Chapter 8

Magnetism

We begin by considering a system of N magnetic dipoles, each with a magnetic dipole moment μ. Let's further assume that these are spin $\frac{1}{2}$ dipoles so that there are two energy states for them, which we will denote as *up* and *down*. The multiplicity for having $n_\uparrow$ up magnetic dipoles and $n_\downarrow$ down magnetic dipoles out of a total of N magnetic dipoles is

$$\Omega = \frac{N!}{n_\uparrow! n_\downarrow!}$$

We can also express this multiplicity as

$$N = n_\uparrow + n_\downarrow \quad \rightarrow \quad \Omega = \frac{N!}{n_\uparrow!\,(N - n_\uparrow)!}$$

This expression is identical to Equation 3.1 if we define $n = n_\uparrow$. This makes sense, of course, as both systems are binary - up/down vs heads/tails.

In the presence of an external magnetic field B, there are two equilibrium energy states for a magnetic dipole. In one of these states the dipole is aligned with the magnetic field and in the other the dipole is aligned opposite the magnetic field[1]. We can express the energies of these two equilibrium states as

$$\epsilon = -\vec{\mu} \cdot \vec{B} \quad \rightarrow \quad \epsilon = \pm \mu B$$

The negative sign occurs when μ and B are parallel and the positive sign occurs when μ and B are anti-parallel. The partition function associated with these energy states is determined using Equation 3.16.

$$Z = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)} \quad \rightarrow \quad Z = e^{\beta \mu B} + e^{-\beta \mu B}$$

The partition function for a system of N distinguishable magnetic dipoles is therefore given by Equation 8.1.

$$Z = \left[e^{\beta \mu B} + e^{-\beta \mu B}\right]^N = 2\cosh^N (\beta \mu B) \tag{8.1}$$

[1]Other orientations are possible when the dipole is not in equilibrium, but when in those orientations a net torque will be exerted on the dipole moving it toward equilibrium.

8.1 Magnetic Properties

As discussed in Chapter 5, the Helmholtz Free Energy is

$$F = E - TS \quad \rightarrow \quad dF = dE - TdS - SdT$$

Since the magnetization (M) and magnetic field (B) are a conjugate pair, we can express the 1$^{\text{st}}$ law of thermodynamics for a magnetic system as

$$dE = TdS - MdB$$

Substitution then gives us

$$dF = (TdS - MdB) - TdS - SdT \quad \rightarrow \quad dF = -MdB - SdT$$

Thus,

$$M = -\left(\frac{\partial F}{\partial B}\right)_T \tag{8.2}$$

The magnetic susceptibility, denoted by χ denotes the dependence of the magnetization on the external magnetic field.

$$\chi = \frac{1}{V}\frac{\partial M}{\partial B} \tag{8.3}$$

As implied by the name, the magnetic susceptibility reflects how susceptible a system is to being magnetized (*i.e.*, how easily the system will develop magnetization).

8.2 Paramagnetism

We can calculate the magnetization of the system of magnetic dipole described above using Equation 8.1 and Equation 8.2. We begin by determining the Helmholtz Free Energy for the system.

$$F = -k_B T \ln\left(2\cosh^N(\beta\mu B)\right) \quad \rightarrow \quad F = -Nk_B T \ln(2\cosh(\beta\mu B))$$

The magnetization is thus

$$M = -\left(\frac{\partial}{\partial B}\right)_T [-Nk_B T \ln(2\cosh(\beta\mu B))]$$

$$M = Nk_B T\left(\frac{2\sinh(\beta\mu B)}{2\cosh(\beta\mu B)}(\beta\mu)\right)$$

$$M = N\mu\tanh(\beta\mu B)$$

The magnetization of the system is zero when the external magnetic field is zero, but non-zero when an external magnetic field is applied. This is referred to as *paramagnetism*.

