# Chapter 1

# Mean field theories of phase transitions and variational mean field

## 1.1 Mean field theories

Increasing the dimension of the systems, the effort to solve analitically the problems increase; indeed, we have seen that

- In $d = 1$: many (simple) models can be solved exactly using techniques such as the transfer matrix method.
- In $d = 2$: few models can still be solved exactly (often with a lot of effort).
- In $d = 3$: almost no model can be exactly solved.

Hence, approximations are needed. The most important and most used one is the *mean field approximation*. It has different names depending on the system considered:

- Magnetic systems: Weiss theory.
- Fluids systems: Van der Walls.
- Polymers: Flory's theory.

The idea is trying to simplify the problem by neglecting the correlation between the fluctuations of the order parameter. It is equivalent to a statistical independence of the microscopic degrees of freedom.

### 1.1.1 Mean field for the Ising model (Weiss mean field)

Let us start from the generic Ising model

$$\mathcal{H}[\{S\}] = -\frac{1}{2}\sum_{ij} J_{ij} S_i S_j - H \sum_i S_i \tag{1.1}$$

where the double sum over $i$ and $j$ have no restrictions, while $H$ is homogeneous.

The partition function is

$$Z_N(T, H, \{J_{ij}\}) = \sum_{\{S\}} e^{-\beta\mathcal{H}[\{S\}]} = \exp(-\beta F_N(T, H, \{J_{ij}\})) \tag{1.2}$$

Since $H$ is uniform, the magnetization per spin is

$$\langle S_i \rangle = \langle S \rangle \equiv m$$

Let us now consider the identity

$$\begin{aligned} S_i S_j &= (S_i - m + m)(S_j - m + m) \\ &= (S_i - m)(S_j - m) + m^2 + m(S_j - m) + m(S_i - m) \end{aligned}$$

*Remark.* The mean field approximation consists in neglecting the term

$$(S_i - m)(S_j - m) = (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle)$$

that measures correlation between fluctuations.

Hence, using the mean field approximation, the above identity becomes

$$S_i S_j \approx m^2 + m(S_i - m) + m(S_j - m)$$

and

$$\frac{1}{2}\sum_{i,j} J_{ij} S_i S_j \overset{MF}{\approx} \frac{1}{2}\sum_{i,j} J_{ij}\left[-m^2 + m(S_i + S_j)\right]$$

Let us focus on the term

$$\frac{1}{2}\sum_{i,j} J_{ij} m(S_i + S_j) = 2\frac{1}{2} m \sum_{i,j} J_{ij} S_i \tag{1.3}$$

If we do not make any assumption on $J_{ij}$, the mean field Hamiltonian is

$$\mathcal{H}_{MF}[\{S\}] = \frac{1}{2} m^2 \sum_{ij} J_{ij} - m \sum_{ij} J_{ij} S_i - H \sum_i S_i \tag{1.4}$$

and by calling

$$\bar{J}_i \equiv \sum_j J_{ij}$$

we get

$$\mathcal{H}_{MF}[\{S\}] = \frac{1}{2} m^2 \sum_i \bar{J}_i - \frac{m}{2} \sum_i \bar{J}_i S_i - H \sum_i S_i$$

*Remark.* Note the coefficient emphasized in green (1/2) is needed to avoid the double counting of bonds.

Moreover, if we suppose that

$$\bar{J}_i \to \bar{J}$$

we have

$$\boxed{\mathcal{H}_{MF}[\{S\}] = \frac{1}{2} m^2 N \bar{J} - \left(\frac{m}{2}\bar{J} + H\right) \sum_i S_i} \tag{1.5}$$

*Remark.* In the standard Ising model, where

$$\frac{1}{2}\sum_{ij} J_{ij} S_i S_j \to \sum_{\langle ij \rangle} J_{ij} S_i S_j$$

the term $2m \sum_{\langle ij \rangle} J_{ij} S_i$ of Eq.(1.3) can be written as follows. Let

$$\sum_{j \in n.n. \text{ of } i} J_{ij} = z \hat{J}_i$$

where $z$ is the coordination number of the underlying lattice (for the hypercubic lattice $z = 2d$). By assuming $\hat{J}_i = \hat{J}$ and inserting the 1/2 to avoid double counting, we have that equation (1.3) becomes

$$2m \sum_{\langle ij \rangle} J_{ij} S_i = 2m \frac{1}{2} z \hat{J} \sum_{i=1}^{N} S_i \tag{1.6}$$

Hence, in this case the Hamiltonian is

$$\boxed{\mathcal{H}_{MF}[\{S\}] = \frac{1}{2}m^2 Nz\hat{J} - (mz\hat{J} + H)\sum_{i=1}^{N} S_i} \tag{1.7}$$

The partition function becomes

$$\begin{aligned} Z_N(T,H,\hat{J}) &= e^{-N\beta\hat{J}\frac{z}{2}m^2}\sum_{\{S\}} e^{\beta(\hat{J}zm+H)\sum_{i=1}^{N} S_i} \\ &= e^{-N\beta\hat{J}\frac{z}{2}m^2}\sum_{\{S\}}\prod_{i=1}^{N}\exp\Big(\beta\Big(\hat{J}zm+H\Big)S_i\Big) \\ &= e^{-N\beta\hat{J}\frac{z}{2}m^2}\left(\sum_{S=\pm1}\exp\Big(\beta\Big(\hat{J}zm+H\Big)S\Big)\right)^N \\ &= e^{-N\beta\hat{J}\frac{z}{2}m^2}\Big(2\cosh\Big[\beta\Big(\hat{J}zm+H\Big)\Big]\Big)^N \end{aligned} \tag{1.8}$$

*Remark.* We are replacing the interaction of the J with a field close to the $S_i$. We called $\hat{J}zm = H_{eff}$, the mean field!

The free energy per spin is

$$\begin{aligned} \frac{F_N(T,H,\hat{J})}{N} &= \frac{1}{N}\Big(-k_BT\ln Z_N(T,H,\hat{J})\Big) \\ &= \frac{1}{2}\hat{J}zm^2 - k_BT\ln\Big[\cosh\Big(\beta(\hat{J}zm+H)\Big)\Big] - k_BT\ln 2 \end{aligned} \tag{1.9}$$

Sometimes it is useful to use the *dimensionless variables* defined as

$$\bar{f} \equiv \frac{F_N}{Nz\hat{J}}, \quad \theta \equiv \frac{k_BT}{z\hat{J}}, \quad \bar{H} \equiv \frac{H}{z\hat{J}} \tag{1.10}$$

Hence,

$$\bar{f}(m,\bar{H},\theta) = \frac{1}{2}m^2 - \theta\ln\big(2\cosh\big(\theta^{-1}(m+\bar{H})\big)\big) \tag{1.11}$$

In order to be a self-consistent, the last equation has to satisfy the thermodynamic relation:

$$m = -\left(\frac{\partial f}{\partial H}\right)_T \quad \Rightarrow m = \tanh\Big(\beta(\hat{J}zm+H)\Big)$$

*Remark.* The results of $m$ is similar to the Ising with infinite range ($\hat{J}z \leftrightarrow J$).

Now, let us consider the $H = 0$ case, we have

$$m = \tanh\Big(\beta(\hat{J}zm)\Big) \tag{1.12}$$

and the graphical solution is shown in Figure 1.1 (hyperbolic function). We can distinguish three cases:

- Case $\beta\hat{J}z > 1$: there are three solutions, one at $m = 0$ and two symmetric at $m = \pm m_0$. Magnetization is $\neq 0\,(= |m_0|)$ for $H = 0$ (*ordered phase*). The two solution are symmetric because they are related by the $\mathbb{Z}^2$ symmetry.
- Case $\beta\hat{J}z < 1$: single solution at $m = 0$ (*disordered or paramagnetic phase*).
- Case $\beta\hat{J}z = 1$: the three solutions coincide at $m = 0$ (*critical point*). The critical temperature $T_c$ is given by

  $$\beta_c\hat{J}z = 1 \Rightarrow \frac{z\hat{J}}{k_BT_c} = 1 \Rightarrow T_c = \frac{z\hat{J}}{k_B} \neq 0!$$

  *Remark.* $T_c$ depends on $z$ and hence on $d$!

