

Thermodynamic Relations in Magnetism

In studying thermodynamic properties of any system (as, for example, a gas) with a fixed number of particles, the relevant thermodynamic variables are the volume (V), the entropy (S), the temperature (T) and the pressure (P). It is usual to work with the *thermodynamic potentials* $U(S, V)$ (energy), $F(T, V)$ (Helmholtz free energy), and $G(T, P)$ (Gibbs free energy). These functions are related through Legendre transforms:

$$\begin{aligned} F &= U - TS, \\ G &= F + PV. \end{aligned} \quad (1)$$

The *equation of state* may be expressed by the relation

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (2)$$

In magnetic systems, and specially in the case of solids, we do not worry about volume changes, but the presence of a magnetic field (H) is relevant. The other relevant thermodynamic quantity, instead of pressure, is obviously the magnetization (M). It is usually convenient to deal with quantities per unit volume, that we will denote with lowercase letters ($u = U/V$, $s = S/V$, $f = F/V$, $g = G/V$). The thermodynamic potentials of interest are the energy $u(s, H)$, the (magnetic) Helmholtz free energy $f(T, H)$, and the (magnetic) Gibbs free energy $g(T, M)$. Note that the magnetization is represented by a capital letter, despite it being a quantity defined per unit volume. The equation of state is given by

$$M = -T \left(\frac{\partial f}{\partial H} \right)_T. \quad (3)$$

If the microscopic interactions in the system are known, the free energy could, in principle, be obtained from the partition function:

$$\begin{aligned} Z &= \text{Tr} e^{-\mathcal{H}/T}, \\ f &= -\frac{T}{V} \ln Z. \end{aligned} \quad (4)$$

For a magnetic system in a lattice, it is usual to define the free energy per site (i.e., per primitive cell) instead of per unit volume. In this case, supposing that it is possible to obtain the partition function Z_N by solving the problem for a lattice of N sites (usually with periodic boundary conditions), the free energy is given by

$$f = -T \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z_N. \quad (5)$$

We have already seen that an exact evaluation of the free energy is only possible for a few simplified models, or using mean-field approximations. However, we can focus on the region around the transition between paramagnetic and ordered phase, where some rigorous relations can be obtained.

Thermodynamic properties near a critical point

In the mean field approximation as well as in the exact solution of the Ising model in $d = 2$, it is observed that the phase transition is characterized by *singular* behavior of various thermodynamic properties. In particular, in the absence of applied magnetic field, one finds that magnetization, uniform susceptibility (let's consider only the PM-FM transition) and specific heat behave as

$$\begin{aligned} M &\sim |t|^\beta, & t &\rightarrow 0-, \\ \chi &\sim |t|^{-\gamma}, & t &\rightarrow 0+, \\ c_{H=0} &\sim |t|^{-\alpha}, & t &\rightarrow 0+, \end{aligned} \quad (6)$$

as functions of the *reduced temperature*

$$t \equiv \frac{T - T_c}{T_c}. \quad (7)$$

On the other hand, on the critical isotherm $T = T_c$, an applied magnetic field eliminates the transition, so that the magnetization has a singular dependence on H in the limit $H \rightarrow 0$:

$$M \sim \text{sgn}(H) |H|^{1/\delta}. \quad (8)$$

For quantities that are singular on the other side of the transition, i.e., in the ordered phase, new exponents are defined, like γ' for χ and α' for c_H . However, both model calculations and experimental results indicate that the equalities $\gamma' = \gamma$, $\alpha' = \alpha$, etc. are verified.

The exponents that appear in the above relations are called ***critical exponents***, and the singular behavior of thermodynamic quantities characterizes the so-called *critical phenomena*. They are not restricted to magnetic systems, but appear whenever there is a second-order phase transition associated with a critical point in the phase diagram of any thermodynamic system.

For magnetic systems, focusing on the PM-FM transition, we know, for example, the values of the critical exponents obtained in the mean-field approximation, as well as those from the exact solution of the Ising model in two dimensions, summarized below.

