Second-Order Phase Transition
In Magnetism Through Mean-field Approach

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March 2025

Abstract

Using the mean-field approach, I will show two way to calculate and model a second-phase transition system from partition function and linking them together with the classical limit and also showing the equivalent between both in Landau theory.

1 Missionary Expected Value:

1.1 Semi-classical approach

An independence particle placed inside a magnetic field $\vec{H}$ will have the single-body Hamiltonian, which is equivalent with the many-body electrons system in the independence particle approximation:

$$\mathcal{H} = -\vec{M} \cdot \vec{H}. \tag{1}$$

Choosing the convention for the magnetic field **H** will be placed along the z axis, the Hamiltonian should be express in the sphere coordinate:

$$\mathcal{H} = -m_z.H = -mH.\cos\theta. \tag{2}$$

Therefore, we can calculate the canonical partition function for an electron:

$$Z = \int e^{-\beta\mathcal{H}} d\Omega. \tag{3}$$

In this equation, the integral over radius r will be neglect since the total moment m is constant for a particle. Therefore:

$$Z = 2\pi \int_0^{\pi} e^{\beta mH\cos\theta} \sin\theta d\theta = 2\pi \int_{-1}^{1} e^{\beta mHx} dx = 4\pi \frac{sinh(\beta mH)}{\beta mH}. \tag{4}$$

In the canonical, the average value of magnetic moment along z m_z axis can be calculated through:

$$\langle m_Z \rangle = \frac{1}{Z} \int m_z e^{\beta H m_z} = \frac{\partial_{\beta H} Z}{Z} \tag{5}$$

$$= -\frac{1}{(\beta H)} + m\coth\beta mH = mL(\beta mH), \tag{6}$$

in which the $L(x)$ is the Langevin function:

$$L(x) = \coth x - \frac{1}{x} \tag{7}$$

The second phase-transition however, come from the idea that the self interaction between the particle inside the system make the magnetic momentum when into two energy minimize states, all up or all down. We will including the mean-field approximation through the total field:

$$H \rightarrow H_{total} = H_{ext} + \Gamma \langle m_z \rangle, \tag{8}$$

with the Γ acting as a phenomenon parameter. These approach will give us the self consistent equation:

$$\langle m_z \rangle = mL(\beta m(H_{ext} + \Gamma \langle m_z \rangle)) \tag{9}$$

The transition can appear without the external field, therefore $H_{ext} \rightarrow 0$ give us:

$$\langle m_z \rangle = mL(\beta m\Gamma \langle m_z \rangle) \tag{10}$$

The second-order phase transition happens when $\langle m_z \rangle \to 0$ at $T \to T_c$, therefore allow us to approximate the Langevin function to the first order of the limit $x \ll 1$:

$$L(x \ll 1) = \frac{1}{x} + \frac{x}{3} + O(x^3) - \frac{1}{x} \approx \frac{x}{3}, \tag{11}$$

give us:

$$\begin{aligned} \langle m_z \rangle =& \frac{m^2 \beta \Gamma \langle m_z \rangle}{3} \\ k_B T_c =& \frac{m^2 \Gamma}{3}, \end{aligned} \tag{12}$$

and when we consider a higher expansion on the Langevin function:

$$\begin{aligned} \langle m_z \rangle \frac{\beta m \Gamma}{m^2} =& \frac{x}{3} - \frac{x^3}{45} \\ \frac{T}{T_c} =& 1 - \frac{x^2}{15} \\ \Rightarrow x =& \pm \sqrt{15 \Gamma k_B m (T_c - T)} = \pm z_0. \end{aligned} \tag{13}$$