We can also define paramagnetism to be the induction of a net magnetic dipole moment in the system by an external magnetic field. To explore this description, let's denote the state where μ is parallel to B as the positive orientation for the dipole and the state where μ is antiparallel to B as the negative orientation. With this definition, the average dipole moment for any individual magnetic dipole can be written in terms of the probability that those states are occupied.

$$\overline{\mu} = \mu p\left(\mu\right) + \left(-\mu\right) p\left(-\mu\right)$$

These probabilities can, of course, be written in terms of the associated Boltzmann factors.

$$\overline{\mu} = \mu\left(\frac{e^{\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}\right) + \left(-\mu\right)\left(\frac{e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}\right)$$

$$\overline{\mu} = \frac{\mu e^{\beta\mu B} + \left(-\mu\right) e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}} \quad \rightarrow \quad \overline{\mu} = \mu\left(\frac{e^{\beta\mu B} - e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}\right)$$

$$\overline{\mu} = \mu \tanh\left(\beta\mu B\right)$$

If $B = 0$, $\overline{\mu} = 0$ and there is no net dipole moment for the system. This occurs because there is an equal probability of the individual dipole moments being aligned in either of the two possible directions. However, if $B = \infty$, $\overline{\mu} = \mu$, indicating that all dipole moments are aligned in the same direction. Similarly results occur when $\beta = 0$ or when $\beta = \infty$ for the same reasons.

We can calculate the magnetic susceptibility using Equation 8.3

$$\chi = \frac{1}{V}\frac{\partial}{\partial B}\left(N\mu \tanh\left(\beta\mu B\right)\right) \quad \rightarrow \quad \chi = \frac{N\beta\mu^2}{V}\text{sech}^2\left(\beta\mu B\right)$$

This expression, $\chi \approx \frac{1}{T}$, is known as Curie's Law, which was empirically derived. The fact that it can be derived from the assumptions of this model suggest that this model may be capturing a good deal of the underlying physics.

Heat Capacity

The mean energy of this system of magnetic dipoles is

$$\overline{E} = -N\overline{\mu}B = -NB\mu \tanh\left(\beta\mu B\right)$$

The heat capacity at constant magnetic field is thus

$$C_B = \left(\frac{\partial \overline{E}}{\partial T}\right)_B = -k_B\beta^2\left(\frac{\partial \overline{E}}{\partial \beta}\right)_B$$

$$C_B = -k_B \beta^2 \left(\frac{\partial}{\partial \beta}\right)_B \left(-NB\mu \tanh\left(\beta\mu B\right)\right)$$

$$C_B = Nk_B \left(\beta B\mu\right)^2 \operatorname{sech}^2\left(\beta\mu B\right)$$

The heat capacity of the system approaches zero at both high temperatures and low temperatures.

8.3 Ferromagnetism

In the previous section we characterized how an external magnetic field will affect the properties of a system of magnetic dipoles. Let's now consider how the magnetic field of the magnetic dipoles themselves contributes to those observed effects. Specifically, let's now assume B that is proportional to M

$$B = \lambda M$$

The parameter λ denotes physical properties of the material exhibiting this behavior. Substitution into the previously derived equation for the magnetization then yields

$$M = N\mu \tanh\left(\beta\mu\lambda M\right)$$

This is a transcendental equation. Let's move forward with finding a solution by defining a new variable $x = \beta\mu\lambda M$, which reflects both the temperature and the magnetization.

$$x = \beta\mu\lambda M \quad \rightarrow \quad \frac{x}{\beta\mu\lambda} = N\mu \tanh\left(x\right) \quad \rightarrow \quad x\left(\frac{1}{N\beta\mu^2\lambda}\right) = \tanh\left(x\right)$$

$$x\left(\frac{k_B T}{N\mu^2\lambda}\right) = \tanh\left(x\right)$$

We now define a *critical* temperature for the system, known as the Curie Temperature[2] and denoted by the variable T_C.

$$T_C = \frac{\mu^2\lambda N}{k_B} \quad \rightarrow \quad x\left(\frac{T}{T_C}\right) = \tanh\left(x\right)$$

Time for a series expansion of tanh.

$$x\left(\tfrac{T}{T_C}\right) = x - \tfrac{1}{3}x^3 + \tfrac{2}{15}x^5 - \tfrac{17}{315}x^7 + \cdots$$

[2]Curie is just as cool as Einstein and Debye.