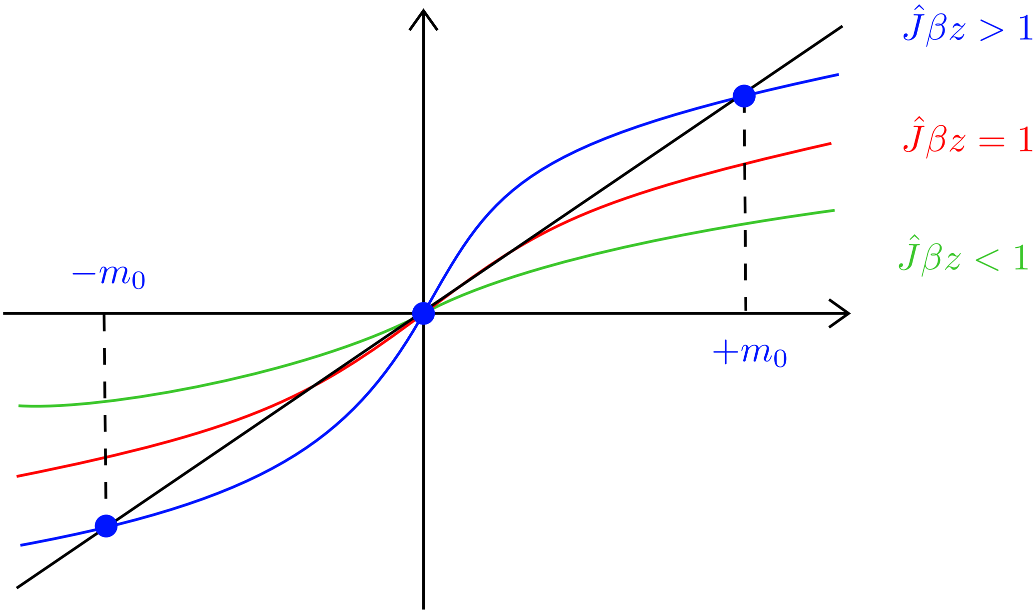



**Figure 1.1:** Graphical solution of equation $m = \tanh\Big(\beta(\hat{J}zm)\Big)$ (case $H = 0$).

### 1.1.2 Free-energy expansion for $m \simeq 0$

The critical point is characterized by the order parameter that is zero. Now, we want to expand the free energy around the critical point. Let us put $H = 0$:

$$f(m, 0, T, \hat{J}) = \frac{1}{2}\hat{J}zm^2 - k_B T \ln\Big[\cosh\Big(\beta\hat{J}zm\Big)\Big] - k_B T \ln 2 \tag{1.13}$$

Define $x \equiv \beta\hat{J}zm \simeq 0$ and by expanding in Taylor series

$$\cosh(x) \simeq 1 + \underbrace{\frac{x^2}{2} + \frac{x^4}{4!}}_{t\simeq 0} + \dots$$

$$\log(1+t) \simeq t - \frac{1}{2}t^2$$

Hence,

$$\log(\cosh x) \simeq \frac{x^2}{2} + \frac{x^4}{4!} - \frac{1}{2}\frac{x^4}{4} + O(x^6) = \frac{x^2}{2} - \frac{x^4}{12} + O(x^6)$$

This gives the result

$$f(m, 0, T, \hat{J}) \simeq const + \frac{A}{2}m^2 + \frac{B}{4}m^4 + O(m^6) \tag{1.14}$$

with

$$A \equiv \hat{J}z\Big(1 - \beta\hat{J}z\Big) \tag{1.15a}$$

$$B \equiv \beta^2\frac{(\hat{J}z)^4}{3} > 0 \tag{1.15b}$$

We have three cases:

- Case $\beta\hat{J}z > 1 \Rightarrow A < 0$: two stable symmetric minima at $m = \pm m_0$ (Figure 1.2). Coexistence between the two ordered phases.

- Case $\beta \hat{J} z < 1 \Rightarrow A > 0$: one minimum at $m = 0$ (Figure 1.3).
- Case $\beta \hat{J} z = 1 \Rightarrow A = 0$: 3 minima coincide at $m = 0$ (Figure 1.4).

*Remark.* Note that in the computations we have just made we have never imposed a particular value for the dimensionality of the system. This means that the results of this approximation should be valid also for $d = 1$, but we know that in one dimension the Ising model does not exhibit a phase transition. This is an expression of the fact that in the one-dimensional case mean field theory is not a good approximation (again, the dimensionality of the system is still too low).

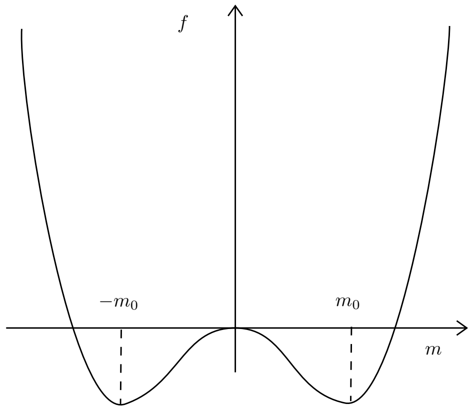



**Figure 1.2:** Plot of the free energy: case $\beta \hat{J} z > 1 \Rightarrow A < 0$.

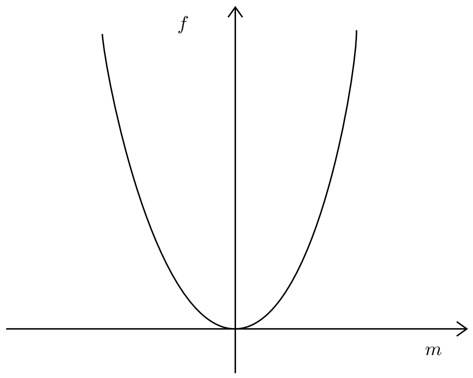



**Figure 1.3:** Plot of the free energy: case $\beta \hat{J} z < 1 \Rightarrow A > 0$.

### 1.1.3 Mean field critical exponents

Let us consider the equation

$$f(m, T, 0) \approx const + \frac{A}{2} m^2 + \frac{B}{4} m^4 + O(m^6)$$

with $B > 0$, so we do not need more term to find the minima of the solution. This is called stabilization. What is most important is the coefficient $A = \hat{J} z (1 - \beta \hat{J} z)$, that means that $A$ can change sign.

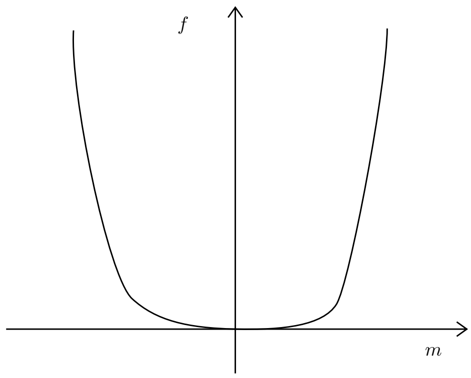



**Figure 1.4:** Plot of the free energy: case $\beta\hat{J}z = 1 \Rightarrow A = 0$.

### $\beta$ exponent

The $\beta$ exponential observe the order parameter. Consider $H = 0$, $t \equiv \frac{T-T_c}{T_c}$ and $m \overset{t\to 0^-}{\sim} -t^\beta$. The condition of equilibrium is

$$\frac{\partial f}{\partial m} = 0$$

which implies

$$\left.\frac{\partial f}{\partial m}\right|_{m=m_0} = Am_0 + Bm_0^3 = \left[\hat{J}z(1-\beta\hat{J}z) + Bm_0^2\right]m_0 = 0$$

Since at the critical point we have $T_c = \frac{\hat{J}z}{k_B}$ :

$$0 = \frac{k_B T_c}{T}(T - T_c)m_0 + Bm_0^3$$

The solution are $m_0 = 0$ and

$$m_0 \simeq (T_c - T)^{1/2} \tag{1.16}$$

Hence, the mean field value is $\beta = 1/2$.

### $\delta$ exponent

Now, let us concentrate in the $\delta$ exponent. We are in the only case in which we are in $T = T_c$ and we want to see how the magnetization decrease: $H \sim m^\delta$.

Starting from the self-consistent equation, we have

$$m = \tanh\Big(\beta(\hat{J}zm + H)\Big) \tag{1.17}$$

Inverting it

$$\beta(\hat{J}zm + H) = \tanh^{-1} m$$

On the other hand, for $m \sim 0$

$$\tanh^{-1} m \simeq m + \frac{m^3}{3} + \frac{m^5}{5} + \dots$$

Therefore, by substituting

$$\begin{aligned} H = k_B T\left(m + \frac{m^3}{3} + \dots\right) - \hat{J}zm &= \left(k_B T - \hat{J}z\right)m + k_B T\frac{m^3}{3} + \dots \\ &\simeq k_B(T - T_c)m + \frac{k_B T}{3}m^3 \end{aligned}$$

At $T = T_c = \frac{\hat{J}z}{k_B}$, we have

$$H \sim k_B T_c \frac{m^3}{3} \tag{1.18}$$

The mean field value is $\delta = 3$.

