

Lecture 05: Free Energy and Order Parameters

In these notes we define the Helmholtz free energy using the second law of thermodynamics, and we use the free energy to understand why some systems appear more ordered than the second law of thermodynamics seemingly allows. Finally, we use a quantitative definition of free energy to study the a simple model of magnetism.

1 The excessiveness of the 2nd law

The second law of thermodynamics states that the entropy of the universe (or any isolated system) always increases in time, until that entropy reaches a constant value. When the entropy of such a system has reached a constant value, we say that the system is in **thermal equilibrium**. The second law applies to the universe at large, however, in physics, we are rarely ever interested in the *entire* universe¹. Rather, we are often just interested in a small part of the universe, a part much smaller than the surroundings representing everything else.

More specifically, in physics we often divide the universe into a **system** containing all the the parts of the universe we are trying to understand and a **surroundings** containing all the parts outside this system. We can alternatively assume that the system and the surroundings exchange matter and energy or just energy², but the two of them together define the proverbial universe. See Fig. 1.

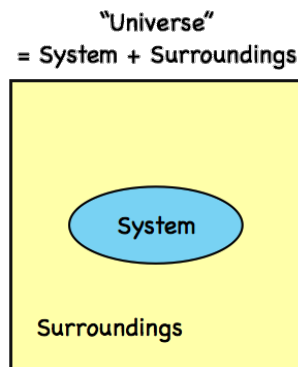


Figure 1: In physics, we are often interested in a specific system, and everything in the universe outside this system defines the surroundings. The term "universe" is also a catchall term for an "isolated" system, one that is separated, with regard to matter and energy transfer, from everything that exists outside of it.

Often the sizes of the two are quite different. For example, if a room defined our system of interest, then everything in the universe outside this room would define the surroundings. Now, the second law of thermodynamics applies to the universe (i.e., the system + surroundings) as a whole, but it does not manifestly say anything about the system alone. Therefore, although we can take the fact that the entropy of the universe increases until it reaches thermal equilibrium as a fundamental principle of physics, it is often somewhat excessive when the only thing that interests us are the gas particles in a room. Therefore, it would be much better if we could find some proxy for "entropy of the universe" which allows us to analyze the microstate and macrostate properties of systems much smaller than the universe. Achieving this objective will be the purpose of these notes.

¹I'm ignoring cosmology and much of late 20th and early 21st century physics here.

²At a classical level there is a distinction between the two.

Framing Question

How can we use the second law of thermodynamics to constrain the properties of a system without taking into account the entropy of the entire universe?

2 Helmholtz Free Energy

Our objective is to use the second law of thermodynamics to constrain the properties of a system without having to consider the entire universe. By the second law, the entropy of the universe increases in time until it reaches a constant value. If we let the entropy change of the universe be ΔS_{univ} , we can divide this entropy change into two parts: the entropy change of the system ΔS_{sys} , and the entropy change of the surroundings ΔS_{surr} :

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}. \quad (1)$$

Let us consider a situation in which the system and the surroundings can exchange energy but not particles (i.e., the system is **closed**, but not **isolated**) and in which surroundings exist at the temperature T . We are interested in the unconstrained evolution of the system, a case in which the surroundings do no work on the system and the system does no work on the surroundings.

For a system which is evolving freely, the reason we would observe an increase in the entropy of the surroundings is that a heat ΔQ_{exits} leaves the system and enters the surroundings. By Clausius's definition of entropy, the entropy of the surroundings must therefore increase by

$$\Delta S_{\text{surr}} = \frac{\Delta Q_{\text{exits}}}{T}, \quad (2)$$

where T is the temperature of the surroundings. By conservation of energy, we know that the energy change of a system is given by $\Delta E_{\text{sys}} = \Delta W_{\text{on sys}} - \Delta Q_{\text{exits}}$. If we are considering the case in which no work is done on the system (i.e., we have unconstrained evolution of the system), then $\Delta W_{\text{on sys}} = 0$, and

$$\Delta E_{\text{sys}} = -\Delta Q_{\text{exits}} \quad [\text{For } \Delta W_{\text{on sys}} = 0]. \quad (3)$$

Inserting Eq.(3) into Eq.(2), we find

$$\Delta S_{\text{surr}} = -\frac{\Delta E_{\text{sys}}}{T}. \quad (4)$$

Finally, inserting Eq.(4) into Eq.(1), we find

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta E_{\text{sys}}}{T}, \quad (5)$$

or, multiplying through by T ,

$$T\Delta S_{\text{univ}} = -\Delta F_{\text{sys}}, \quad (6)$$

where we defined F_{sys} as

$$\boxed{F_{\text{sys}} = E_{\text{sys}} - TS_{\text{sys}}} \quad [\text{Helmholtz Free Energy}] \quad (7)$$

Eq.(7) is termed the **Helmholtz³ free energy** of the system. From Eq.(6), we see that when the entropy of the universe increases, the Helmholtz free energy of our system decreases. Therefore, if the second law of thermodynamics asserts that the entropy of the universe (or any isolated system) increases until ther-

³You might be more familiar with the Gibbs free energy associated with chemical reactions. The two quantities both represent free energies but are applied in different circumstances. For gaseous systems, we apply the Helmholtz free energy when the *volume* of our system can be held fixed, and we apply the Gibbs free energy when the *pressure* can be held fixed.

mal equilibrium is reached, then Eq.(6) tells us that the free energy of our system decreases until thermal equilibrium is reached.