This equation will have a solution as long as $T < T_C$. There is thus spontaneous magnetization ($M \neq 0$) for temperatures below the Curie temperature, but not for temperatures above the Curie temperature. This spontaneous magnetization is referred to as *ferromagnetism*.

When $T > T_C$, an external magnetic field must be applied to obtain nonzero magnetization.

$$M = N\mu \tanh\left[\beta\mu\left(\lambda M + B\right)\right]$$

When the external magnetic field is weak or when the temperature of the system is high, this equation can be approximated as

$$M = N\mu\left[\beta\mu\left(\lambda M + B\right)\right] \quad \rightarrow \quad M = N\beta\mu^2\left(\lambda M + B\right)$$

$$M\left(1 - N\beta\lambda\mu^2\right) = B \quad \rightarrow \quad M = \frac{B}{1 - N\beta\lambda\mu^2}$$

We can rewrite this expression in terms of the Curie Temperature.

$$M = \frac{B}{1 - \frac{N\lambda\mu^2}{k_B T}} \quad \rightarrow \quad M = \frac{B}{1 - \frac{T_C}{T}}$$

Solving for the magnetic susceptibility using Equation 8.3 then yields

$$\chi = \frac{1}{V}\frac{\partial}{\partial B}\left(\frac{B}{1 - \frac{T_C}{T}}\right) \quad \rightarrow \quad \chi = \frac{1}{V}\left(\frac{1}{1 - \frac{T_C}{T}}\right)$$

Phase Transitions

Since this system of spins has a fixed volume, the Gibbs free energy is equal to the Helmholtz free energy. Therefore, the Gibbs free energy per particle is

$$g = \frac{G}{N} = \frac{F}{N}$$

Derivatives of g are equivalent to derivatives of F. Thus, the magnetization and magnetic susceptibility can be expressed as

$$M = -\left(\frac{\partial F}{\partial B}\right)_T = -\frac{1}{N}\left(\frac{\partial g}{\partial B}\right)_T$$

$$\chi = \frac{1}{V}\left(\frac{\partial M}{\partial B}\right)_T \quad \rightarrow \quad \chi = -\frac{1}{NV}\left(\frac{\partial^2 g}{\partial B^2}\right)_T$$

The magnetization is therefore the first order parameter for the system and the magnetic susceptibility is the second order parameter for the system. The magnetization of the ferromagnetic system was determined by solving the transcendential equation

$$M = N\mu \tanh\left[\beta\mu\left(\lambda M + B\right)\right]$$

The magnetization is zero for all temperatures above T_C and non-zero for all temperatures below T_C. The magnetization also continuously approaches zero as the temperature is lowered to T_C from higher temperatures. Since the magnetization is discontinuous for the transition from paramagnetism to ferromagnetism (*i.e.*, for the transition of temperature from above T_C to below T_C), the phase transition from paramagnetism to ferromagnetism is not a first order phase transition.

There is, of course, a discontinuity in the expression for the magnetic susceptibility at high temperatures or weak external magnetic fields. Therefore, the transition from paramagnetism to ferromagnetism (*i.e.*, for the transition of temperature from above T_C to below T_C) is a second order phase transition.

