

Lecture 06: Boltzmann Distribution and Partition Function

In these notes, we introduce the method of Lagrange multipliers and use it to derive the Boltzmann distribution. From the Boltzmann distribution, we relate the Helmholtz free energy to the spectrum of probabilities to be in various microstates. This relation justifies the importance of the partition function, and as an example calculation of the utility of the partition function, we consider a spin system in an external magnetic field.

1 Returning to Microstates

In the previous notes, we showed that for closed systems¹ at fixed temperature, the second law of thermodynamics implies

$$F = E - TS, \quad (1)$$

defined as the Helmholtz free energy of these systems, is minimized at equilibrium. In applying this result, we considered a system in which this free energy was written as a function of a macroscopic quantity, and we were thus able to determine the macrostate corresponding to the free energy minimum and, equivalently, the thermal equilibrium of the system. However, by focusing only on the macrostate (i.e., some description of the system at large), we were ignoring possibly interesting properties of the microstate. In particular, each macrostate can be associated with many different microstates and at thermal equilibrium it would be interesting to know the probability distribution to be in various microstates. Such a probability distribution could not be obtained from the macrostate analysis of the previous notes.

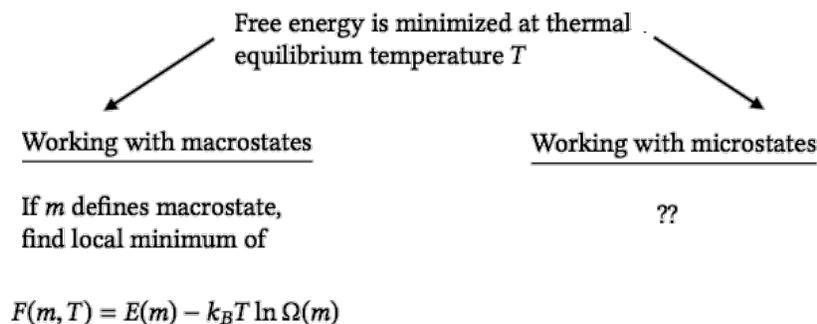


Figure 1: We previously found the thermal equilibrium of a system at a temperature T by analyzing the macrostate. Can we do the same by analyzing the properties of the microstate?

Instead, in order to be able to determine the probabilistic properties of microstates at thermal equilibrium, we need a formalism for minimizing free energy in terms of the properties of the microstate (see Fig. 1). This task is what we turn to in these notes.

¹That is systems that can exchange energy but not matter with their surroundings

Framing Question

We previously used the free energy $F = E - TS$ to determine the macrostate of a system at equilibrium. How can we use the free energy to determine the probabilistic properties of microstates?

2 Free energy and microstates

In our objective to determine how free energy minimization constrains the properties of microstates, we must first find a relation between free energy and microstates. Calculating free energy requires that we calculate energy and entropy, so from our discussion in Lecture Notes 3 on "Entropy and Information", we are already part of the way towards achieving a relation between free energy and microstates. We noted that the most general form for the entropy of a system consisting of a set of microstates $\{i\}$ where microstate i occurs with probability p_i is

$$S = -k_B \sum_{\{i\}} p_i \ln p_i, \quad (2)$$

where the summation $\sum_{\{i\}}$ represents a sum over the set of all microstates. Now, if we say that each microstate i has the energy E_i , then we can define the average energy across all microstates as

$$\langle E \rangle = \sum_{\{i\}} p_i E_i. \quad (3)$$

If we have a system composed of many different microstates, the energy defined in Eq.(3) gives us the average energy of our system. From Eq.(2) and Eq.(3), and the fact that free energy is $F = E - TS$, we can define the free energy of a system with a set of microstates $\{i\}$ as

$$F = \langle E \rangle - TS = \sum_{\{i\}} p_i (E_i + k_B T \ln p_i), \quad (4)$$

where p_i is again the probability to be in the microstate i . In Eq.(4), we use $\langle E \rangle$ instead of simply the energy of a single microstate because the free energy describes the entire system and must therefore include an energy term representing the whole system.

Eq.(4) is the free energy of our system written in terms of the probability to be in a microstate i . If we can minimize Eq.(4) as a function of our p_i , we can find the probability spectrum of the microstates when our system is in thermal equilibrium at a temperature T . However, there is a caveat to this minimization procedure. The probability p_i is *constrained* by normalization; the probability to be in *any* microstate must be 1. Therefore, we cannot simply find the raw local minimum of Eq.(4); we need to find the local minimum, subject to the constraint that $\sum_{\{i\}} p_i = 1$.