MF:	$\beta = 1/2,$	$\gamma = 1,$	$\alpha = 0$ (disc.),	$\delta = 3$
Ising 2D:	$\beta = 1/8,$	$\gamma = 7/4,$	$\alpha = 0$ (log.),	$\delta = 15$

Note that, although the exponent α is zero in both cases, these are distinct singularities: a finite discontinuity in MFA, and a logarithmic divergence in the 2d Ising model.

Experimental results on ferromagnets indicate concentrated values in narrow regions:

$$\beta \simeq 0.33 \rightarrow 0.37, \quad \gamma \simeq 1.21 \rightarrow 1.37, \quad \alpha \simeq -0.1 \rightarrow 0.1, \quad \delta \simeq 4.2 \rightarrow 4.4.$$

Since experimental results mostly refer to three-dimensional systems, it would be interesting to obtain theoretical predictions for such systems. One possibility is by extrapolating high-temperature series. For example, we saw that the susceptibility can be written as the series

$$\chi = \sum_{n=0}^{\infty} a_n T^{-n}, \quad \beta = 1/T. \quad (9)$$

On the other hand, we should have

$$\chi \sim A \left(1 - \frac{T_c}{T}\right)^{-\gamma}, \quad \beta \rightarrow \beta_c. \quad (10)$$

Expanding the last equation in powers of β , and comparing the terms, we obtain

$$a_n \sim \frac{A(n + \gamma - 1)!}{T_c^{-n} n! (\gamma - 1)!}, \quad n \rightarrow \infty. \quad (11)$$

Therefore,

$$r_n \equiv \frac{a_n}{a_{n-1}} \sim T_c \left(1 + \frac{\gamma - 1}{n}\right). \quad (12)$$

We see that the critical temperature T_c and the exponent γ can be obtained from the asymptotic linear behavior of r_n as a function of $1/n$. With an equivalent procedure for other thermodynamic quantities, the results obtained for the Ising model in 3 dimensions are

$$\alpha = 1/8, \quad \beta = 5/16, \quad \gamma = 5/4, \quad \delta = 5.$$

The value of δ is not directly determined by a high-temperature series, but is deduced from relations with the other exponents, as we will see later. The above values are much closer to the experimental results. The remaining differences can be attributed to the fact that real systems are usually closer to the Heisenberg model, instead of Ising. This shows that critical exponents, in addition to depending on the system's spatial dimension, also depend on the number of components (symmetry) of the order parameter. We already know the critical exponents for $d = 2, n = 1$ (2d Ising), and for $d \rightarrow \infty$, any n (MF). A complementary case, for $n \rightarrow \infty$ and any dimension, is provided by the *spherical model*. It is classical, like the Ising model, but with n -component spins, taking the limit $n \rightarrow \infty$ with the condition $\frac{1}{n} \sum_{\alpha=1}^n s_{\alpha}^2 = 1$. The resulting critical exponents are

$$\begin{array}{llll} \alpha = \frac{4-d}{d-2}, & \beta = \frac{1}{2}, & \gamma = \frac{2}{d-2} & \longrightarrow & 2 < d \leq 4 \\ \alpha = 0, & \beta = \frac{1}{2}, & \gamma = 1 & \longrightarrow & d \geq 4 \end{array}$$

Note that the exponents for $d \geq 4$ are the same as in MF. This is not a peculiarity of the spherical model, but actually a general result. So, although the MF approximation becomes correct only for $d \rightarrow \infty$, as discussed in Text 10, its critical exponents are already correct at $d = 4$.

At this point, it is worth mentioning that there are methods, like the *Renormalization Group*, that deal specifically with critical phenomena and the evaluation of critical exponents, but they are out of the scope of the present course.

Free energy and phase transitions

Since we are addressing the statistical mechanics of magnetism, it is interesting to focus on the free energy and its behavior in a range of temperatures that include a magnetic phase transition.