### $\alpha$ exponent

Consider the $\alpha$ exponent, for $H = 0$, $c_H \sim t^{-\alpha}$ and $t = (T - T_c)/T_c$. Compute the specific heat at $H = 0$. Consider first $T > T_c$, where $m_0 = 0$,

$$f(m, H) = \frac{\hat{J}zm^2}{2} - \frac{1}{\beta} \ln\left(2\cosh\Big(\beta(\hat{J}zm + H)\Big)\right) - k_B T \ln 2$$

If $m = 0$, $\cosh 0 = 1$ and

$$f = -k_B T \ln 2$$

it is called paramagnetic phase. Indeed,

$$c_H = -T\left(\frac{\partial^2 f}{\partial T^2}\right) = 0 \tag{1.19}$$

The mean field value is $\alpha = 0$.

*Remark.* For $T < T_c$, $m = m_0 \neq 0$. This implies that $c_H \neq 0$, but still $f = -k_B T \ln A$ with $A = const$. We obtain $\alpha = 0$ also in this case.

$$m_0 = \pm\sqrt{-\frac{\hat{J}z}{2T_c}(T - T_c)}$$

### $\gamma$ exponent

Now we consider the $\gamma$ exponent, for $H = 0$, $\chi \sim t^{-\gamma}$. Starting again from equation (1.17):

$$m = \tanh\Big(\beta(\hat{J}zm + H)\Big)$$

and developing it around $m \simeq 0$, as shown before we get

$$H = mk_B(T - T_c) + \frac{k_B T}{3} m^3$$

$$\Rightarrow \chi_T = \frac{\partial m}{\partial H} = \frac{1}{\frac{\partial H}{\partial m}}$$

Since $\frac{\partial H}{\partial m} \simeq k_B(T - T_c) + K_B T m^2$, as $m \to 0$

$$\chi \sim (T - T_c)^{-1} \tag{1.20}$$

The mean field value is $\gamma = 1$.

### Summary

The mean field critical exponents are

$$\beta = \frac{1}{2}, \quad \gamma = 1, \quad \delta = 3, \quad \alpha = 0 \tag{1.21}$$

We can immediately note that these exponents are different from those found by Onsager for the Ising model in two dimensions, so the mean field theory is giving us wrong predictions. This is because mean field theories are good approximations only if the system has a high enough dimensionality (and $d = 2$ is still too low for the Ising model, see Coarse graining procedure for the Ising model).

*Remark.* In the mean field critical exponents the dimension $d$ does not appear. $T_c$ instead depends on the number of $z$ of neirest neighbours and hence on the embedding lattice (on the dimension)!

*Remark.* (lesson) The $\nu$ exponent define the divergence of the correlation lengths. In order to do that, in principle we should compute the correlation function, but which are the correlation we are talking about? The correlation or the fluctuation with to respect the average? In the ferromagnetic we have infinite correlation lengths, but it is not true, because instead of that we consider the variation correlated! Which is the problem here? In mean field we were neglecting correlation between fluctuation. We thought: let us compute neglecting correlation. How we can compute the correlation function within the mean field theory with thermal fluctuations? We look at the response of the system. Experimentally what can we do? It is a magnetic field, but we cannot use homogeneous magnetic field. Another way to compute the correlation function without looking at thermal fluctuation it is by considering a non homogeneous magnetic field. If we make a variation in $H_i$ in the system, what happened in the $H_j$? This is an important point.

## 1.2 Mean field variational method

The mean field variational method is a general approach to derive a mean field theory. The method is valid for all $T$ and is sufficiently flexible to deal with complex systems. The method is similar to the one used in quantum mechanics, namely it is based on the following inequality

$$E_\alpha = \langle\psi_\alpha|\,\hat{H}\,|\psi_\alpha\rangle \geq E_0 \tag{1.22}$$

valid for all trial function $\psi_\alpha$.

*Remark.* $E_0$ is the ground state energy.

**Example 1**

In many body problem we have Hartree and Hartree-Fock variational methods.

The closest bound to $E_0$ is the one that is obtained by minimizing $E_\alpha$, i.e. $\langle\psi_\alpha|\,\hat{H}\,|\psi_\alpha\rangle$ over $|\psi_\alpha\rangle$, where the $|\psi_\alpha\rangle$ are functions to be parametrized in some convenient way.

The method is based on the following inequalities

1. Let $\Phi$ be a random variable (either discrete or continuous) and let $f(\Phi)$ be a function of it.

   For all function $f$ of $\Phi$, the mean value with respect to a distribution function $p(\Phi)$ is given by
   $$\langle f(\Phi)\rangle_p \equiv \mathrm{Tr}(p(\Phi)f(\Phi)) \tag{1.23}$$
   If we consider the function
   $$f(\Phi) = \exp[-\lambda\Phi] \tag{1.24}$$
   it is possible to show the inequality
   $$\left\langle e^{-\lambda\Phi}\right\rangle_p \geq e^{-\lambda\langle\Phi\rangle_p}, \quad \forall p \tag{1.25}$$

   **Proof of inequality** (1.25)**.** $\forall\Phi\in\mathbb{R}$, $e^\Phi \geq 1+\Phi$. Hence,
   $$e^{-\lambda\Phi} = e^{-\lambda\langle\Phi\rangle}e^{-\lambda[\Phi-\langle\Phi\rangle]} \geq e^{-\lambda\langle\Phi\rangle}(1-\lambda(\Phi-\langle\Phi\rangle))$$
   Taking the average of both sides, we get
   $$\to \left\langle e^{-\lambda\Phi}\right\rangle_p \geq \left\langle(1-\lambda(\Phi-\langle\Phi\rangle))e^{-\lambda\langle\Phi\rangle}\right\rangle_p = e^{-\lambda\langle\Phi\rangle_p}$$
   ■

2. The second inequality refers to the free energy. Let $\rho(\Phi)$ be a probability distribution, i.e. such that
$$\mathrm{Tr}(\rho(\Phi)) = 1, \quad \rho(\Phi) \geq 0 \quad \forall \Phi \tag{1.26}$$
Hence,
$$e^{-\beta F_N} = Z_N = \mathrm{Tr}_{\{\Phi\}}\, e^{-\beta \mathcal{H}[\{\Phi\}]} = \mathrm{Tr}_{\{\Phi\}}\, \rho e^{-\beta\mathcal{H} - \ln\rho} = \left\langle e^{-\beta\mathcal{H}-\ln\rho} \right\rangle_\rho$$
From the inequality (1.25),
$$e^{-\beta F_N} = \left\langle e^{-\beta\mathcal{H}-\ln\rho} \right\rangle_\rho \geq e^{-\beta\langle\mathcal{H}\rangle_\rho - \langle \ln\rho\rangle_\rho}$$
Taking the logs one has
$$F \leq \langle \mathcal{H}\rangle_\rho + k_B T \langle \ln\rho\rangle_\rho = \mathrm{Tr}(\rho\mathcal{H}) + k_B T\, \mathrm{Tr}(\rho\ln\rho) \equiv F_\rho \tag{1.27}$$
Whenever we are able to write the last equation by using a $\rho$, then we will minimize it. This is the variational approach of statistical mechanics. The question is: which is the $\rho$ that minimizes?

The functional $F_\rho$ will reach its minimum value with respect to the variation of $\rho$ with the constraint $\mathrm{Tr}(\rho) = 1$, when
$$\boxed{\bar{\rho} = \rho_{eq} = \frac{1}{Z} e^{-\beta\mathcal{H}}} \tag{1.28}$$
So far so good but not very useful, since we are back to the known result that the distribution that best approximately the free energy of the canonical ensemble is given by the Gibbs-Boltzmann distribution. To compute $\rho_{eq}$, we need some approximation!