At this point, our problem is well formulated. We would like to determine the probability spectrum of the microstates in this system. Namely, we want to find the probability p_i to be in microstate i . To find this probability, we need to minimize Eq.(4) subject to the constraint of probability normalization. That is,

Problem

We want to find the set of p_i s that minimize $F = \sum_{\{i\}} (p_i E_i + k_B T p_i \ln p_i)$ subject to the constraint $\sum_{\{i\}} p_i = 1$.

The problem given above represents a type of calculus problem that we have not encountered before. Consequently, instead of solving it directly we will begin with a simpler example. Ultimately, by working through this example, we seek to answer the following question

Question

How do we maximize or minimize quantities when the independent variables are subject to a constraint?

3 Optimization Under Constraints

Our goal is to find a way to maximize a function when the function's independent variables are constrained in some way. We will begin with an example framed around a question: If a rectangle has a fixed perimeter P , what dimensions of the rectangle maximize the area A . In this problem, the area A is the quantity we are seeking to maximize, and the claim that it has a perimeter P is the constraint.

Let x and y be the dimensions of the rectangle. Then by simple geometry, twice the width plus twice the height is equal to the perimeter and the width times the height is equal to the area:

$$P = 2x + 2y, \quad A = xy. \quad (5)$$

We are still trying to find the dimensions x and y which maximize $A = xy$, subject to the condition that $2x + 2y = P$. A is a multivariable function, and when we are trying to find a point defining the optimum of a multivariable function we must find the point where the partial derivatives of the function are zero. Thus given the constraint, we are trying to find the x and y which satisfy

$$\frac{\partial}{\partial x} A_{P=2x+2y} = 0 \quad \text{and} \quad \frac{\partial}{\partial y} A_{P=2x+2y} = 0. \quad (6)$$

One way to approach this problem is to eliminate one of the dimensions by using the constraint to solve for this dimension in terms of the other dimension, and then to implement the standard maximization algorithm. For example, from the first equation in Eq.(5), we can solve for y to obtain

$$y = \frac{P}{2} - x. \quad (7)$$

If we substitute, Eq.(7) into the equation for A in Eq.(5) we find

$$A = \frac{P}{2}x - x^2, \quad (8)$$

which is the equation for the area with the incorporated perimeter constraint. Applying the standard maximization algorithm in calculus, we find that Eq.(8) is maximized for $x = P/4$. From Eq.(7), this in turn implies $y = P/4$. Therefore, the dimensions of a rectangle with maximum area given a perimeter P are

$$x = y = \frac{P}{4}. \quad (9)$$

In other words, for a fixed perimeter, the area of a rectangle is maximized if that rectangle is in fact a square.

The above solution is one approach to finding a maximization with a constraint: Use the constraint to eliminate one of the independent variables, and then proceed with the standard algorithm from calculus. Another approach uses the constraint in a more clever way.

Let's say we introduce the variable λ into the problem by defining the function

$$H(x, y, \lambda) = xy + \lambda(P - 2x - 2y). \quad (10)$$

How would we find the local minimum of Eq.(10)? Well, $H(x, y, \lambda)$ is a multivariable function, and a point at an optimum of a multivariable function is partly defined by all partial derivatives of the function being

zero at that optimum. So the local minimum of Eq.(10) is partly defined by

$$\frac{\partial}{\partial x} H(x, y, \lambda) = x - 2\lambda = 0 \quad (11)$$

$$\frac{\partial}{\partial y} H(x, y, \lambda) = y - 2\lambda = 0 \quad (12)$$

$$\frac{\partial}{\partial \lambda} H(x, y, \lambda) = P - 2x - 2y = 0 \quad (13)$$

$$(14)$$

Solving the system of equations given by Eq.(11), Eq.(12), and Eq.(13), we find that the values of x and y for which $H(x, y, \lambda)$ is maximized are

$$x = y = \frac{P}{4}, \quad (15)$$

and $\lambda = P/8$. In Eq.(15), we see we have reproduced Eq.(9), the dimensions which maximize the area of a rectangle subject to a given perimeter. The intuition behind this new procedure is that since the derivative along every coordinate direction must be zero at a maximum, we can incorporate the variable constraint into a new function $H(x, y, \lambda)$ (with a new variable λ) by defining the function in such a way that requiring all partial derivatives to be zero simply gives us our original constraint as one of the zero derivatives. In the above example, we incorporated the constraint into the maximization algorithm by defining the new variable λ and adding $\lambda(P - 2x - 2y)$ to the quantity we intended to maximize. The more general procedure is as follows:

Optimization subject to a constraint

If we are trying to optimize (that is minimize or maximize) the N variable function

$$f(x_1, x_2, \dots, x_N), \quad (16)$$

subject to the constraint

$$g(x_1, x_2, \dots, x_N) = C, \quad (17)$$

then we define

$$H(x_1, x_2, \dots, x_N, \lambda) = f(x_1, x_2, \dots, x_N) + \lambda(C - g(x_1, x_2, \dots, x_N)), \quad (18)$$

and we solve the system of equations given by

$$\frac{\partial}{\partial x_1} H = 0, \quad \dots, \quad \frac{\partial}{\partial x_N} H = 0, \quad \frac{\partial}{\partial \lambda} H = 0. \quad (19)$$

The solutions to the above conditions will give us a set of values of x_1, x_2, \dots, x_N values where Eq.(16) is optimized under constraint of Eq.(17), but we will also obtain the value of λ . However, λ is an auxiliary parameter which is introduced for the procedure, but does not have any deeper meaning other than its utility in parameterizing the constraint.

The above procedure is called the **method of Lagrange multipliers**, and the parameter λ is termed a **Lagrange multiplier**. This method is used in all areas of physical sciences and mathematical modeling when equations need to be optimized under constraints of the independent variables.

One important fact that we have swept under the rug is that this procedure allows us to find the local optima of functions where the independent variables are subject to constraints, but it does not tell us whether those optima are local minima or local maxima. For multivariable functions, the procedure for determining

whether an optimum of a function is a maximum or a minimum is more complicated (see [Second partial derivatives test](#)) than it is for single-variable functions. So, moving forward, we will make the somewhat ad-hoc claim that we know which optimum we are aiming for when we implement the method of Lagrange multipliers.

4 Boltzmann and the probability to be in a microstate

With the procedure discussed above, we now have a way to answer our question from the previous two sections. We wanted to know how to find the probabilities p_i that minimize the function

$$F = \sum_{\{i\}} \left(p_i E_i + k_B T p_i \ln p_i \right), \quad (20)$$

when we know that the probabilities have the normalization constraint $\sum_{\{i\}} p_i = 1$. As per, the Lagrange multipliers procedure, we define the function H as

$$H(\{p_i\}, \lambda) = \sum_{\{i\}} \left(p_i E_i + k_B T p_i \ln p_i \right) + \lambda \left(1 - \sum_{\{i\}} p_i \right). \quad (21)$$

Computing the p_j partial derivative of H and setting the result to zero, we have

$$\frac{\partial}{\partial p_j} H(\{p_i\}, \lambda) = E_j + k_B T (\ln p_j + 1) + \lambda = 0. \quad (22)$$

Solving Eq.(22) for p_j gives us

$$p_j = e^{(-\lambda - E_j)/k_B T - 1} = e^{-\lambda/k_B T - 1} e^{-E_j/k_B T}. \quad (23)$$

In Eq.(23) the only undetermined variable is the Lagrange multiplier λ . We determine this variable by considering the final partial derivative of H . Computing the λ partial derivative of H and setting the result to zero gives us

$$\frac{\partial}{\partial \lambda} H(\{p_i\}, \lambda) = 1 - \sum_{\{i\}} p_i = 0, \quad (24)$$

Inserting Eq.(23) into Eq.(24), we obtain

$$1 = \sum_{\{i\}} p_i = \sum_{\{i\}} \left(e^{-\lambda/k_B T - 1} e^{-E_i/k_B T} \right) = e^{-\lambda/k_B T - 1} \sum_{\{i\}} \left(e^{-E_i/k_B T} \right), \quad (25)$$

which implies

$$e^{-\lambda/k_B T - 1} = \frac{1}{\sum_{\{i\}} \left(e^{-E_i/k_B T} \right)}. \quad (26)$$

Finally, returning to Eq.(23), we find that the probability p_j to be in a microstate j is

$$\boxed{p_j = \frac{e^{-E_j/k_B T}}{\sum_{\{i\}} \left(e^{-E_i/k_B T} \right)}. \quad \text{[Boltzmann distribution]} \quad (27)}$$

Eq.(27) represents the probability to be in microstate j (given that this microstate has energy E_j) when the system is at thermal equilibrium with temperature T . Formally, it is called the **Boltzmann distribution**.