Free energy in MF

As we saw earlier, the mean-field Hamiltonian for a system of localized spins has the form

$$\mathcal{H} = -H^{\text{eff}} \sum_i S_i^z + NJ(0)M^2, \quad (13)$$

where M is the magnetization, $J(0)$ is the uniform Fourier component of the exchange interaction, and $H^{\text{eff}} = H + 2J(0)M$ is the effective magnetic field acting on every one of the N spins in the system, each occupying a lattice site.

The partition function is separable, i.e., $Z = Z_i^N$, with

$$Z_i = e^{J(0)M^2/T} \text{Tr} e^{H^{\text{eff}} S_i^z / T}. \quad (14)$$

For simplicity, let us consider the case $S = 1/2$ e $H = 0$. Then,

$$Z_i = 2e^{J(0)M^2/T} \cosh(H^{\text{eff}}/2T). \quad (15)$$

The free energy per site, $f = -\frac{1}{N}T \ln Z = -T \ln Z_i$ is given by

$$f = -T \ln 2 + J(0)M^2 - T \ln [\cosh(J(0)M/T)]. \quad (16)$$

It is important to note that equating to zero the derivative of f with respect to M we reobtain exactly the equation for M obtained through the self-consistency condition $M = \langle S_i^z \rangle$. Therefore, considering f as dependent on the *variable* M , the equilibrium value of this variable it is the one that minimizes the free energy.

Remembering that $T_c = 2S(S + 1)J(0)/3 = J(0)/2$, we can eliminate the exchange interaction, writing it in terms of the Curie temperature. It is also convenient to define the variable $\sigma \equiv 2M$. With this, we have

$$f = -T \ln 2 + \frac{1}{2}J(0)\sigma^2 - T \ln \left[\cosh \left(\frac{T_c}{T} \sigma \right) \right]. \quad (17)$$

Taking into account that σ is small near T_c , we can use as the expansions of $\cosh(x)$ and $\ln(1 + y)$ for low values of x or y , obtaining

$$\ln \left[\cosh \left(\frac{T_c}{T} \sigma \right) \right] = \frac{1}{2} \left(\frac{T_c}{T} \right)^2 \sigma^2 - \frac{1}{12} \left(\frac{T_c}{T} \right)^4 \sigma^4 + \dots \quad (18)$$

Therefore,

$$f = f_0(T) + \frac{1}{2}a(T)\sigma^2 + \frac{1}{4}b\sigma^4 + \dots, \quad (19)$$

where $f_0(T) = -T \ln 2$ and

$$\begin{aligned} a(T) &= T_c \left(1 - \frac{T_c}{T} \right) = T_c t + O(t^2), \\ b(T) &= \frac{T_c}{3} \left(\frac{T_c}{T} \right)^4 = \frac{T_c}{3} + O(t). \end{aligned} \quad (20)$$

So, starting with a mean-field formulation, we arrive at a free energy written as a power series in the order parameter. It is usually called *Landau free energy* because it corresponds to a proposal by L. Landau in 1937.

Minimizing the free energy (19) with respect to σ , we obtain

$$\frac{\partial f}{\partial \sigma} = a\sigma + b\sigma^3 = \sigma(a + b\sigma^2) = 0. \quad (21)$$

The possible solutions are $\sigma = 0$ e $\sigma = \pm\sqrt{a/b}$. Taking the second derivative, it follows that

$$\frac{\partial^2 f}{\partial \sigma^2} = a + 3b\sigma^2 = \begin{cases} a, & \text{se } \sigma = 0, \\ -2a, & \text{se } \sigma = \pm\sqrt{a/b}. \end{cases} \quad (22)$$

Therefore, a solution $\sigma = 0$ is possible for $a > 0$, which means, $t > 0$, while the solutions $\sigma = \pm\sqrt{a/b}$ are possible for $a < 0$, i.e, $t < 0$. The existence of two solutions for the ordered phase reflects the spin-inversion symmetry, but present the same absolute value, satisfying the relation $|\sigma| \sim |t|^{1/2}$.