In other words, when the entropy of the universe reaches a *local maximum*, then the system and surroundings are in thermal equilibrium. At the same time, Eq.(6) indicates that when the free energy of the system reaches a *local minimum*, then the system and surroundings are in thermal equilibrium.

This point is so important it deserves to be repeated:

Relationship between $F_{\text{sys.}}$ and $S_{\text{univ.}}$: As the universe (or any isolated system consisting of a subsystem and its surroundings) works to maximize entropy $S_{\text{univ.}}$, any closed subsystem at constant temperature, works to minimize free energy $F_{\text{sys.}}$.

Thus the free energy is the quantity we are looking for: It is written in terms of system dependent quantities (namely the system energy and the system entropy), and by seeking the local minimum of the free energy for closed systems, we can use the free energy to determine the properties of a system in thermal equilibrium with its surroundings.

But it is important to remember that the Helmholtz free energy is applied to closed systems, while the second law of thermodynamics considers the entropy of isolated systems.

To clarify when we apply entropy maximization and when we apply free energy minimization, it would be worthwhile to distinguish between the various types of systems that can or cannot exchange energy with one another.

3 Open, Closed, or Isolated

When we discuss physical systems in this class we will be primarily concerned with **closed** systems. **Closed systems** are systems that can exchange energy but not matter with their surroundings. A related system is an open system. **Open systems** are systems that can exchange both matter and energy with their surroundings. Finally, **isolated system** can exchange neither matter nor energy with their surroundings. The canonical "isolated system" is our physical universe. We cannot observe anything outside this universe so we assume that said universe does not exchange matter nor energy with anything outside itself.

A picture is useful in understanding and remembering the differences. Consider Fig. 2.

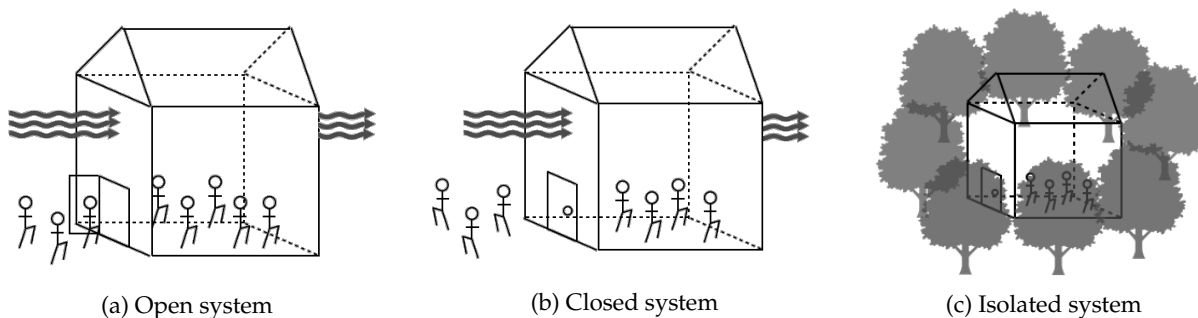


Figure 2: Open, closed, and isolated systems

- An open system is like a house with glass walls and an open door. Light (i.e., energy) can flow into and out of the house and people (i.e., matter) can enter and exit.
- A closed system is like a house with glass walls and a closed door. Light can flow into and out of the house, but people cannot enter or exit.
- An isolated system is like a house in the woods which is completely obscured by trees and has a closed door. Light cannot flow into or out of the house because the trees prevent it, and people cannot enter or exit the house. Our universe is such an isolated system.

With regard to the laws of thermodynamics and our newly formulated concept of free energy, the second law of thermodynamics asserts that the entropy of isolated systems increases in time until that entropy reaches a constant maximum. Our calculation in the previous section (in particular Eq.(6)) shows that the Helmholtz free energy of closed systems contained within those isolated systems decreases in time until that free energy reaches a constant minimum.

The energy of an isolated system is constant because no heat leaves the system and no work can be done on the system to add energy to it. We can always embed a closed or open system inside a larger isolated system in which the energy is conserved. For Fig. 1, the region in yellow is a closed system that exchanges energy with its surroundings, but the entire rectangle (i.e., system+surroundings or the universe) is an isolated system. Therefore, there is an alternative way to express the relationship between free energy and entropy:

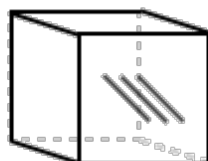
Relationship between $F_{\text{sys.}}$ and $S_{\text{univ.}}$ (alternative): The thermal equilibrium of an isolated system is defined by the maximum of entropy. The thermal equilibrium of a closed system at a constant temperature is defined by the minimum of the free energy.

4 Examples of the relevance of free energy

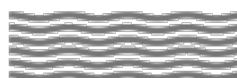
We have found the answer to our framing question. We can analyze the thermal equilibrium of a system without having to take into account the entropic properties of the evolution, by instead analyzing the free energy of the system. Now, let's consider some examples:

- **Ice vs. Water**

Just from looking at it, we can tell that a volume of ice has less entropy than the same volume of water: In water, the molecules of H_2O are constantly in motion and thus require more information to specify their positions than it takes to specify the positions of the molecules that make up ice.