### 1.2.1 Mean field approximation for the variational approach

Let us now try to compute the $Z$ by starting from the inequality (1.27). Up to now everything is exact. The idea is to choose a functional form of $\rho$ and then minimize $F_\rho$ with respect to $\rho$. Note that $\rho$ is the $N-$point probability density function (it is a function of all the degrees of freedom):
$$\rho = \rho(\Phi_1, \ldots, \Phi_N)$$
it is a $N-$body problem, where $\Phi_\alpha$ is the random variables associated to the $\alpha-$esim degree of freedom. This is in general a very difficult distribution to deal with. This is equivalent exactly at
$$\psi_\alpha(\vec{\mathbf{r}}_1, \vec{\mathbf{P}}_1, \ldots, \vec{\mathbf{r}}_N, \vec{\mathbf{P}}_N)$$
The mean-field approximation consists in factorising $\rho$ into a product of $1-$point distribution function:
$$\boxed{\rho(\Phi_1, \ldots, \Phi_N) \overset{MF}{\simeq} \prod_{\alpha=1}^{N} \rho^{(1)}(\Phi_\alpha) \equiv \prod_{\alpha=1}^{N} \rho_\alpha} \tag{1.29}$$
where we have used the short-hand notation $\rho^{(1)}(\Phi_\alpha) \to \rho_\alpha$.

*Remark.* Approximation (1.29) is equivalent to assume statistical independence between particles (or more generally between different degrees of freedom). The independence of the degree of freedom is a very strong assumption!

**Example 2**

Let us consider the spin model on a lattice; what is the $\Phi_\alpha$? We have:
$$\Phi_\alpha \to S_i$$

Hence, $\rho = \rho(S_1, S_2, \dots, S_N)$ and (1.29) becomes

$$\rho \overset{MF}{\simeq} \prod_{i=1}^{N} \rho^{(1)}(S_i) \equiv \prod_{i=1}^{N} \rho_i$$

With Eq.(1.29) and the condition $\mathrm{Tr}(\rho_\alpha) = 1$, we compute the two averages in the Eq.(1.27) given the field. We have:

$$\mathrm{Tr}_{\{\Phi\}}(\rho \ln \rho) = \mathrm{Tr}\left(\prod_\alpha \rho_\alpha \left(\sum_\alpha \ln \rho_\alpha\right)\right) \overset{\text{to do}}{=} \sum_\alpha \mathrm{Tr}^{(\alpha)}(\rho_\alpha \ln \rho_\alpha) \tag{1.30}$$

where $\mathrm{Tr}^{(\alpha)}$ means sum over all possible values of the random variable $\Phi_\alpha$ (with $\alpha$ fixed and $\mathrm{Tr}^{(\alpha)}\, \rho_\alpha = 1$).

We end up that

$$F_{\rho_{MF}} = \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \sum_\alpha \mathrm{Tr}^{(\alpha)}(\rho_\alpha \ln \rho_\alpha) \tag{1.31}$$

*Remark.* $F_{\rho_{MF}} = F(\{\rho_\alpha\})$ and we have to minimize it with respect to $\rho_\alpha$.

How can we parametrize $\rho_\alpha$? There are two approaches that are mostly used:

1. Parametrize $\rho_\alpha \equiv \rho^{(1)}(\Phi_\alpha)$ by the average of $\Phi_\alpha$ with respect to $\rho_\alpha$, $\langle \Phi_\alpha \rangle_{\rho_\alpha}$ (in general is the local order parameter):
$$\rho_\alpha = \rho^{(1)}(\Phi_\alpha) \to \langle \Phi_\alpha \rangle_{\rho_\alpha}$$
This means that there are two constraints in the minimization procedure:
$$\mathrm{Tr}^{(\alpha)}\, \rho_\alpha = 1, \quad \mathrm{Tr}^{(\alpha)}(\rho_\alpha \Phi_\alpha) = \langle \Phi_\alpha \rangle$$
where the second is the self-consistent equation.
*Remark.* In this case the variational parameter coincides with the order parameter.

2. In the second approach is $\rho_\alpha$ itself the variational parameter. $F_{\rho_{MF}}$ is minimized by varying $\rho_\alpha$. It is a more general approach, that involves functional minimization.

### 1.2.2 First approach: Bragg-Williams approximation

We apply this approach to the Ising model with non uniform magnetic field. The Hamiltonian of such a system is

$$\mathcal{H}[\{S\}] = -J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i \tag{1.32}$$

It means that

$$\Phi_\alpha \to S_i = \pm 1$$

and that the variational parameter becomes the order parameter

$$\langle \Phi_\alpha \rangle \to \langle S_i \rangle \equiv m_i$$

*Remark.* Note that this time $H \to H_i$ (non-uniform), hence $m_i$ depends on the site $i$.

We have to define a $1-$particle probability density distribution $\rho_i \equiv \rho^{(1)}(S_i)$ such that

$$\rho_i \equiv \rho^{(1)}(S_i) \to \begin{cases} \mathrm{Tr}\, \rho_i = 1 \\ \mathrm{Tr}\, \rho_i S_i = m_i \end{cases} \tag{1.33}$$

Since we have to satisfy these two constraints, we need two free parameters. A linear functional form is sufficient. Denoting by:

- $a$: statistical weight associated to the value $S_i = -1$.
- $b$: statistical weight associated to all the remaining possible values of $S_i$ (for an Ising only one value remains, i.e. $S_i = +1$).

The simplest function form with two parameters is the linear function, namely

$$\rho_i \equiv \rho^{(1)}(S_i) = a(1 - \delta_{S_i,1}) + b\delta_{S_i,1} \tag{1.34}$$

Using the constraints

$$\begin{cases} \mathrm{Tr}^{(i)}(\rho_i) = 1 & \to a + b = 1 \\ \mathrm{Tr}^{(i)}(\rho_i S_i) = m_i & \to b - a = m_i \end{cases}$$

where $a, b$ are the functions of the order parameter. In that case we have not to write the functions for all the $i$. For $S_i = 1$ we have one value, for all the other values another one. The results of the previous equation are:

$$\begin{cases} a = \frac{1-m_i}{2} \\ b = \frac{1+m_i}{2} \end{cases}$$

Hence,

$$\rho_i = \frac{1 - m_i}{2}(1 - \delta_{S_i,1}) + \frac{1 + m_i}{2}\delta_{S_i,1} \tag{1.35}$$

that in matrix form can be expressed as

$$\rho_i = \begin{pmatrix} \frac{(m_i+1)}{2} & 0 \\ 0 & \frac{(1-m_i)}{2} \end{pmatrix} \tag{1.36}$$

**Mean field energy term**

Let us consider the average of the Hamiltonian

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = \left\langle -J \sum_{\langle ij \rangle} S_i S_j - \sum_i H_i S_i \right\rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_{\rho_{MF}} - \sum_i H_i \langle S_i \rangle_{\rho_{MF}} \tag{1.37}$$

Since we have

$$\rho_{MF} = \prod_{i=1}^{N} \rho_i$$

the term $\langle S_i S_j \rangle_{\rho_{MF}}$ will transform into

$$\langle S_i S_j \rangle_{\rho_{MF}} = \langle S_i \rangle_{\rho_{MF}} \langle S_j \rangle_{\rho_{MF}}$$

Moreover, for all function $g$ of $S_i$ we can write

$$\begin{aligned} \langle g(S_i) \rangle_{\rho_{MF}} = \mathrm{Tr}^{(i)}(g(S_i)\rho_i) &= \sum_{S_i=\pm 1} g(S_i)\rho_i \\ &= \sum_{S_i=\pm 1} g(S_i) \left[ \frac{1 + m_i}{2}\delta_{S_i,1} + \frac{1 - m_i}{2}(1 - \delta_{S_i,1}) \right] \\ &= \frac{1 + m_i}{2} g(1) + \frac{1 - m_i}{2} g(-1) \end{aligned}$$

Note that, if $g(S_i) = S_i$, we have $g(1) = +1$ and $g(-1) = -1$, hence

$$\langle S_i \rangle_{\rho_{MF}} = m_i$$

as expected. Taken this into account, the Hamiltonian can be rewritten as

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} m_i m_j - \sum_i H_i m_i \tag{1.38}$$

*Remark.* This has the form of the original Hamiltonian where $S_i$ had been replaced by their statistical averages.