Figure 1 shows schematically the evolution of the free energy as a function of the order parameter as the temperature changes near a second-order phase transition.

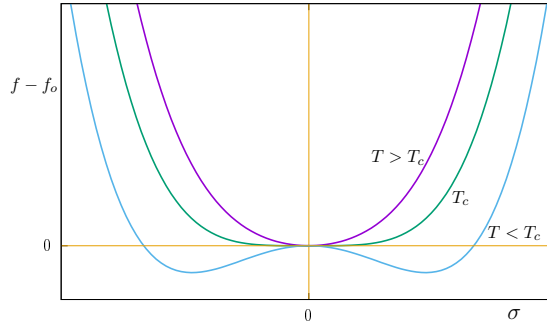


Figure 1: Free energy as a function of the order parameter in the case of a second-order phase transition.

Ginzburg-Landau Theory

The Landau free energy may be seen as a particular case of a more general form, the Ginzburg-Landau free energy. It is also written as power series on the order parameter, but the latter does not have to be uniform. Its variation in space give rise to gradient terms, which prevent strong variations of the order parameter, thus reflecting the effect of exchange interactions.

Taking into account the quadratic and quartic terms that appear in MF, plus the first term involving the gradient compatible with the symmetries of the problem, and including the presence of a magnetic field, the Ginzburg-Landau free energy is written as

$$f = f_0 + \frac{1}{V} \int d^d r \left[\frac{1}{2} a \sigma^2(\mathbf{r}) + \frac{1}{4} \sigma^4(\mathbf{r}) + \frac{1}{2} c [\nabla \sigma(\mathbf{r})]^2 - H(\mathbf{r}) \sigma(\mathbf{r}) \right]. \quad (23)$$

Now, the minimization condition leads to an equation of the Euler-Lagrange type,

$$\frac{\partial \mathcal{L}}{\partial \sigma} - \nabla \cdot \frac{\partial \mathcal{L}}{\partial (\nabla \sigma)} = 0, \quad (24)$$

where \mathcal{L} represents the integrand in Eq. (23). The mean field result is reobtained for $H = 0$, when the uniform solution corresponds to the lowest free energy because the gradient term contributes positively.

The Ginzburg-Landau free energy can describe other physical situations. For example, even considering the uniform case, and without applied field, but including a term in σ^3 , a **first order** phase transition occurs, as shown in Fig. 2. In this case, the behavior of free energy as a function of the parameter order undergoes several changes as the temperature is reduced:

- In the high temperature region, we have a single minimum, at $\sigma = 0$.
- When T is reduced below a first characteristic temperature T^* , a secondary minimum appears for $\sigma \neq 0$, characterizing a metastable phase.

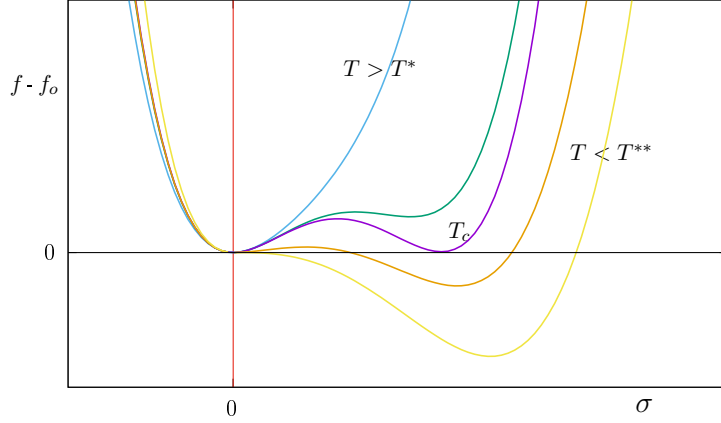


Figure 2: Free energy as a function of the order parameter for the case of a first-order transition.