(a) Water as a solid



(b) Water as a liquid

Figure 4: At a low enough temperature (i.e., $T < 0^\circ \text{C}$), the free energy of the solid form of water is less than the free energy of the liquid form of water. Therefore, at these temperatures, water assumes its solid form.

Knowing the second law of thermodynamics, this may appear anomalous, unless we also note that the second law applies to *isolated* systems, and an ice cube of water is not an isolated system. Rather an ice cube constitutes a *closed* system, one that can exchange energy but not matter with its surroundings⁴. The surroundings of the ice cube are at a fixed temperature, and thus by our discussion above, the thermodynamic quantity we are optimizing is the free energy rather than the entropy. More precisely, we are seeking a macrostate for the system that minimizes that free energy.

At cold enough temperatures (i.e., $T < 0^\circ \text{C}$), the free energy of solid water F_{solid} is less than the free energy of liquid water F_{liquid} , so water assumes its solid form at these temperatures:

⁴This is true assuming we are considering a system in which the evaporation of water into water vapor and the sublimation of water vapor into liquid water and ice are not relevant to first order.

$$\text{Water: For } T \text{ sufficiently low, } F_{\text{solid}} < F_{\text{liquid}} \quad (8)$$

- **Paramagnet vs. Ferromagnet**

In metals that can create them⁵, magnetic fields result from the collective alignment of many (on the order of 10^{26}) magnetic dipoles within the solid (Fig. 5a). It is only when these magnetic dipoles are all pointing in the same direction, that a magnetic field is generated. We call materials that generate their own magnetic field, **ferromagnetic**.

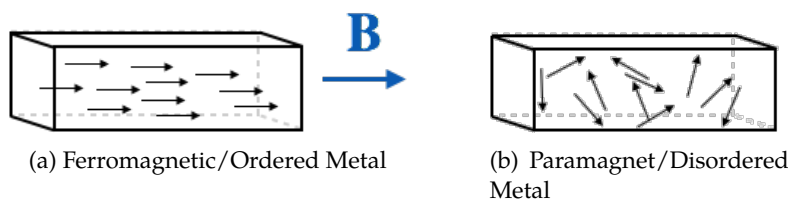


Figure 6: At a low enough temperature (which varies from metal to metal) and for certain metals, the free energy of the ordered form (i.e., ferromagnetic form) of the metal is less than the free energy of the disordered form (i.e., the paramagnetic form) of the metal. Therefore, at these temperatures, the metal is in its ordered or ferromagnetic form. This is the form that gives rise to the magnetic behavior of magnets.

Such states of aligned magnetic dipoles occur in some metals at certain temperatures. However, it is entropically more favorable for these magnetic dipoles to *not* all be pointing in the same direction. That is, when the metal has magnetic dipoles which are not constrained to point in a single direction it has a higher entropy than when these dipoles do point in a single direction. When a metal has dipoles that do not, on their own, point in a single direction, we call that metal **paramagnetic**. Paramagnetic metals can generate magnetic fields, but they require some external magnetic field to first align their magnetic dipoles for them.

A naive application of the second law of thermodynamics would suggest that ordered magnetic dipoles are not possible since they represent lower entropy states. However, the reason this lower entropy state can be adopted is that such a macrostate has overall a lower free energy (again at certain temperatures) than the more disordered macrostate. Thus, for metals that can create them⁶, for sufficiently low temperature, we have $F_{\text{ordered}} < F_{\text{disordered}}$:

$$\text{Magnet: For sufficiently low } T, F_{\text{ordered}} < F_{\text{disordered}} \quad (9)$$

- **Folded vs. Unfolded Protein**

Proteins are manufactured in the cell by continuously joining amino acids together to create a chain of amino acids called a polypeptide. After all necessary amino acids have been added to the chain (and sometimes even beforehand), the chain conforms itself into a specific configuration (Fig. 7a) necessary to perform the function for which it was manufactured.

However, such a specific configuration has a much lower entropy than the a random collection of non-specific interactions (Fig. 7b).

Why does the protein adopt its lower entropy state, when the second law of thermodynamics suggests that systems seek to maximize their entropy? The system adopts the lower entropy conformation because the folding process (i.e., the process in which the chain of amino acids becomes a specific

⁵Whether a metal can create a magnetic dipole has to do with the electron configurations of the atoms that compose it.

⁶See above footnote.

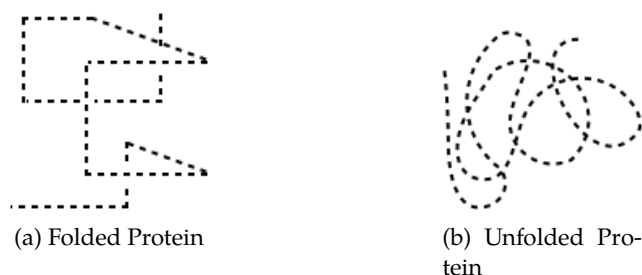


Figure 8: Proteins are composed of ordered sequences of amino acids. After the sequence is assembled (or sometimes during), the sequence folds into a specific protein conformation dictated by its order of amino acids. Such a conformation is referred to as a “folded” protein and this folded protein has less entropy than just a random collection of non-specific interactions.