This expression give us two states that can happens when the $T < T_c$, we neglect the trivial $\langle m_z \rangle = 0$ in the previous calculation due to the unstable of this point in compare with the stable points z_0. From the Langevin function, we also can derive Curie's law:

$$\begin{aligned} \langle m_z \rangle \approx& \frac{m^2 H}{3 k_B T} \\ \chi_0 =& \frac{N}{V} \lim_{H \to 0} \frac{M_z}{H} = \frac{n_0 m^2}{3 k_B T} \equiv \frac{C}{T} \quad \text{(Q.E.D)} \end{aligned} \tag{14}$$

Curie law is derived in assumption that the spin will not "talk" (interact) to other spins in the system. In contract, we can use the same mean-field approach to derive the Curie-Weiss law:

$$\begin{aligned} \langle m_z \rangle \approx& \frac{m^2 H_{ext}}{3 k_B T} + \frac{m^2 \Gamma \langle m_z \rangle}{3T} = \frac{m^2 H_{ext}}{3 k_B T} + \frac{T_c \langle m_z \rangle}{T} \\ \chi =& \frac{N}{V} \lim_{H_{ext} \to 0} \frac{m^2}{3 k_B T} + \frac{T_c N}{TV} \lim_{H_{ext} \to 0} \frac{\langle m_z \rangle}{H_{ext}} = \chi_0 + \chi \frac{T_c}{T} \\ \Rightarrow \chi =& \frac{\chi_0}{1 - \frac{T_c}{T}} \equiv \frac{C}{T - T_c} \quad \text{(Q.E.D)} \end{aligned} \tag{15}$$

1.2 Quantum Approach

The same approach can be used but the angular momentum along the z direction will be quantized. In this case, it should be best to considering the picture that a whole particle will have the total angular momentum compose of angular momentum $\vec{L}$ and spin $\vec{S}$:

$$\vec{J} = \vec{S} + \vec{L}. \tag{16}$$

The same degeneracy of the angular- and spin-momentum for these momenta give total degeneracy of $2J+1$ for $m_j \in [-J, J]$. In this scenario, we will expressing the interaction between the total momentum J and field H:

$$\mathcal{H} = - \vec{M} \cdot \vec{H} \tag{17}$$

$$\vec{M} = g_J \mu_B \vec{J}, \tag{18}$$

in which g_J is the Landé factor define as[1]:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \tag{19}$$

Partition function is:

$$\begin{aligned} Z_J =& \sum_{m=-J}^{J} e^{\beta g_J \mu_B H m} = e^{-\beta g_J \mu_B H J} + e^{-\beta g_J \mu_B H (J-1)} + ... + e^{\beta g_J \mu_B H J} \\ =& e^{-\beta g_J \mu_B H J} (1 + e^{\beta g_J \mu_B H} + e^{2 \beta g_J \mu_B H} + ... + e^{2 \beta g_J \mu_B H J}) \\ =& e^{-\beta g_J \mu_B H J} \frac{1 - e^{\beta g_J \mu_B H (2J+1)}}{1 - e^{\beta g_J \mu_B H}} = \frac{e^{-\beta g_J \mu_B H J} - e^{\beta g_J \mu_B H (J+1)}}{1 - e^{\beta g_J \mu_B H}} \\ =& \frac{e^{-\beta g_J \mu_B H (J+1/2)} - e^{\beta g_J \mu_B H (J+1/2)}}{e^{-\beta g_J \mu_B H/2} - e^{\beta g_J \mu_B H/2}} = \frac{\sinh(\beta g_J \mu_B H (J+1/2))}{\sinh(\beta g_J \mu_B H/2)} \end{aligned} \tag{20}$$

[1]The definition above actually a pretty good approximation, the full expression can be derived from the perturbation theory

From this generalize partition function, we can recover the familiar partition function for the electron case $J = S = \frac{1}{2}$:

$$Z_{1/2} = \frac{\sinh\left(g_{1/2}\beta\mu_B H\right)}{\sinh\left(g_{1/2}\beta\mu_B H/2\right)} = \frac{2\sinh\left(g_{1/2}\beta\mu_B H/2\right)\cosh\left(g_{1/2}\beta\mu_B H/2\right)}{\sinh\left(g_{1/2}\beta\mu_B H/2\right)} = 2\cosh\left(\frac{g_{1/2}\beta\mu_B H}{2}\right) \tag{21}$$