The entropy term is:

$$\begin{aligned}
\langle \ln \rho \rangle_{\rho_{MF}} &= \mathrm{Tr}(\rho \ln \rho) \overset{MF}{=} \sum_i \mathrm{Tr}^{(i)}(\rho_i \ln \rho_i) \\
&= \sum_i \left[ \frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right]
\end{aligned} \tag{1.39}$$

The total free energy in Eq.(1.27) becomes:

$$\begin{aligned}
F_{\rho_{MF}} &= \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \langle \ln \rho \rangle_{\rho_{MF}} \\
&= -J \sum_{\langle ij \rangle} m_i m_j - \sum_i H_i m_i + k_B T \sum_i \left[ \frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right]
\end{aligned} \tag{1.40}$$

We now look for the values $m_i = \bar{m}_i$, that minimizes $F_{\rho_{MF}}$ (equilibrium phases):

$$\left. \frac{\partial F_{\rho_{MF}}}{\partial m_i} \right|_{m_i = \bar{m}_i} = 0$$

This gives:

$$0 = -J \sum_{j \in n.n.\,\mathrm{of}\, i} \bar{m}_j - H_i + \frac{k_B T}{2} \ln \left[ \frac{1+\bar{m}_i}{1-\bar{m}_i} \right]$$

To solve it, remember that

$$\tanh^{-1}(x) = \frac{1}{2} \ln \frac{1+x}{1-x} \qquad |x| < 1$$

Hence,

$$k_B T \tanh^{-1}(\bar{m}_i) = J \sum_{j \in n.n.\,\mathrm{of}\, i} \bar{m}_j + H_i$$

which implies

$$\bar{m}_i = \tanh \left[ (k_B T)^{-1} \left( J \sum_{j \in n.n.\,\mathrm{of}\, i} \bar{m}_j + H_i \right) \right]$$

We have again found the self-consistency equation for the magnetization that we have already encountered in the Weiss mean field theory for the Ising model! This is again a confirmation that all mean field theories are equivalent. Defining

$$z \bar{m}_i \equiv \sum_{j \in n.n.\,\mathrm{of}\, i} \bar{m}_j$$

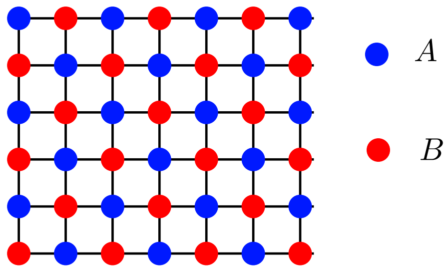
we get

$$\bar{m}_i = \tanh \left[ \beta (J z \bar{m}_i + H_i) \right] \tag{1.41}$$

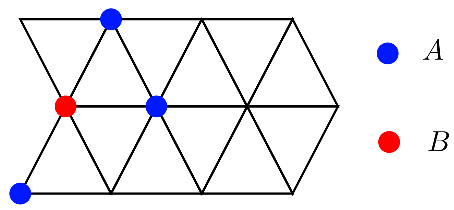
this is the Bragg-William approximation.

**Example 3: Ising anti-ferromagnet in an external field**

Let us consider the model




**(a)** Square lattice is bipartite.




**(b)** Triangular lattice is not bipartite.

**Figure 1.5:** Ising anti-ferromagnet in an external field.

$$\mathcal{H} = \boxed{+} J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i, \tag{1.42}$$

Note the $+$ sign before $J$, this means that the interactions are anti-ferromagnetic. Let us consider two cases:

- If $H = 0$ ferromagnetic and anti-ferromagnetic behave similarly when the interactions are between nearest neighbours on a *bipartite lattice*, i.e. a lattice that can be divided into two sublattices, say $A$ and $B$, such that a $A$ site has only $B$ neighbours and a $B$ site only $A$ ones.

  *Remark.* FCC is not bipartite, while BCC it is. See Figure 1.5.

  If the lattice is bipartite and $J_{ij}$ is non zero only when $i$ and $j$ belong to different sublattices (they do not have to be only n.n.!), one can redefine the spins such that

  $$S'_j = \begin{cases} +S_j & j \in A \\ -S_j & j \in B \end{cases}$$

  Clearly, $S'_i S'_j = -S_i S_j$. It is like if the $J_{ij}$ have changed sign and we are formally back to ferromagnetic model for the two sublattices:

  $$\mathcal{H}^* = \boxed{-} J \sum_{\langle ij \rangle} S'_i S'_j \tag{1.43}$$

  i.e. a ferromagnetic Ising.

- In presence of a magnetic field $H$, we need to reverse its sign when applied to sites $B$.

  The thermodynamic of a ferromagnetic Ising model on a bipartite lattice in a uniform magnetic field $H$ is identical to the one of the Ising antiferromagnetic model in presence of the so called *staggered field*, i.e. $H_A = H$ and $H_B = -H$. The Hamiltonian is

  $$\mathcal{H}^*[S] = -J \sum_{\langle r_A r_B \rangle} S(r_A) S(r_B) - H \sum_{r_A} S(r_A) + H \sum_{r_B} S(r_B), \quad J > 0, H > 0 \tag{1.44}$$

  The average magnetization per spin is

  $$m \equiv \frac{1}{2}(m_A + m_B)$$

while

$$m_S = \frac{1}{2}(m_A - m_B)$$

is the *staggered magnetization.*

In order to use the variational density matrix method for this problem we consider two independent variational parameters $m_A$ and $m_B$ for sublattice $A$ and $B$ respectively. On each sublattice, the model is like the standard Ising

$$\begin{cases} \rho_A^{(1)}(S) = \frac{1+m_A}{2}\delta_{S,1} + \frac{1-m_A}{2}\delta_{S,-1} \\ \rho_B^{(1)}(S) = \frac{1+m_B}{2}\delta_{S,1} + \frac{1-m_B}{2}\delta_{S,-1} \end{cases}$$

*Remark.* Note that, being $H$ uniform, $\langle S_i \rangle = m$, i.e. does not depend on $i$. Same for the 1−particle distribution functions $\rho_A^{(1)}(S)$ and $\rho_B^{(1)}(S)$.

By performing the calculation for the terms

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_{\rho_{MF}} - H \sum_i \langle S_i \rangle_{\rho_{MF}}$$

$$\langle \ln \rho \rangle_{\rho_{MF}} = \sum_i \mathrm{Tr}^{(i)}(\rho_i \ln \rho_i)$$

as before, but remembering to partition the procedure into the two sublattices $A$ and $B$, one can show that the variational free energy is given by

$$\frac{F(m_A, m_B)}{N} = \frac{z\hat{J}}{2} m_A m_B - \frac{1}{2}H(m_A + m_B) - \frac{1}{2}k_B T s(m_A) - \frac{1}{2}k_B T s(m_B) \quad (1.45)$$

where the entropy term is

$$s(m) = \left[\frac{1+m}{2}\ln\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\ln\left(\frac{1-m}{2}\right)\right]$$

By differentiating $\frac{F}{N}$ with respect to $m_A$ and $m_B$, one gets

$$\begin{aligned} \frac{\partial(F/N)}{\partial m_A} = 0 \qquad & \Rightarrow m_B = \frac{H}{z\hat{J}} - \frac{k_B T}{z\hat{J}} \ln\left(\frac{1+m_A}{1-m_A}\right) \\ \frac{\partial(F/N)}{\partial m_B} = 0 \qquad & \Rightarrow m_A = \frac{H}{z\hat{J}} - \frac{k_B T}{z\hat{J}} \ln\left(\frac{1+m_B}{1-m_B}\right) \end{aligned}$$

As before, since

$$\tanh^{-1}(x) = \frac{1}{2}\ln\frac{1+x}{1-x}$$

these self-consistent equations can be written as

$$\begin{cases} m_A = \tanh\Big(\beta\Big(H - z\hat{J}m_B\Big)\Big) \\ m_B = \tanh\Big(\beta\Big(H - z\hat{J}m_A\Big)\Big) \end{cases} \quad (1.47)$$

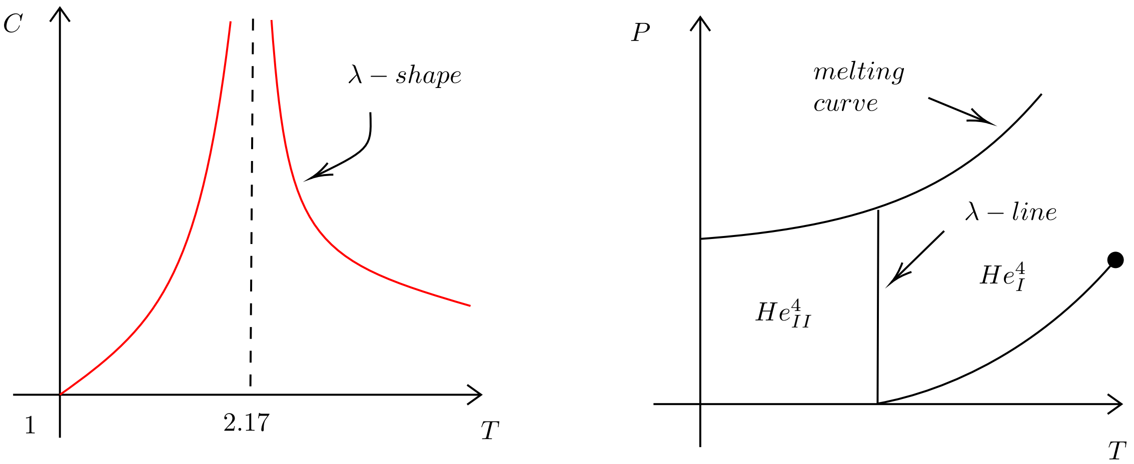
The sites $\in A$ experience an internal field $H_{A,MF} = -z\hat{J}m_B$ from the $B$ neighbours and vice versa for the sites $\in B$.