3D protein) occurs at constant temperature in a system that is not isolated, and, consequently, the system seeks to minimize the free energy⁷. Again the system only adopts the folded protein state for certain temperatures. If we heat the system up, the protein becomes unfolded and becomes the random collection of amino-acid interactions.

Therefore

$$\text{Proteins: For sufficiently low } T, F_{\text{folded}} < F_{\text{unfolded}} \quad (10)$$

5 Order Parameters and Phase Transition

Our discussion in the previous section was entirely qualitative. We can make the concept of free energy more useful by using it to build of physical phenomena. We will do so in the next section by analyzing a model of the paramagnetic vs. ferromagnetic metals of our second example. But first, we should summarize the main takeaway from our previous discussions. As we increase the temperature of our specific system of interest, (e.g., take the ice cube out of the fridge, heat up a bar magnet, or boil a protein), the macrostate that defines the free energy minimum becomes one with more disorder (e.g., the ice melts, the bar magnetic becomes non-magnetic, the protein becomes unfolded). Conversely, as we lower the temperature of our system of interest, the macrostate becomes one of more order (e.g., water becomes ice, the non-magnetic material becomes magnetic, the protein refolds).

The reason for this temperature dependent transition between order and order arises from the form of the free energy. The free energy is written as

$$F = E - TS \quad (11)$$

In Eq.(11), the energy term E is typically one which induces *order* in the system, binding water molecules together or making dipoles align. However the entropy term $-TS$ typically induces *disorder* in the system, encouraging water molecules to separate or making dipoles unalign. As we change T , we change the relative contributions of the energy and entropy terms in the free energy, and we thereby change whether order or disorder dominates in the system. At sufficiently high temperatures, disorder dominates and at sufficiently low temperatures order dominates.

⁷The free energy being minimized in this example is actually the Gibbs free energy rather than the Helmholtz free energy. The former is used for constant pressure systems at variable volume and the latter is used for constant volume systems at variable pressure.

Thermodynamics' fundamental contest: In all thermal systems there is a contest between energy and entropy, and the arbiter that determines which one wins is often⁸ temperature. At sufficiently high temperature, entropy (and disorder) win. At sufficiently low temperature, energy (and order) win.

In either case (energy domination or entropy domination) we can define the resulting system in terms of an **order parameter**. The order parameter is taken to be a macroscopic quantity which changes drastically⁹ as we change the temperature of our system. When the order parameter has made such a drastic change, we say a **phase transition** has occurred. In fact, all of the examples of the previous section are examples of phase transitions with their own associated order parameters

- **From ice to water:** Solid-liquid phase transition; order parameter: density.
- **From bar magnet to hunk of metal:** Ferromagnetic-paramagnetic phase transition; order parameter: average magnetization of material.
- **From folded to unfolded protein:** Folded-unfolded phase transition; order parameter: contact matrix of protein.

To precisely model all of the above systems requires some statistical mechanics machinery beyond the methods of this course. However, it is possible to consider a concrete but approximate model of the ferromagnetic-paramagnetic phase transition which illustrates how free energy, order parameters, and phase transitions relate to one another.

6 Mean-Field Ising Model

In this section we will build a model of magnetism. In particular, we will show how changing the temperature of a magnetic system changes the free energy minimum, and thus changes whether the system has aligned spins or not. Our framing question is as follows

Framing Question

Can we use free energy to understand why at low temperatures the macrostate of a magnet consists of spins pointing in one direction and at higher temperatures the macrostate consists of disordered spins?

We will consider a simple system consisting of a volume of arbitrary dimensions and size, inside which there are many magnetic dipoles represented by arrows. Due to the quantum mechanical origin of these dipoles, we denote them as spins—quantities that can take on one of two values.

Let's say we have a lattice of N of these spins denoted s_1, s_2, \dots, s_N . Each spin s_i can have the value $+1$ or -1 denoting "up" and "down" spins, respectively. Such a model is called an **Ising model** after **Ernst Ising** who studied the first example of such a system as a Ph.D student.

In general, for a collection of spins $\{s_i\}$ —each with magnetic moment μ (Greek lowercase letter mu pronounced "mew")—in an external magnetic field H , the energy of the spin system is

$$E = -\mu H \sum_{i=1}^N s_i. \quad (12)$$

⁸Sometimes external conditions like external magnetic fields or system volume can also act as arbiters.

⁹"Drastically" has a mathematical meaning. We mean that as a function of temperature this order parameter (or one of its derivatives) makes a discontinuous transition at some temperature value.

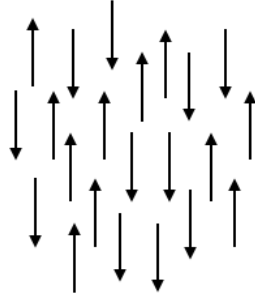


Figure 9: Ising system consisting of “spins” pointing up or down. For the system in this section, each spin interacts with every other spin.