- At $T = T_c < T^*$ the two minima have the same free energy, which characterizes the first order transition, involving a discontinuity in the order parameter.
- Immediately below T_c , it is the minim at $\sigma = 0$ that becomes metastable.
- Finally, at a temperature $T^{**} < T_c$ the metastable minimum at $\sigma = 0$ disappears, and the only phase present in the system becomes the ordered phase.

Relation to Field Theory

The Ginzburg-Landau free energy, Eq. (23), can be seen as an *action integral*, with the function \mathcal{L} playing the role of a Lagrangian. Replacing the order parameter $\sigma(\mathbf{r})$ by a **field** $\phi(\mathbf{r})$, we can divide the Lagrangian, that becomes a functional of ϕ , in two parts:

$$\mathcal{L}[\phi] = \mathcal{L}_0[\phi] + \mathcal{L}_1[\phi], \quad (25)$$

where

$$\mathcal{L}_0[\phi] = \frac{1}{2} [(\nabla\phi)^2 + m^2\phi^2], \quad \mathcal{L}_1[\phi] = \frac{1}{4}\lambda_4\phi^4. \quad (26)$$

Note that we redefined the coefficients, even absorbing the temperature, so that the partition function is written as

$$Z = \int [\mathcal{D}\phi] \exp \left\{ - \int d^d r \mathcal{L}[\phi(\mathbf{r})] \right\}. \quad (27)$$

The term \mathcal{L}_0 can be interpreted as the Lagrangian of a free particle of mass m . Note that $m^2 \sim a(T)$, which means that the theory is only defined for $T > T_c$ and $m \rightarrow 0$ when $T \rightarrow T_c$.

The term containing the field's gradient can be seen as the continuous limit of the exchange interaction. If we go to the reciprocal space, this term becomes $k^2\phi^2$, that is directly related to the difference $J(0) - J(\mathbf{k})$ in the limit $k \rightarrow 0$. The interaction Lagrangian, \mathcal{L}_1 , on the other hand, has the role of limiting field fluctuations, being, therefore, a *kinematic* interaction.

From the point of view of a field theory, the Ginzburg-Landau theory may be seen as a *classical* limit. It is worth noting that, although we started from the Ginzburg-Landau formulation (motivated by the mean-field approximation), it is possible to write rigorously the partition function of a spin Hamiltonian in the form of a functional integral. This involves the so-called *Hubbard-Stratonovich transformation*, but we will not go into details about this.

To finish up, it is interesting to comment on the physical dimensions of the field and parameters of the theory. Denoting by L and Λ the dimensions of length and momentum, respectively, we see that the Lagrangian has dimension L^{-d} , because its integral in d dimensions must be a dimensionless quantity [see Eq. (27)]. Therefore, the dimension of the field ϕ is $L^{1-d/2}$, so that $(\nabla\phi)^2$ has dimension L^{-d} . In consequence, m^2 has dimension L^{-2} (or Λ^2). Finally, counting the powers, one concludes that the coefficient λ_4 of the interaction term has dimension Λ^{4-d} . This result is relevant in the context of the Renormalization Group, previously mentioned. Under a change of length scale by a factor b , λ_4 is multiplied by b^{4-d} . For $d > 4$, iteration of this procedure reduces progressively this coefficient, showing that the critical exponents are determined by the **free** theory, described by \mathcal{L}_0 . For $d < 4$, the perturbative treatment of the interaction will be reflected in quantities that are written as power series of the parameter $\epsilon = 4 - d$. It can be verified that the exponents of the free theory are mean-field ones: $m^2 \sim t$ indicates that $\beta = 1/2$; the shape of correlation functions in a massive particle theory, $\xi \sim m^{-1}$, results in $\nu = 1/2$; it is also verified that $\mathcal{C}(\mathbf{q}) = (q^2 + m^2)^{-1}$, immediately resulting in $\eta = 0$ and $\gamma = 1$. The other exponents can be obtained by the scaling relations.

Complementary references:

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