Which in turn give us the expected value both generalize and spin 1/2 case:

$$\begin{aligned}\langle J_z\rangle =& \frac{1}{Z}\sum_{m=-J}^{J} m e^{g_J\mu_B H m} = \frac{1}{Z g_J\mu_B H}\frac{\partial Z}{\partial\beta} \\ =& \left(J+\frac{1}{2}\right)\coth\left(\beta g_J\mu_B H\left(J+\frac{1}{2}\right)\right) - \frac{1}{2}\coth\left(\frac{\beta g_J\mu_B H}{2}\right) \\ =& J\left[\left(1+\frac{1}{2J}\right)\coth\left(y\left(1+\frac{1}{2J}\right)\right) - \frac{1}{2J}\coth\left(\frac{y}{2J}\right)\right] = JB_J(y), \qquad y = \beta g_J\mu_B HJ\end{aligned} \tag{22}$$

in which $B_J(y)$ is the Brillouin function, which defined as:

$$B_J(y) = \left(1+\frac{1}{2J}\right)\coth\left(y\left(1+\frac{1}{2J}\right)\right) - \frac{1}{2J}\coth\frac{y}{2J} \tag{23}$$

As shown in Fig. 1, the Brillouin's function $B_J(x)$will converge to Langevin's $L(x)$ function as $J \to \infty$.

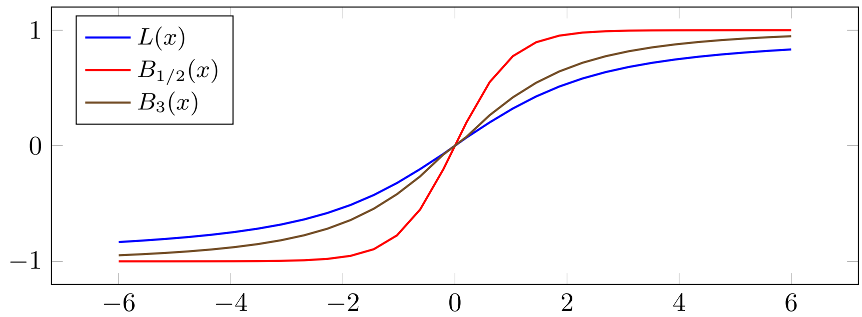

Figure 1: Brillouin's and Langevin's functions on the same graph

Proof.

$$\begin{aligned}B_J(y) =& \left(1+\frac{1}{2J}\right)\coth\left(y\left(1+\frac{1}{2J}\right)\right) - \frac{1}{2J}\coth\frac{y}{2J} \\ \xrightarrow{J\to\infty}& \coth(y) - \lim_{J\to\infty}\frac{1}{2J}\left(\frac{2J}{y}+\frac{y}{2J}+...\right) = \coth(y) - \frac{1}{y} = L(y).\end{aligned}$$

Therefore, at classical limit $J \to \infty, B_J(y) \to L(y)$ □

For the electron $S = 1/2$, we recover the usual relation:

$$\begin{aligned}B_{1/2}(y) = 2\coth(2y) - \coth(y) = \frac{1+\tanh^2(y)}{\tanh(y)} - \frac{1}{\tanh(y)} = tanh(y) \\ \langle J_z\rangle = JB_J(\beta g_J\mu_B H/2J) = \frac{1}{2}\tanh\left(\beta g_{1/2}\mu_B H\right)\end{aligned}$$

The phase transition relation can be achieved by using the mean-field approach for the total field H, through the self-consistence equation:

$$\langle M_z\rangle = g_J\mu_B JB_J(\beta g_{1/2}\mu_B\left(H_{ext}+\Gamma\langle M_z\rangle\right)) \xrightarrow{H_{ext}} g_J\mu_B JB_J(\beta g_{1/2}\mu_B\Gamma\langle M_z\rangle) \tag{24}$$