In the **mean-field** Ising model, we assume the magnetic field H is proportional to the mean of the spin system. Namely, we take

$$H = \frac{H_0}{N} \sum_{j=1}^N s_j, \quad [\text{Assumption of mean-field Ising model}] \quad (13)$$

where H_0 is a constant with the units of magnetic field. When we plug Eq.(13) into Eq.(12), we find

$$E = -\mu \frac{H_0}{N} \sum_{j=1}^N s_j \sum_{i=1}^N s_i = -\mu \frac{H_0}{N} \sum_{j=1}^N \sum_{i=1}^N s_j s_i. \quad (14)$$

Defining the parameter J as

$$J \equiv 2\mu H_0, \quad (15)$$

we can write Eq.(14) in a more condensed form as

$$E_N = -\frac{J}{2N} \sum_{i=1}^N \sum_{j=1}^N s_i s_j. \quad (16)$$

The model defined by the energy Eq.(16) is called a **mean-field** model because each spin s_i interacts with the mean-spin $\sum_i s_i/N$ of the entire system. We define the energy in terms of J because the result Eq.(16) provides a different picture of how we can view interactions in this system. From Eq.(16), we can say a spin s_i interacts with a spin s_j to produce the energy term $-\frac{J}{N} s_i s_j$. If s_i and s_j are both $+1$ or both -1 (i.e., if they are pointing in the same direction), the energy of the system drops and the system becomes more stable by an energy amount $-J/N$. Alternatively, if s_i and s_j are pointing in opposite directions, the energy of the system increases and the system becomes less stable by an energy amount $+J/N$. Eq.(16) also includes unphysical “self-interaction” terms like s_i^2 , but we can keep such terms because they do not affect our final results; $s_i^2 = 1$ for any s_i so such terms lead to a spin-independent additive constant.

Now, In order to determine the thermal equilibrium properties of this system, we need to first find the free energy. By Eq.(11), the free energy is composed of the energy and the entropy. With Eq.(16) we have the energy, but it will prove useful to write this energy in terms of a macroscopic quantity. We define the average magnetization of our system as the sum of all the spins divided by the number of spins:

$$m = \frac{1}{N} \sum_{i=1}^N s_i. \quad (17)$$

With Eq.(17), Eq.(16) becomes

$$E_N(m) = -\frac{JN}{2}m^2, \quad (18)$$

where we made the energy's dependence on m , explicit. With Eq.(18) we have the energy written as a function of the macrostate m . Now, we need only determine the entropy before we find the free energy. Generally, given a system defined by the macrostate m , we expect our free energy to have the form

$$F_N(m, T) = E_N(m) - TS_N(m), \quad (19)$$

where T is the temperature of the surroundings and $S_N(m)$ is the entropy of the system written as a function of the macrostate. To determine Eq.(19), we need to determine $S_N(m)$. To determine $S_N(m)$, we will use the Boltzmann definition of entropy:

$$S_N(m) = k_B \ln \Omega_N(m), \quad (20)$$

where $\Omega_N(m)$ is the number of microstates associated with the macrostate m . We use Eq.(20) instead of the Clausius definition $\Delta Q/T$ because the heat exchange ΔQ cannot (currently) be expressed in terms of the macrostate m of the system and thus cannot help us determine the free energy as a function of that macrostate. We also do not (apparently) use the Gibbs definition of entropy $S = -k_B \sum_i p_i \ln p_i$ because the Gibbs definition reduces to Eq.(20) when each microstate i is equally probable for a given macrostate, as is the case here. The microstates for each macrostate m are equally probable in this situation because all microstates that are associated with the macrostate m also have the common energy $E(m)$, and if microstates have the same energy then they are equally probable.

Therefore, what remains in determining Eq.(19) is determining $\Omega_N(m)$, the number of microstates associated with the macrostate m . We can determine $\Omega_N(m)$ in a number of steps. We have an average number of spins $m = \frac{1}{N} \sum_{i=1}^N s_i$. Therefore the sum of all the values of the spins is

$$\sum_{i=1}^N s_i = mN. \quad (21)$$

Because our spins can only be up or down and each up spin contributes $+1$ to Eq.(21) and each down spin contributes -1 to Eq.(21), we can write Eq.(21) as

$$n_+ - n_- = mN, \quad (22)$$

where n_+ is the number of up spins and n_- is the number of down spins. Because we have N total spins, the number of up spins added to the number of down spins should be equal to N :

$$n_+ + n_- = N. \quad (23)$$

Now, we can find Ω , the number of microstates in our system by asking the following question:

In order to determine Ω : We have N spins in our system. In how many ways can we select n_+ up spins and n_- down spins in this system?

The answer to the above question is a simple combinatorics problem. We are essentially asking in how many ways can we choose n_+ up spins from N total spins. The answer is

$$\Omega_N = \binom{N}{n_+} = \frac{N!}{n_+!n_-!}, \quad (24)$$

where in the last equality we used Eq.(23) to write $n_- = N - n_+$. Now, in order to have a free energy $F(m, T)$ written in terms of the macrostate m , we need to also write the entropy in terms of the macrostate m . This in turn means writing Eq.(24) in terms of m . We can achieve this by turning to Eq.(22) and Eq.(23) to allow

us to write n_+ and n_- in terms of m . Using both of these equations, we can show

$$n_+ = \frac{N}{2}(1+m), \quad n_- = \frac{N}{2}(1-m). \quad (25)$$

And therefore, Eq.(24) becomes

$$\Omega_N(m) = \frac{N!}{\left[\frac{N}{2}(1+m)\right]! \left[\frac{N}{2}(1-m)\right]!} \quad (26)$$

where we made the functional dependence of Ω_N on m explicit. Taking the logarithm of Eq.(26) as it appears in Eq.(20), we have

$$\ln \Omega_N(m) = \ln N! - \ln \left[\frac{N}{2}(1+m)\right]! - \ln \left[\frac{N}{2}(1-m)\right]! \quad (27)$$