### 1.2.3 Second approach: Blume-Emery-Griffith model

We apply this approach to the so called *Blume-Emery-Griffith model*. This is a spin model with vacancies that describes the phase diagram and the critical properties of an interacting system displaying a *tricritical point*. Perhaps the most famous of these systems is the $\mathrm{He}^3 - \mathrm{He}^4$ mixture undergoing a fluid-superfluid transition.

*Remark.* $\mathrm{He}^4$ is a non radiative isotope with two protons and two neutrons. Roughly 1/4 of the universe matter is $\mathrm{He}^4$! From a quantum statistical point of view $\mathrm{He}^4$ is a *boson*.

A gas of $\mathrm{He}^4$ undergoes a fluid-superfluid transition at $T_\lambda = 2.17K$ and $P = P_0$. It is known as $\lambda-$transition since at $T \sim T_\lambda$ the specific heat $c(T)$ behaves as in Figure 1.6a: the plot of the specific heat as a function of the temperature has a shape that resembles a $\lambda$. The $\lambda-$transition is a genuine critical point (second order). For $T < T_\lambda$, $\mathrm{He}^4$ is in the superfluid phase and it can be described by a two-fluids model in which one component has zero viscosity and zero entropy.




**(a)** Plot of the specific heat $c(T)$. It has the shape of a $\lambda$.

**(b)** $(P, T)$ phase diagram.

**Figure 1.6**

The BEG model is used to describe what happens when we add some $\mathrm{He}^3$ to the system constituted by $\mathrm{He}^4$; it does not consider quantum effects, but only the "messing up" due to the $\mathrm{He}^3$ impurities.

*Remark.* $\mathrm{He}^3$ is a non-radioactive isotope with 2 protons and 1 neutron. From a quantum statistical point of view is a *fermion*.

Experimentally when $\mathrm{He}^3$ is added to $\mathrm{He}^4$ the temperature of the fluid-superfluid transition decreases. More specifically, if inserted in a system of $\mathrm{He}^4$ it will "dilute" its bosonic property. Then, one expects that $T_\lambda$ decreases, as observed. Denoting by $x$ the concentration of $\mathrm{He}^3$, one observes

$$T_\lambda = T_\lambda(x)$$

with $T_\lambda(x)$ that decreases as $x$ increases.

For small concentration of $\mathrm{He}^3$ the mixture remains homogeneous, and the only effect is the change of $T_\lambda$. However, when the concentration $x$ of $\mathrm{He}^3$ reaches the critical value $x_t$

$$x > x_t = \frac{n_3}{n_3 + n_4} \sim 0.67$$

$\mathrm{He}^3$ and $\mathrm{He}^4$ separate into two phases (just like oil separates from water, the mixture undergoes a separation between a phase rich and a phase poor of $\mathrm{He}^3$) and the $\lambda$ transition becomes first-order (namely, discontinuous). The transition point $(x_t, T_t)$ where the system shifts from a continuous $\lambda$-transition to a discontinuous one is that where the phase separation starts and is called tricritical point (i.e. it is a critical point that separates a line of second order transition from a line of first order transition). The BEG model was introduced to describe such a situation.

### BEG Model

As we have anticipated, the BEG Model is a lattice gas model and so it is based on an Ising-like Hamiltonian. In particular, it is the model of a diluted ferromagnetic system. On the sites of this lattice we define a variable $S_i$ which can assume the values $-1$,0 and $+1$: we decide that when an $He^4$ atom is present in a lattice site then $S_i = \pm 1$, while when $S_i = 0$ it means that the site is occupied by an $He^3$ atom. We then define our order parameter to be

$$\langle S_i \rangle = m_i$$

In the Ising model $\left\langle S_i^2 \right\rangle$ can only be equal to 1, while in this case it can be either 0 or 1: we can thus interpret $\left\langle S_i^2 \right\rangle$ as the concentration of $He^4$ atoms, and

$$x \equiv 1 - \left\langle S_i^2 \right\rangle$$

as the fraction of $He^3$. We also define

$$\Delta \propto \mu_{\mathrm{He}^3} - \mu_{\mathrm{He}^4}$$

to be the difference of the chemical potentials of $He^3$ and $He^4$; since this parameter is related to the number of $He^3$ and $He^4$ atoms, we expect that when

- $x \to 0$ (namely, there is only $He^4$), we have $\Delta \to -\infty$.
- $x \to 1$ (namely, there is only $He^3$), we have $\Delta \to +\infty$.

and the order parameter for the $\lambda-$transition becomes

$$\langle S_i \rangle = \begin{cases} 0 & T > T_\lambda \\ m & T < T_\lambda \end{cases}$$

We consider the following Hamiltonian for the system:

$$\mathcal{H} = -J \sum_{\langle ij \rangle}^{N} S_i S_j + \Delta \sum_{i=1}^{N} S_i^2 - \Delta N \tag{1.48}$$

*Remark.* $N$ is the total number of lattice sites The $\Delta N$ term is a typical term for a gas in gran canonical ensemble.

### Variational mean field approach to BEG

Since we want to apply the second variational method that we have seen, we write the mean field probability density as:

$$\rho_{MF} = \prod_i \rho_i = \prod_i \rho^{(1)}(S_i)$$

and the free energy:

$$G(T, J, \Delta) = \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \sum_i \mathrm{Tr}^{(i)}(\rho_i \ln \rho_i) \tag{1.49}$$

The mean value of the Hamiltonian is:

$$\langle \mathcal{H} \rangle_{\rho_{MF}} = -J \sum_{\langle ij \rangle} \langle S_i S_j \rangle + \Delta \sum_i \left\langle S_i^2 \right\rangle - N\Delta$$

and since $\langle S_i S_j \rangle = \langle S_i \rangle \langle S_j \rangle$ (it's the fundamental hypothesis of mean field theories) we get

$$\langle \mathcal{H} \rangle_{\rho_{MF}} \overset{MF}{\simeq} -J \sum_{\langle ij \rangle} \langle S_i \rangle \langle S_j \rangle + \Delta \sum_i \left\langle S_i^2 \right\rangle - N\Delta$$

We have also

$$\langle S_i \rangle = \langle S_j \rangle \equiv m$$

Therefore, the free energy of the system is:

$$G(T, J, \Delta)_{MF} = -\frac{1}{2} NJz(\mathrm{Tr}_{S_i}(\rho_i S_i))^2 + N\Delta\,\mathrm{Tr}_{S_i}(\rho_i S_i^2) - N\Delta + Nk_B T\,\mathrm{Tr}_{S_i}(\rho_i \ln \rho_i) \tag{1.50}$$

where $z$ is the coordination number of the lattice.