At the transition point $\langle M_z\rangle \to 0$, we can approximate the $B_\nu(y) \approx \frac{y}{3}\frac{J+1}{J}$:

$$\begin{aligned}\langle M_z\rangle =& g_J\mu_B J\beta g_J\mu_B J\frac{H_{ext}+\Gamma\langle M_z\rangle}{3}\frac{J+1}{J} \\ \xrightarrow{H_{ext}\to 0} k_B T_c =& (g_J\mu_B)^2 J\frac{J+1}{3}\Gamma\end{aligned} \tag{25}$$

The J^2 term in the equation give the idea of corresponding with the m^2 term in semi-classical ansatz, in which $J^2 \gg J$. Which the same proceed, Curie's law and Curie-Weiss's law can easily computed without and with mean-field approach, respectively:

$$\begin{aligned}
\chi_0 &= \frac{N}{V} \lim_{H_{ext}\to 0} \frac{\langle M_z \rangle}{H_{ext}} = n \frac{g_J^2 \mu_B^2}{3k_B T} \frac{J+1}{J} = \frac{C}{T} \qquad \text{(Q.E.D)} \\
\chi &= \frac{N}{V} \lim_{H_{ext}\to 0} \frac{\langle M_z \rangle}{H_{ext}} = \chi_0 + \frac{T_c}{T}\chi \\
\Rightarrow \chi(T) &= \frac{\chi_0}{T - T_c} \qquad \text{(Q.E.D)}
\end{aligned}$$

2 Free Energy Ansatz:

2.1 The Idea:

Landau theory place a key role in describe the phase transition of the system, by writing the free energy of the system in term of order parameter η (the physical value depend on the system that will drop to and remains at 0 as $T > T_c$). We will skip some argument about the symmetry of the system to arrive with the final expression:

$$F = F_0 + \alpha(T - T_c)\eta^2 + b(T_c)\eta^4 - h\eta, \quad (\alpha, b > 0) \tag{26}$$

For the magnetism system, the wise value to be choose as the order parameter will be the component of magnetism of the system (in this case is the $\langle m_z \rangle$).

2.2 The Missionary One:

Start from the partition function of the semi-classical case, we have the free energy of the homogeneous system:

$$\begin{aligned}
F &= -k_b T \ln Z + \frac{\vec{H}\vec{M}}{2} \\
&= -k_B T \ln\left(\frac{1}{x}\sinh x\right) + \frac{H\langle M_z \rangle}{2}, \quad x = \beta m H \\
&= -k_B T\left(\frac{x^2}{6} - \frac{x^4}{180}\right) + \frac{1}{2}H\langle M_z \rangle
\end{aligned} \tag{27}$$

Again, we use the mean-field to modify the total field $H \to H_{ext} + \Gamma\langle M_z \rangle$. A little arrange and we will have:

$$\begin{aligned}
F &= -k_B T\frac{(\beta m H)^2}{6} + \frac{1}{2}H\langle M_z \rangle + \frac{k_B T}{180}(\beta m H)^4 \\
&= -\frac{1}{6k_B T}(m(H_{ext} + \Gamma\langle M_z \rangle))^2 + \frac{1}{2}(H_{ext} + \Gamma\langle M_z \rangle)\langle M_z \rangle + \frac{m^4}{180k_b^3 T^3}H^4 \\
&\approx \frac{1}{2}\langle M_z \rangle^2\left(\Gamma - \frac{m^2}{3k_B T}\Gamma^2\right) + \frac{m^4\Gamma^4}{180k_b^3 T_c^3}\langle M_z \rangle^4 + \langle M_z \rangle\left(\frac{1}{2} - \frac{m^2\Gamma}{3k_B T}\right)H_{ext}
\end{aligned} \tag{28}$$