With Eq.(27) we are essentially done in computing the free energy as a function of the macrostate m . However, Eq.(27) is not in its most useful form to us because it contains factorial symbols. We can eliminate the factorials by making repeated use of Stirling's approximation. **Stirling's approximation** (which we will prove in a future problem set) states that for any number $N \gg 1$, we can approximate $N!$ as

$$N! = \sqrt{2\pi N} \left(\frac{N}{e}\right)^N + \mathcal{O}(N^{-1}). \quad (28)$$

In Eq.(27), our factorials appear as the arguments of logarithms, so we have

$$\ln N! = \frac{1}{2} \ln(2\pi N) + N \ln N - N + \mathcal{O}(N^{-1}). \quad (29)$$

However, because $N \gg 1$ the first term in Eq.(29) is much less than the subsequent two terms (e.g., consider $N = 100$ as a test case). Therefore, in what follows we can neglect this first term and simply take

$$\ln N! = N \ln N - N + \mathcal{O}(\ln N), \quad (30)$$

for any number $N \gg 1$. Applying Eq.(30) to the three terms in Eq.(27), and working through some algebra, we ultimately find

$$\ln \Omega_N(m) = N \ln 2 - \frac{N}{2} \ln(1-m^2) - \frac{N}{2} m \ln \frac{1+m}{1-m} + \mathcal{O}(\ln N). \quad (31)$$

Inserting Eq.(31) into Eq.(20) and inserting the resulting entropy into Eq.(19) (along with Eq.(18), we find that the free energy has the functional form

$$\begin{aligned} F_N(m, T) &= E_N(m) - TS_N(m) \\ &= -\frac{JN}{2}m^2 - k_B T \left[N \ln 2 - \frac{N}{2} \ln(1-m^2) - \frac{N}{2} m \ln \frac{1+m}{1-m} + \mathcal{O}(\ln N) \right] \end{aligned} \quad (32)$$

or

$$F_N(m, T) = \frac{N}{2} \left[-Jm^2 + k_B T \left(\ln(1-m^2) + m \ln \frac{1+m}{1-m} \right) \right] + F_N(0), \quad (33)$$

where $F_N(0)$ represents all the terms which remain in Eq.(32) when we take $m = 0$.

Eq.(33) gives us the free energy of our system as a function of the macrostate m representing the average spin. By the second law of thermodynamics, we know that the entropy of the universe increases in time, but we also showed that the *free energy of a closed system decreases in time* until it reaches thermal equilibrium at a free energy minimum. We would like to determine the macrostate m corresponding to the free energy minimum of this system. Thus given Eq.(33) we need only determine the value of m which minimizes the

given free energy. That is, we need to find $m = \bar{m}$ such that

$$\frac{\partial}{\partial m} F_N(m = \bar{m}, T) = 0, \quad \frac{\partial^2}{\partial m^2} F_N(m = \bar{m}, T) > 0. \quad (34)$$

From the first condition in Eq.(34) and using Eq.(33), we have (after some algebra)

$$\begin{aligned} 0 &= \frac{\partial}{\partial m} F_N(m = \bar{m}, T) \\ &= \frac{N}{2} \left[-Jm + k_B T \left(-\frac{2m}{1-m^2} + \ln \frac{1+m}{1-m} - m \frac{1}{1+m} - m \frac{1}{1-m} \right) \right] \Big|_{m=\bar{m}} \\ &= \frac{N}{2} \left[-2J\bar{m} + k_B T \ln \frac{1+\bar{m}}{1-\bar{m}} \right], \end{aligned} \quad (35)$$

which yields the condition

$$\frac{2J\bar{m}}{k_B T} = \ln \frac{1+\bar{m}}{1-\bar{m}}. \quad (36)$$

We can write Eq.(36) in a more useful form by inverting it. First we take the exponential of both sides to yield

$$e^{2\bar{m}J/k_B T} = \frac{1+\bar{m}}{1-\bar{m}}. \quad (37)$$

Then, if we solve Eq.(37) for \bar{m} in terms of $e^{2\bar{m}J/k_B T}$ we find

$$\bar{m} = \frac{e^{2\bar{m}J/k_B T} - 1}{e^{2\bar{m}J/k_B T} + 1} = \frac{e^{\bar{m}J/k_B T} - e^{-\bar{m}J/k_B T}}{e^{\bar{m}J/k_B T} + e^{-\bar{m}J/k_B T}}, \quad (38)$$

where in the final equality of Eq.(38) we multiplied the numerator and the denominator by $e^{-\bar{m}J/k_B T}$. Finally, using the definition of the **hyperbolic tangent function**

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}}, \quad (39)$$

we can write Eq.(38) as

$$\bar{m} = \tanh \left(\frac{J\bar{m}}{k_B T} \right) \quad [\text{Condition for } \partial_m F_N(m, T) = 0]. \quad (40)$$

Eq.(40) defines the value of the average spin m when our spin system is in thermal equilibrium at temperature T . However, it cannot be solved analytically to obtain \bar{m} as an explicit function of T . Instead, we can plot the left and the right sides of Eq.(40) for various choices of $J/k_B T$ to see how choices of this parameter affect the solutions we find. Doing so we can create Fig. 10. From Fig. 10. we see that Eq.(40) either has one solution or three solutions contingent on how T compares to J/k_B . When $T > J/k_B$, there is only one solution at $\bar{m} = 0$. When $T < J/k_B$ there are three solutions: one at $\bar{m} = 0$, and two others which are non-zero and symmetric.

