduced in Sec. VI B 4. For a Hermitian operator $A$, $A_A(\tau)$ is purely imaginary and $\chi(\tau)$ is real. We now perform the Fourier transform:

$$\begin{aligned} \hbar\chi(\omega) &= \int d\tau\, \chi(\tau) e^{i\omega\tau} = 2i\int\limits_0^\infty d\tau\, A_A(\tau) e^{i\omega\tau - \delta\tau} \\ &= 2i\int\limits_0^\infty d\tau \int \frac{d\nu}{2\pi}\, A_A(\nu) e^{-i\nu\tau} e^{i\omega\tau-\delta\tau} = \int \frac{d\nu}{\pi}\, \frac{A_A(\nu)}{\nu-\omega-i\delta} \ . \end{aligned} \tag{365}$$

Since $A_A(\nu)$ is real (a Fourier transform of a purely imaginary anti-symmetric function) we obtain $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$, where

$$\hbar\chi''(\omega) = A_A(\omega) \ . \tag{366}$$

Finally, the FDT in this case gives for the symmetrised correlator

$$S_A(\omega) = A_A(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) = \hbar\chi''(\omega)\coth\left(\frac{\beta\hbar\omega}{2}\right) \ . \tag{367}$$

This is the ultimate relation between fluctuations $S_A(\omega)$ and dissipation $\chi''(\omega)$.

### D. Boltzmann equation

This is a famous kinetic equation describing relaxation and transport in gases. One considers the quantity $f(r,p,t)$. This is proportional to the average number of particles having the coordinate $r$ and the momentum $p$ (we have to do it quasi-classically, otherwise one could not define sharp values for $r$ and $p$ simultaneously. More precisely

$$\frac{1}{(2\pi\hbar)^d}\, f(r,p,t)\Delta r^d \Delta p^d \tag{368}$$

is the number of particles in the phase space volume element $\Delta r^d \Delta p^d$. The particles satisfy the equation of motion

$$\frac{d\vec{r}}{dt} = \vec{v}(\vec{p}) \quad , \quad \vec{v} = \vec{p}/m \ , \tag{369}$$

$$\frac{d\vec{p}}{dt} = \vec{F} \ . \tag{370}$$

Here $\vec{F}$ is the external force (it can be $r$ and even $p$ dependent, e..g, Lorentz force). If these equations of motion would provide the full description we would have

$$f(r(t),p(t),t) = f(r(t_0),p(t_0),t_0) \ , \tag{371}$$

or equivalently the vanishing of the full $t$-derivative:

$$\frac{df}{dt} = 0 \ . \tag{372}$$

This is equivalent to the Liouville theorem about the conservation of the phase volume. This would give

$$\frac{\partial f}{\partial t} + \vec{v}(\vec{p})\,\frac{\partial f}{\partial \vec{p}} + \vec{F}(\vec{r},\vec{p},t)\,\frac{\partial f}{\partial \vec{r}} = 0 \ . \tag{373}$$

Collisions between the particles lead to transitions into and from the volume element of the phase space. The equation is then modified as

$$\frac{\partial f}{\partial t} + \vec{v}(\vec{p})\,\frac{\partial f}{\partial \vec{p}} + \vec{F}(\vec{r},\vec{p},t)\,\frac{\partial f}{\partial \vec{r}} = I[f] \ , \tag{374}$$

where the functional $I[f]$ is called the collision integral. We will not derive or specify $I[f]$ but just mention that in many cases it can be reduced to a very simple form $I[f] = -(f - f_0)/\tau$, where $f_0$ is the equilibrium distribution and $\tau$ is the relaxation time.

Boltzmann has proven the so called $H$-theorem. He has introduced a quantity of the type entropy

$$H(t) = -\int d^d r d^d p\, f(r,p,t)\, \ln f(r,p,t) \ . \tag{375}$$

Further, Boltzmann has shown that the entropy does not decrease, i.e.,

$$\frac{dH}{dt} \geq 0 \ . \tag{376}$$

Moreover, if there are no collisions, i.e., $I[f] = 0$, then $dH/dt = 0$. Historically, this was the starting point of the modern statistical physics.