8.4 1-D Ising Model

Let's now consider a 1 dimensional chain of N magnetic dipoles. Let's further assume that each magnetic dipole has spin $\frac{1}{2}$ (*i.e.*, each magnetic dipole can assume only two orientations) and that each magnetic dipole moment can interact with nearest-neighbor magnetic dipole moments. The energy for this system would then be

$$E = -\epsilon \sum_{k=1}^{N} s_k s_{k+1} - \mu B \sum_{k=1}^{N} s_k$$

The variable ϵ in this equation denotes the energy associated with the interaction between nearest-neighbor magnetic dipole moments, the variable s_k denotes the orientation of the k^{th} magnetic dipole moment, and the variable B denotes the magnitude of an external magnetic field applied to this system. We will use ± 1 as the values for s_k to denote the two different possible orientations of each magnetic dipole moment. Let's next apply a boundary condition by assuming the two ends of the chain are connected to one another.

$$s_{N+1} = s_1$$

The partition function of this system can then be calculated by summing all possible orientations for all magnetic dipoles in the system.

$$Z = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} e^{\beta \sum\limits_{k=1}^{N} (\epsilon s_k s_{k+1} + \mu B s_k)}$$

We can rewrite this equation using the system's boundary condition.

$$Z = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} e^{\beta \sum\limits_{k=1}^{N} \left(\epsilon s_k s_{k+1} + \frac{1}{2} \mu B (s_k + s_{k+1})\right)}$$

Let's now define a matrix P as follows

$$P = \begin{bmatrix} e^{\beta(\epsilon+\mu B)} & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & e^{\beta(\epsilon-\mu B)} \end{bmatrix}$$

We see that the matrix elements of the matrix P with the different magnetic dipole orientations are

$$\langle +1| P |+1\rangle = e^{\beta(\epsilon+\mu B)}$$
$$\langle -1| P |-1\rangle = e^{\beta(\epsilon-\mu B)}$$
$$\langle +1| P |-1\rangle = \langle -1| P |+1\rangle = e^{-\beta\epsilon}$$

Thus,

$$\langle s| P |s'\rangle = e^{\beta\left(\epsilon s s' + \frac{1}{2}\mu B\left(s+s'\right)\right)}$$

This allows us to write the sum over k in the partition function for the system as a product of matrix elements.

$$Z = \sum_{s_1}\sum_{s_2}\cdots\sum_{s_N} \langle s_1| P |s_2\rangle \langle s_2| P |s_3\rangle \cdots \langle s_N| P |s_1\rangle$$

$$Z = \sum_{s_1} \langle s_1| P^N |s_1\rangle = \mathrm{Tr} P^N = \lambda_1^N + \lambda_2^N$$

Where λ_1 and λ_2 are the eigenvalues of the matrix P.

$$\lambda_1 = e^{\beta\epsilon}\left[\cosh\left(\beta\mu B\right) + \sqrt{\sinh^2\left(\beta\mu B\right) + e^{-4\beta\epsilon}}\right]$$

$$\lambda_2 = e^{\beta\epsilon}\left[\cosh\left(\beta\mu B\right) - \sqrt{\sinh^2\left(\beta\mu B\right) + e^{-4\beta\epsilon}}\right]$$

The partition function for the system is thus

$$\begin{aligned} Z &= e^{N\beta\epsilon}\left[\cosh\left(\beta\mu B\right) + \sqrt{\sinh^2\left(\beta\mu B\right) + e^{-4\beta\epsilon}}\right]^N \\ &+ e^{N\beta\epsilon}\left[\cosh\left(\beta\mu B\right) - \sqrt{\sinh^2\left(\beta\mu B\right) + e^{-4\beta\epsilon}}\right]^N \end{aligned} \tag{8.4}$$

Let's now examine the behavior of this system in different limits. First, since $\lambda_1 > \lambda_2$ for all values of B, as N becomes large, only λ_1 will contribute significantly to the partition function.

$$Z = e^{N\beta\epsilon}\left[\cosh\left(\beta\mu B\right) + \sqrt{\sinh^2\left(\beta\mu B\right) + e^{-4\beta\epsilon}}\right]^N$$