We will call the $\bar{m} = 0$ solution \bar{m}_0 , and we will call the symmetric solutions which appear for $T < J/k_B$, $\bar{m}_+(T)$ and $\bar{m}_-(T)$.

Given that Eq.(40) admits multiple solutions for $T < J/k_B$, we need to check which of these solutions occur at a local minimum of the free energy Eq.(33). That is, we need to check which solutions satisfy the second condition in Eq.(34). Using Eq.(35) to compute the second derivative of the free energy, we find

$$\frac{\partial^2}{\partial m^2} F_N(m = \bar{m}, T) = \frac{\partial}{\partial m} \frac{N}{2} \left[-2Jm + k_B T \ln(1+m) - k_B T \ln(1-m) \right] \Big|_{m=\bar{m}}$$

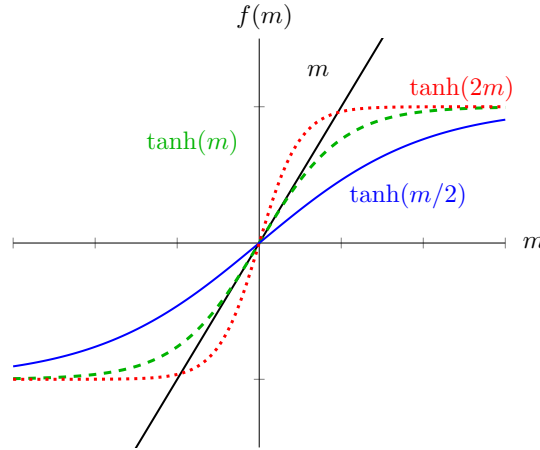


Figure 10: Plot of m and $\tanh(Jm/k_B T)$ for $J/k_B T = 1$, $J/k_B T = 2$, and $J/k_B T = 1/2$. We see that for $J/k_B T < 1$ there is only one solution to the equation $m = \tanh(J/k_B T)$: the one at $m = 0$. But for $J/k_B T > 1$ (or $T < J/k_B$), there are three solutions to the equation $m = \tanh(Jm/k_B T)$: the one at $m = 0$ and two which are symmetric and for which $m \neq 0$.

$$= N \left(-J + \frac{k_B T}{1 - \bar{m}^2} \right). \quad (41)$$

Requiring that Eq.(41) be greater than zero we have

$$\bar{m}^2 > 1 - \frac{k_B T}{J} \quad [\partial_m^2 F_N(m, T) > 0] \quad (42)$$

We see that when $T > J/k_B$, the solution $\bar{m} = 0$ satisfies the inequality Eq.(42), and so, for this temperature range, $\bar{m} = 0$ is a local minimum of the free energy. However, for $T < J/k_B$, the solution $\bar{m} = 0$ no longer satisfies the inequality, and therefore only the symmetric non-zero solutions to Eq.(40) are local minima.

6.1 Summary and Meaning

The preceding pages contained a lot of mathematics, so it would be useful to recap what we were doing and why we were doing it.

We previously established that for a closed system at a fixed temperature, the second law of thermodynamics asserts that the Helmholtz free energy $F = E - TS$ is minimized. We then considered the specific system of N spins where each spin interacts with every other spin. We defined the macroscopic quantity $m = \sum_i s_i / N$ which represents the average spin of the system. We then computed the energy as a function of m to find

$$E_N(m) = -\frac{JN}{2} m^2. \quad (43)$$

We also computed the entropy of this system and used Stirling's approximation to write the entropy as a continuous function of m :

$$S_N(m) = k_B \ln \Omega_N(m) = k_B \left[N \ln 2 - \frac{N}{2} \ln(1 - m^2) - \frac{N}{2} m \ln \frac{1 + m}{1 - m} + \mathcal{O}(\ln N) \right]. \quad (44)$$

The objective in computing Eq.(43) and Eq.(44) was to find an expression for the free energy in terms of the macroscopic quantity m so that we could determine what value of m is associated with a local minimum of