$$\tag{29}$$

According to Landau's theory's equation (27), we define and rearrange:

$$F = F_0 + \alpha(T - T_c)\langle M_z \rangle^2 + b(T_c)\langle M_z \rangle^4 + h\langle M_z \rangle \tag{30}$$

in which,

$$k_B T_c = \frac{m^2\Gamma}{3}, \quad \alpha = \frac{\Gamma}{2T_c}, \quad b = \frac{m^2\Gamma^3}{60k_b^2 T_c^2}, \quad h = \frac{H_{ext}}{2} \tag{31}$$

The self-consistence equation can be recovered through the derivative of the Free energy according to Landau's theory's idea of the minimum of the potential at the limit $H_{ext} = 0$:

$$\begin{aligned}
\frac{\partial F}{\partial\langle M_z \rangle} &= \frac{\Gamma(T - T_c)}{T_c}\langle M_z \rangle + \frac{m^2\Gamma^3}{15k_B^2 T_c^2}\langle M_z \rangle^3 = 0 \\
\frac{T}{T_c} &= 1 - \frac{m^2\Gamma^2\beta^2}{15}\langle M_z \rangle^2 = 1 - \frac{x^2}{15}
\end{aligned} \tag{32}$$

2.3 The Other One:

In the quantum ansatz, as we have discuss:

$$
\begin{aligned}
F = -k_BT\ln Z + \frac{\vec{H}\vec{M}}{2} &= -k_BT\ln\frac{\sinh\left(x\left(J+\frac{1}{2}\right)\right)}{\sinh\left(\frac{x}{2}\right)} + \frac{\vec{H}\vec{M}}{2} \\
&= -k_BT\left(\ln(2J+1) + \frac{J(J+1)}{6}x^2 - \frac{J(2J^3+4J^2+3J+1)}{360}x^4\right) + \frac{x^2}{2\Gamma(\beta g_J\mu_B)^2}.
\end{aligned} \tag{33}
$$

In this scenario, since I am really lazyyyyyy!, I will treat and choose $x = \beta g_J\mu_B\Gamma\langle M_z\rangle$ as the order parameter, they still the same, just difference by some constant. What we want to focus in here is the numeric factor:

$$
\begin{aligned}
F =& F_0 + \left(\frac{1}{\Gamma g_J^2\mu_B^2\beta^2} - \frac{J(J+1)}{3\beta}\right)\frac{x^2}{2} - \frac{J(2J^3+4J^2+3J+1)}{360\beta}x^4 \\
=& F_0 + \left(\frac{3-\beta\Gamma g_J^2\mu_B^2 J(J+1)}{3\Gamma g_J^2\mu_B^2\beta^2}\right)\frac{x^2}{2} - \frac{J(2J^3+4J^2+3J+1)}{360\beta}x^4.
\end{aligned}
$$

Compare with the Landau equation (27), we can easily see the critical point:

$$
k_BT_c = \frac{J(J+1)\Gamma}{3}(g_J^2\mu_B^2), \tag{34}
$$

which give us:

$$
F = k_B^2T_c(T-T_c)\frac{x^2}{2} - \frac{J(2J^3+4J^2+3J+1)}{360\beta}x^4 + hx \tag{35}
$$

The x^4 term can be easily deal when take the classical limit to gain:

$$
\frac{J(2J^3+4J^2+3J+1)}{360\beta}x^4 \xrightarrow{J\to\infty} \frac{J^4x^4}{180}.
$$

And we can treat it as in the semi-classical case. And again, I'm very lazy to normal exact the term h in x representation, but it will be it, still there and have a minus sign $h < 0$.

3 Conclusion

As we have discussed above, two way of calculating the order parameter in the canonical ensemble have been proof to be equivalent. The expression of Landau theory is an interesting example for the application in real problem.