In this limit, the Helmholtz free energy is

$$F = -k_B T \ln \left[e^{N\beta\epsilon} \left[\cosh(\beta\mu B) + \sqrt{\sinh^2(\beta\mu B) + e^{-4\beta\epsilon}} \right]^N \right]$$

$$F = -N k_B T \left(\beta\epsilon + \ln \left[\cosh(\beta\mu B) + \sqrt{\sinh^2(\beta\mu B) + e^{-4\beta\epsilon}} \right] \right)$$

And thus the magnetization is

$$M = -\frac{\partial}{\partial B} \left[-N k_B T \left(\beta\epsilon + \ln \left[\cosh(\beta\mu B) + \sqrt{\sinh^2(\beta\mu B) + e^{-4\beta\epsilon}} \right] \right) \right]$$

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

Since the system has a fixed volume, the Gibbs free energy is equal to the Helmholtz free energy. Therefore, the Gibbs free energy per particle is

$$g = \frac{G}{N} = \frac{F}{N} = -k_B T \left(\beta\epsilon + \ln \left[\cosh(\beta\mu B) + \sqrt{\sinh^2(\beta\mu B) + e^{-4\beta\epsilon}} \right] \right)$$

The first derivative of g with respect to B is

$$\left(\frac{\partial g}{\partial B} \right)_T = -\frac{N \sinh(\beta\mu B)\, \mu}{\sqrt{\sinh^2(\beta\mu B) + e^{-4\beta\epsilon}}}$$

$$\lim_{B \to 0} \left(\frac{\partial g}{\partial B} \right)_T = 0$$

Since this derivative is continuous, there is no first order phase transition in this system.

Let's now examine the behavior of this model in a few limiting cases.

Paramagnetism

If there is no interaction between the spins (*i.e.*, if $\epsilon = 0$, the magnetization of the system is

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

$$M = N\mu \tanh(\beta\mu B)$$

This is identical to the expression we derived previously for a system of N magnetic dipoles.

No External Magnetic Field

If there is no external magnetic field present (*i.e.*, if $B = 0$), the partition function for the system becomes

$$Z = e^{N\beta\epsilon}\left[1+\sqrt{0+e^{-4\beta\epsilon}}\right]^N \quad \rightarrow \quad Z = \left[e^{\beta\epsilon}+e^{-\beta\epsilon}\right]^N$$

$$Z = 2\cosh^N(\beta\epsilon)$$

This is identical to what we derived previously for the paramagnetic system of N magnetic dipole moments that we derived previously if we define $\epsilon = \mu B$. In other words, for the paramagnetic system described earlier, an external magnetic field B defined the energy states for the orientation of the magnetic dipole moments, whereas in the Ising model, it is the interaction energy ϵ that is defining those energy states for the orientations.

The mean energy of this system is

$$\overline{E} = -\frac{\partial}{\partial\beta}\ln\left[2\cosh^N(\beta\epsilon)\right]$$

$$\overline{E} = -N\left[\frac{2\epsilon\sinh(\beta\epsilon)}{2\cosh(\beta\epsilon)}\right] \quad \rightarrow \quad \overline{E} = -N\epsilon\tanh(\beta\epsilon)$$

This result is also identical to our previous derivation with the definition $\epsilon = \mu B$. Since the system has a fixed volume, the Gibbs free energy is equal to the Helmholtz free energy and, thus, the Gibbs free energy per particle is

$$g = \frac{G}{N} = \frac{F}{N} = -k_B T\ln(2\cosh(\beta\epsilon))$$

Since the mean energy is proportional to the first derivative of Gibbs free energy and is also continuous, there is no first order phase transition in this system. The heat capacity of the system can be calculated from this mean energy.

$$C_V = -k_B\beta^2\frac{d}{d\beta}\left[-N\epsilon\tanh(\beta\epsilon)\right] \quad \rightarrow \quad C_V = k_B\beta^2 N\epsilon\,\text{sech}^2(\beta\epsilon)\,\epsilon$$

$$C_V = Nk_B(\beta\epsilon)^2\,\text{sech}^2(\beta\epsilon)$$

Since the heat capacity is proportional to the second derivative of Gibbs free energy and is also continuous, there is no second order phase transition in this system.