We now must minimize this expression with respect to $\rho_i$, with the constraint $\mathrm{Tr}_{S_i}(\rho_i) = 1$:

$$\frac{\mathrm{d}G}{\mathrm{d}\rho_i} = 0$$

Let us consider each term

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}\rho_i}(\mathrm{Tr}(\rho_i S_i))^2 &= 2(\mathrm{Tr}(\rho_i S_i))S_i = 2\langle S_i \rangle S_i = 2mS_i \\
\frac{\mathrm{d}}{\mathrm{d}\rho_i}\left(\mathrm{Tr}\left(\rho_i S_i^2\right)\right) &= S_i^2 \\
\frac{\mathrm{d}}{\mathrm{d}\rho_i}(\mathrm{Tr}(\rho_i \ln \rho_i)) &= \ln \rho_i + 1
\end{aligned}$$

then,

$$\frac{\mathrm{d}G}{\mathrm{d}\rho_i} = -JNzmS_i + N\Delta S_i^2 + Nk_B T \ln \rho_i + Nk_B T = 0$$

Dividing by $Nk_BT$,

$$\ln \rho_i \equiv \ln \rho^{(1)}(S_i) = \beta JzmS_i - \beta\Delta S_i^2 - 1$$

which leads to

$$\rho^{(1)}(S_i) = \frac{1}{A} e^{\beta(zJmS_i - \Delta S_i^2)} \tag{1.52}$$

where we have reabsorbed $e^{-1}$ into the normalization constant $A$. The constant $A$ can be found by imposing the constraint $\mathrm{Tr}_{S_i}\,\rho^{(1)}(S_i) = 1$, we find

$$A = 1 + 2e^{-\beta\Delta}\cosh(\beta zJm) \tag{1.53}$$

**Example 4: How to compute $A$**

By imposing the constraint $\mathrm{Tr}_{S_i}\,\rho^{(1)}(S_i) = 1$ (recall that $S_i = \pm 1, 0$), we get

$$1 = \frac{1}{A}\left(e^{\beta(zJm(+1) - \Delta(+1)^2)} + e^{\beta(zJm(-1) - \Delta(-1)^2)} + e^{\beta(zJm(0) - \Delta(0)^2)}\right)$$

Hence, by rearranging

$$1 = \frac{1}{A}\left(2e^{-\beta\Delta}\cosh\left(\beta zJm\right) + 1\right) \Rightarrow A = 1 + 2e^{-\beta\Delta}\cosh(\beta zJm)$$

Given $\rho^{(1)}(S_i)$ it is possible to show

$$\left\langle S_i^2 \right\rangle = \mathrm{Tr}_{S_i}(\rho_i S_i^2) = \frac{1}{A} 2e^{-\beta\Delta}\cosh(\beta zJm)$$

and

$$x = 1 - \left\langle S_i^2 \right\rangle = \frac{A - 2e^{-\beta\Delta}\cosh(\beta zJm)}{A} \qquad \Rightarrow x = \frac{1}{A}$$

Hence, substituting this expression of $\rho_i$ into $G$, after some mathematical rearrangement we get:

$$\boxed{\frac{G(T,\Delta,m,J)}{N} = \frac{z}{2}Jm^2 - \Delta - k_BT\ln A} \tag{1.54}$$

In order to find the equilibrium state for any $T$ and $\Delta$, we must minimize this expression of $G(T,\Delta,m,J)$ with respect to $m$. If we expand $G$ for small values of $m$, keeping in mind the Taylor expansions

$$\cosh(t) = 1 + \frac{t^2}{2} + \frac{t^4}{24}, \quad \ln(1+t) = t - \frac{t^2}{2}$$

we get

$$G(T,\Delta,J,m) = a_0(T,\Delta) + a(T,\Delta)m^2 + b(T,\Delta)m^4 + \frac{c(T,\Delta)}{6}m^6 \tag{1.55}$$

where

$$\begin{cases} a_0(T,\Delta) = -k_BT\ln\left(1 + 2e^{-\beta\Delta}\right) - \Delta \\ a(T,\Delta) = \frac{zJ}{2}\left(1 - \frac{zJ}{\delta k_BT}\right) \\ b(T,\Delta) = \frac{zJ}{8\delta^2}(\beta zJ)^3\left(1 - \frac{\delta}{3}\right) \\ c(T,\Delta) > 0 \end{cases} \tag{1.56}$$

and the parameter $\delta$ is

$$\delta \equiv 1 + \frac{e^{\beta\Delta}}{2} = \delta(T,\Delta) \tag{1.57}$$

Note that unlike the Ising model in the Weiss approximation in this case both the quadratic and the quartic terms, $a$ and $b$, can change sign when the parameters assume particular values. Let us also note that the order parameter of the system, namely the concentration of $He^3$, is:

$$x(T,\Delta,J) = 1 - \left\langle S_i^2 \right\rangle = \frac{1}{A} = \frac{1}{1 + 2e^{-\beta\Delta}\cosh(\beta zJm)}$$

Therefore, in the disordered phase (both $He^3$ and $He^4$ are present) we have $m = 0$ and the concentration of $He^3$ becomes:

$$x(T,\Delta,J) = \frac{1}{1 + 2e^{-\beta\Delta}} = 1 - \frac{1}{\delta} \tag{1.58}$$

This way we can determine how the temperature of the $\lambda$-transition depends on $x$; in fact, the critical temperature will be the one that makes $a$ change sign, so we can determine it from the condition $a = 0$:

$$a(T_c(\Delta)) = \frac{zJ}{2}\left(1 - \frac{zJ}{\delta k_BT_c}\right) = 0 \qquad \Rightarrow T_c = \frac{zJ}{k_B\delta}$$

Since as we have just seen $1/\delta = 1 - x$, we have

$$T_c(x) = T_c(0)(1 - x) \tag{1.59}$$

where $T_c(0) = zJ/k_B$. The other transition (from the continuous $\lambda$ to the discontinuous one) will occur when the quartic term $b$ changes sign, and so we can determine the critical value of $x_c$ at which it occurs from the condition $b = 0$. Hence, the tricritical point is the one that satisfies the conditions

$$\begin{cases} a(T_t,\Delta_t) = 0 \\ b(T_t,\Delta_t) = 0 \end{cases} \quad \Rightarrow \begin{cases} \delta_t = \frac{zJ}{k_BT_t} \\ \delta_t = 3 \end{cases}$$

and the value of the concentration of $He^3$ results

$$x(T_t, \Delta_t) = 1 - \frac{1}{\delta_t} = \frac{2}{3} \tag{1.60}$$

which is in astonishingly good agreement with the experimental result of $x_t \sim 0.67$.

**Exercise 1: Expansion of G for small values of m**

Expand the free-energy per site

$$\frac{G}{N} = \frac{z}{2}Jm^2 - \Delta - k_B T \ln A$$

where $A = 1 + 2e^{-\beta\Delta}\cosh(\beta zJm)$ for small values of $m$.

*Solution.* Let us define

$$x \equiv \beta zJm, \quad B \equiv 2e^{-\beta\Delta}$$

Since $\cosh x \simeq 1 + \frac{x^2}{2} + \frac{x^4}{24}$, we can expans $A$ as

$$A = 1 + B\cosh x \simeq 1 + B\left(1 + \frac{x^2}{2} + \frac{x^4}{24}\right)$$

Hence,

$$\begin{aligned}
\ln A &= \ln\left(1 + B + \frac{Bx^2}{2} + \frac{Bx^4}{24}\right) \\
&\simeq \ln\left[(1+B)\left(1 + \frac{B}{2(1+B)}x^2 + \frac{B}{24(1+B)}x^4\right)\right] \\
&= \ln(1+B) + \ln(1+t)
\end{aligned}$$

where

$$t \equiv \frac{B}{2(1+B)}x^2 + \frac{B}{24(1+B)}x^4$$

Let us first consider the term

$$\frac{B}{1+B} = \frac{2e^{-\beta\Delta}}{1+2e^{-\beta\Delta}} = \frac{2}{2+e^{\beta\Delta}} = \frac{1}{\delta}$$

Since $\ln(1+t) = t - \frac{t^2}{2}$, we have

$$\Rightarrow \ln A = \ln(1+B) + \frac{x^2}{2\delta} + \left(\frac{1}{24\delta} - \frac{1}{4\delta^2}\right)x^4 - \frac{1}{24\delta^2}x^6$$

If we remember that $x \equiv \beta zJm$, we obtain

$$\begin{aligned}
-\frac{\ln A}{\beta} + \frac{z}{2}Jm^2 - \Delta \simeq & a_0(T,\Delta) + \left(\frac{z}{2}J - \frac{\beta z^2 J^2}{2\delta}\right)m^2 \\
& + \left(\frac{1}{8\delta} - \frac{1}{24\delta}\right)\beta^3 z^4 J^4 m^4 + \frac{1}{24\delta^2}\beta^5 z^6 J^6 m^6
\end{aligned}$$

Hence, the free energy $G$ for small values of $m$ is

$$G(T,\Delta,J,m) = a_0(T,\Delta) + a(T,\Delta)m^2 + b(T,\Delta)m^4 + c(T,\Delta)m^6$$

where

$$\begin{aligned}
a(T,\Delta) &= \frac{zJ}{2}\left(1 - \frac{\beta zJ}{\delta}\right) \\
b(T,\Delta) &= \frac{\beta^3 z^4 J^4}{8\delta}\left(\frac{1}{\delta} - \frac{1}{3}\right) = \frac{\beta^3 z^4 J^4}{8\delta^2}\left(1 - \frac{\delta}{3}\right) \\
c(T,\Delta) &= \frac{\beta^5 z^6 J^6}{24\delta^2} > 0
\end{aligned}$$