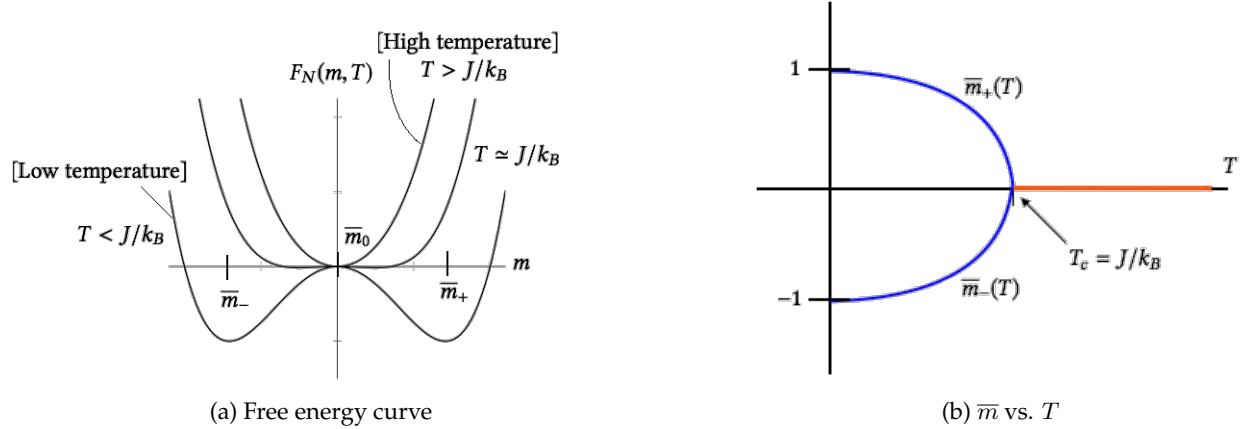


Figure 12: Free energy function Eq.(33) and order parameter as we vary temperature. As we lower the temperature, $F_N(m, T)$ transitions from having one local minimum to two local minima, and \bar{m} changes from the value 0 to a non-zero quantity. The transition shown here is an example of **symmetry breaking** in physics. We also note that as $T \rightarrow 0$, \bar{m} approaches ± 1 , indicating the system has all of its spins pointing in a single direction.

the free energy. Using Eq.(43) and Eq.(44) we found the free energy

$$F_N(m, T) = \frac{N}{2} \left[-Jm^2 + k_B T \left(\ln(1 - m^2) + m \ln \frac{1 + m}{1 - m} \right) \right] + F_N(0). \quad (45)$$

We plot Eq.(45) in Fig. 11a. From the figure, we see that $F_N(m, T)$ has a local minimum at $m = 0$ for high temperatures (specifically $T > J/k_B$) and then two symmetric local minima at low temperatures (specifically $T < J/k_B$). Next, determining (analytically) the *local minima* of Eq.(45), we found that $F_N(m, T)$ has a local minimum at $m = \bar{m}$, where

$$\bar{m} = 0 \quad \text{for } T > J/k_B, \quad (46)$$

and \bar{m} is either one of the non-zero solutions to

$$\bar{m} = \tanh \left(\frac{J\bar{m}}{k_B T} \right) \quad \text{for } T < J/k_B. \quad (47)$$

We plot the composite solution of \bar{m} for all T in Fig. 11b. From Eq.(46) and Eq.(47), we can infer that the quantity \bar{m} is the **order parameter** for this system because it allows us to define two different phases. Here are the two phases:

- **Ordered phase:** For $T < J/k_B$, we have $\bar{m} \neq 0$. Thus the average spin at thermal equilibrium is non-zero, and the system has either more up spins than down spins or vice versa. As $T \rightarrow 0$, all spins either eventually point down or point up, producing $\bar{m} = -1$ or $\bar{m} = +1$, respectively.
- **Disordered phase:** For $T > J/k_B$, we have $\bar{m} = 0$. Thus the average spin at thermal equilibrium is zero, and the system has an equal number of up spins and down spins.

Phase transitions occur at a temperature which separates qualitatively distinct behaviors for the order parameter. We call the temperature at which a phase transition occurs the **critical temperature**. For this system, the critical temperature is

$$T_c = J/k_B \quad \text{[Critical temperature]} \quad (48)$$

Now, we should comment on the ambiguity of the solutions in Fig. 11b. We have two branches of solutions for $T < J/k_B$ indicating that as we lower the temperature of this system below J/k_B , the average

spin which previously had the value of 0, can now take on either a positive or a negative value. Which of these branches the system adopts is completely random unless there is a slight external magnetic field which encourages the system to align along one particular direction. Above $T = J/k_B$, the equilibrium value of m is entirely symmetric with respect to up and down spins, but below this temperature, the symmetry vanishes and the system acquires a bias towards either up or down spins. When a symmetry exists in the system for certain parameter regimes but vanishes under different parameter regimes, we say the system is capable of **symmetry breaking**.

7 Moving from Macrostates to Microstates

In these notes, we have managed to define a system-dependent quantity (i.e., the free energy) for determining the equilibrium of a system, and we used this quantity to investigate the equilibrium properties of a simple model of magnetism. The quantitative model has many features in common with the qualitative examples presented earlier. In particular, our model exhibited a transition at a particular temperature which separated qualitatively distinct types of behavior for the macrostate. In a way similar to how a block of ice turns to water, a bar magnet becomes an ordinary hunk of metal, or a protein denatures into a random globule, our spin system became more disordered at high temperatures.

Our quantitative analysis of equilibrium of the free energy was in terms of the macrostate of the system. However, there is another way to perform this analysis by instead considering the microstates of the system. Using Gibbs definition of entropy and the definition of energy as the average of all the energies of the microstates, we can develop a formalism for computing the free energy in terms of the properties of microstates. Doing so will require that we introduce a new technique from calculus. We will turn to this task in the next notes.