8.5 Negative Temperature

Let's now return to our system of N magnetic dipole moments in an external magnetic field. The entropy of this system can be determined from the system's multiplicity using Equation 5.13.

$$S = k_B \ln\left(\frac{N!}{n_\uparrow!\,(N-n_\uparrow!)!}\right)$$

$$S = k_B\left[N\ln N - n_\uparrow \ln n_\uparrow - (N-n_\uparrow)\ln(N-n_\uparrow)\right]$$

The energy of the system is

$$E(n_\uparrow) = n_\uparrow(-\mu B) + (N-n_\uparrow)(\mu B) \quad \rightarrow \quad E(n_\uparrow) = (N-2n_\uparrow)\,\mu B$$

We can determine the parameter β for the system from the dependence of the entropy on the energy of the system.

$$\beta = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n_\uparrow}\frac{\partial n_\uparrow}{\partial E}$$

Substitution gives us

$$\beta = \left(-\ln n_\uparrow - n_\uparrow\frac{1}{n_\uparrow} + \ln(N-n_\uparrow) - (N-n_\uparrow)\left(\frac{-1}{N-n_\uparrow}\right)\right)\left(-\frac{1}{2\mu B}\right)$$

$$\beta = -\frac{k_B}{2\mu B}\ln\left(\frac{N-n_\uparrow}{n_\uparrow}\right) \quad \rightarrow \quad \beta = \frac{k_B}{2\mu B}\ln\left(\frac{n_\uparrow}{N-n_\uparrow}\right)$$

We see from this expression that $\beta > 0$ when $n_\uparrow > \frac{N}{2}$ and $\beta < 0$ when $n_\uparrow < \frac{N}{2}$. This system will therefore have a negative temperature when more than half of the dipoles are anti-parallel with the external magnetic field. The region of negative temperature thus corresponds to the region where the system has its highest energy. To make things even more amusing, the system has an infinite temperature when $n_\uparrow = \frac{N}{2}$ and since the energy of the system is lower when $n_\uparrow = \frac{N}{2}$ than when $n_\uparrow < \frac{N}{2}$, negative temperature is *hotter* than infinite temperature.

Negative temperature occurs whenever you have a system whose entropy has bounds at the limit of high energy and the limit of low energy. A good example of this is the system of magnetic dipoles discussed above or a system of coin flips. Another example occurs within lasers. Consider a two state system with discrete energy states E_1 and E_2 with $E_2 > E_1$ that contains N particles. The maximum entropy of this system occurs when both energy states contain $\frac{N}{2}$ particles. Increasing the number of particles in the E_2 state (*i.e.*, moving more particles from the E_1 state to the E_2 state) from this point of balanced population will result in an increase in the energy of the system and a decrease in the entropy of the system. Thus, the condition of *population inversion*, where more particles are in the E_2 state than the E_1 state, corresponds to a negative temperature for the system.

We can also think about negative temperature in terms of the Boltzmann factors for the two different energy states in the system. The ratio of the number of particles in each state (N_2 for energy state E_2 and N_1 for energy state E_1) is

$$\frac{N_2}{N_1} = e^{-\beta(E_2 - E_1)} \quad \rightarrow \quad \frac{N_2}{N_1} = e^{\frac{E_1 - E_2}{k_B T}}$$

Since $E_2 > E_1$, a situation where $N_2 > N_1$ would correspond to a negative value for T. A system with a negative temperature is therefore a system that is not in its most thermodynamically favorable state and therefore will give off energy to transition to a more favorable state. This is why we argue that negative temperatures are hotter than positive (and even infinite) temperatures.