### 1.2.4 Mean field again

Another way to introduce the variational approach and the mean field approximation often discussed starts from the general expression of the variational free energy

$$F_{var} = \langle \mathcal{H} \rangle_{\rho_{TR}} + k_B T \langle \ln \rho_{TR} \rangle_{\rho_{TR}} \tag{1.62}$$

We have to choose a family of distribution. If one assumes that the family of trial distribution is of the Gibbs-Boltzmann form

$$\rho_{TR} = \frac{e^{-\beta \mathcal{H}_{TR}}}{Z_{TR}} \tag{1.63}$$

with

$$Z_{TR} = e^{-\beta F_{TR}} = \sum_{\{\Phi_i\}} e^{-\beta \mathcal{H}_{TR}(\{\Phi_i\})} \tag{1.64}$$

then, since

$$\ln \rho_{TR} = -\beta \mathcal{H}_{TR} - \ln Z_{TR}$$

we have

$$k_B T \langle \ln \rho_{TR} \rangle_{\rho_{TR}} = k_B T \left\langle \frac{-\mathcal{H}_{TR}}{k_B T} \right\rangle + k_B T \underbrace{\langle - \ln Z_{TR} \rangle}_{\beta F_{TR}}$$

By rearranging,

$$k_B T \langle \ln \rho_{TR} \rangle_{\rho_{TR}} = \langle -\mathcal{H}_{TR} \rangle + F_{TR}$$

Hence, the variational free energy becomes

$$F_{var} = \langle \mathcal{H} \rangle_{\rho_{TR}} - \langle \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} = \langle \mathcal{H} - \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} \tag{1.65}$$

Clearly, $F \leq F_{var}$ and one has to look for the minima of $F_{var}$ by varying $\rho_{TR}$. Within this approach, the mean field approximation is still given by

$$\rho_{TR}^{MF}(\Phi_1, \dots, \Phi_N) = \prod_{i=1}^{N} \rho_{TR}^{(1)}(\Phi_i)$$

that in this case becomes

$$\prod_{i=1}^{N} \rho_{TR}^{(1)}(\Phi_i) = \frac{1}{Z_{TR}^{MF}} e^{\beta \sum_i b_i \Phi_i} \tag{1.66}$$

and

$$Z_{TR} = \sum_{\{\Phi\}} e^{\beta \sum_i b_i \Phi_i} \tag{1.67}$$

where $b_i$ are the variational parameters. The Hamiltonian is

$$\mathcal{H}_{TR} = -\sum_i b_i \Phi_i \tag{1.68}$$

If we consider again the Ising model (remind that it means $\Phi_i \to S_i = \pm 1$), the Hamiltonian is

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

Hence, Eq.(1.65) becomes

$$
\begin{aligned}
F_{var} &= \langle \mathcal{H} - \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} \\
&= F_{TR} + \left\langle \left( -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i \right) - \left( -\sum_i b_i S_i \right) \right\rangle_{\rho_{TR}} \\
&= F_{TR} + \left\langle -J \sum_{\langle ij \rangle} S_i S_j + \sum_i (b_i - H) S_i \right\rangle_{\rho_{TR}} \\
&= F_{TR} - J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_{\rho_{TR}} + \sum_i (b_i - H) \langle S_i \rangle_{\rho_{TR}}
\end{aligned}
$$

Since $\rho_{TR} = \prod_{i=1}^N \rho_i$, we have

$$
\langle S_i S_j \rangle_{\rho_{TR}} = \langle S_i \rangle_{\rho_{TR}} \langle S_j \rangle_{\rho_{TR}}
$$

Therefore,

$$
F_{var} = F_{TR} - J \sum_{\langle ij \rangle} \langle S_i \rangle_{\rho_{TR}} \langle S_j \rangle_{\rho_{TR}} + \sum_i (b_i - H) \langle S_i \rangle_{\rho_{TR}}
$$

Let us minimize the last equation, we consider the condition:

$$
\frac{\partial F_{var}}{\partial b_i} = 0, \quad \forall i
$$

which gives

$$
0 = \frac{\partial F_{var}}{\partial b_i} = \left[ -J \sum_{j \in n.n.\, i} \langle S_j \rangle_{\rho_{TR}} + b_i - H \right] \frac{\partial \langle S_i \rangle}{\partial b_i}
$$

The variational parameters are equal to

$$
b_i = J \sum_{j \in n.n.\, i} \langle S_j \rangle_{\rho_{TR}} + H
$$

Let us calculate the average of the spin $\langle S_i \rangle_{\rho_{TR}}$:

$$
\begin{aligned}
\langle S_i \rangle_{\rho_{TR}} &= \frac{1}{Z_{TR}} \sum_{\{S\}} S_i e^{\beta \sum_k S_k b_k} = \frac{\prod_k \sum_{S_k} S_i e^{\beta S_k b_k}}{\prod_k \sum_{S_k} e^{\beta S_k b_k}} \\
&= \frac{\sum_{S_i = \pm 1} S_i e^{\beta S_i b_i}}{\sum_{S_i = \pm 1} e^{\beta S_i b_i}} = \frac{\sinh(\beta b_i)}{\cosh(\beta b_i)} = \tanh(\beta b_i)
\end{aligned}
$$

Finally, the variational parameters are

$$
b_i = J \sum_{j \in n.n.\, i} \tanh(\beta b_j) + H \tag{1.69}
$$

*Remark.* The main step to understand is how to derive $F_{var}$ from a $\rho_{TR}$. This is nice to see a variation with respect to the real hamiltonian. Consider a bunch of data, for instance a million of configuration, which is the distribution of the configuration? Usually, we build up a model with a distribution that depends on parameters and what we want to do is statistical inference. Starting from the model and the data we have to obtain the real distribution.

**Exercise 2**

Consider again the antiferromagnetic Ising model

$$\mathcal{H}[\{S\}] = -J \sum_{\langle \vec{\mathbf{r}}_A \vec{\mathbf{r}}_B \rangle} S(\vec{\mathbf{r}}_A) S(\vec{\mathbf{r}}_B) - H \sum_{\vec{\mathbf{r}}_A} S(\vec{\mathbf{r}}_A) + H \sum_{\vec{\mathbf{r}}_B} S(\vec{\mathbf{r}}_B)$$

whith $J > 0$ and $H > 0$. Remember that

- $\vec{\mathbf{r}}_A$ denotes the site on the $A$ sublattice.
- $\vec{\mathbf{r}}_B$ denotes the site on the $B$ sublattice.

Let us find again the mean-field solution, but now using the variational ansatz

$$F \leq F_{var} = \langle \mathcal{H} \rangle_{\rho_{TR}} - \langle \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR} = \langle \mathcal{H} - \mathcal{H}_{TR} \rangle_{\rho_{TR}} + F_{TR}$$

*Remark.* Since the problem can be splitted in two sublattices, it is convenient to use

$$\mathcal{H}_{TR} = -H_A \sum_{r_A} S(r_A) - H_B \sum_{r_B} S(r_B)$$

In particular:

- show that $F_{var}$ has the following expression:

$$\begin{aligned} F_{var} =& F_{TR}(\beta H_A, \beta H_B) - 4NJ \langle S_A \rangle_{\rho_{TR}} \langle S_B \rangle_{\rho_{TR}} \\ &- \frac{1}{2} NH \Big( \langle S_A \rangle_{\rho_{TR}} - \langle S_B \rangle_{\rho_{TR}} \Big) + \frac{1}{2} N \Big( H_A \langle S_A \rangle_{\rho_{TR}} + H_B \langle S_B \rangle_{\rho_{TR}} \Big) \end{aligned}$$

  where

$$\langle S_A \rangle_{\rho_{TR}} \equiv m_A + n$$
$$\langle S_B \rangle_{\rho_{TR}} \equiv m_B - n$$

  with $m = m_A + m_B$, and

$$m_A = \tanh(\beta H - 4\beta J m_B)$$
$$m_B = \tanh(\beta H - 4\beta J m_A)$$

- Expand the free energy $F_{var}$ in powers of $m$ of the form

$$F_{var} = A + Bm^2 + cm^4 + O(m^6)$$

  and find the explicit expression of $A, B$ and $C$ as a function of $T, H$ and $n$.