Again we note that we have derived Eq.(27) only from the condition that the derivatives of Eq.(21) are zero, when in fact to show that Eq.(27) yields a free energy minimum, we would need to do a second derivative test. However,

5 Free Energy and Partition Function

Let us recap our work to this point. We began Section 2 of these notes by arguing that if we are to describe statistical physics systems by microstates, we have to use probabilities since the definition of entropy is written in terms of probabilities of microstates. From here, we postulated that the free energy for a system with a set of microstates $\{i\}$, where a microstate i has energy E_i , is Eq.(20). From Lecture Notes 05, we know that at a thermal equilibrium temperature T , the free energy is minimized. Thus our objective, was then to find the probabilities that minimized Eq.(20) subject to the constraint of probability normalization. Using the method of Lagrange multipliers, we found that these probabilities were given by Eq.(27).

From here, we can do some slight book keeping. For notational simplicity, let us define

$$Z = \sum_{\{i\}} e^{-E_i/k_B T}. \quad (28)$$

We call Eq.(28) the **partition function** of our system. The partition function is important because of its simple relationship with the free energy. Inserting Eq.(27) into Eq.(20), we find

$$\begin{aligned} F &= \sum_{\{i\}} \left(p_i E_i + k_B T p_i \ln p_i \right) \\ &= \sum_{\{i\}} \left(\left(\frac{e^{-E_i/k_B T}}{Z} E_i + k_B T \frac{e^{-E_i/k_B T}}{Z} \left(-\frac{E_i}{k_B T} - \ln Z \right) \right) \right) \\ &= \sum_{\{i\}} \left(\frac{e^{-E_i/k_B T}}{Z} E_i - \frac{e^{-E_i/k_B T}}{Z} E_i - \frac{e^{-E_i/k_B T}}{Z} k_B T \ln Z \right), \end{aligned} \quad (29)$$

which upon canceling the first and second terms, and using probability normalization, gives us

$$F = -k_B T \ln Z. \quad [\text{Free energy and partition function}] \quad (30)$$

Therefore, the free energy is $-k_B T$ times the natural logarithm of the partition function.

There is one more important relation between the partition function and an important physical quantity in our system, but deriving it requires we introduce one last bit of new notation. Because the factor $1/k_B T$ appears so often in statistical physics it is usually redefined as the quantity

$$\beta \equiv \frac{1}{k_B T}, \quad [\text{Definition of } \beta] \quad (31)$$

representing **inverse temperature**. Writing our partition function, in terms of inverse temperature, we have

$$Z = \sum_{\{i\}} e^{-\beta E_i}. \quad (32)$$

Now, let us compute the average energy of our system. Given that Eq.(27) gives the probability to be in a microstate j , the average energy across all microstates is

$$\langle E \rangle = \sum_{\{i\}} p_i E_i = \frac{1}{Z} \sum_{\{i\}} E_i e^{-\beta E_i} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{\{i\}} e^{-\beta E_i}, \quad (33)$$

where in the last line we used $\frac{d}{dx}e^{-ax} = -ae^{-ax}$. By the definition of the derivative of the logarithm, we then have

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z. \quad [\text{Average energy}] \quad (34)$$

So the average energy of the system is the negative of the β derivative of the natural logarithm of the partition function. By a similar procedure, we can show that the variance in the energy (i.e., $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$) is

$$\sigma_E^2 = \frac{\partial^2}{\partial \beta^2} \ln Z. \quad [\text{Variance in energy}] \quad (35)$$

6 Spins in a Magnetic Field

We have largely completed the objective of these notes, but before we conclude let us consider a concrete example.

Say we have a collection of N spins denoted s_1, s_2, \dots, s_N . These spins can take on the values $+1$ or -1 . They also exist in an external magnetic field $H > 0$ which acts on each spin and produces an energy $-\mu H s_k$ for each spin s_k (Fig. 2). The quantity μ is called the magnetic moment of the spin; it is included in the energy to yield the correct units and we assume all spins have the same magnetic moment². We want to use the formalism we just developed to find the probability that this system of spins is in a particular microstate defined by $\{s_1, s_2, \dots, s_N\}$.

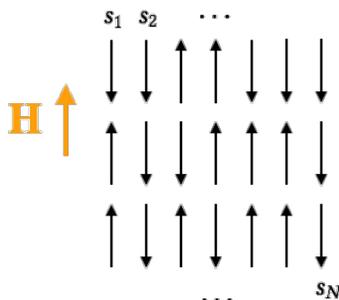


Figure 2: We have N spins in an external magnetic field H . If a spin s_i is pointing in the same direction as the magnetic field, then its energy is $-\mu H$, and if the spin is pointing in the opposite direction as the field, then its energy is $+\mu H$.

First we write, the energy of this system for an arbitrary microstate. Given that the energy of the spin s_k is $-\mu H s_k$, the energy of all the N spins is

$$E(\{s_k\}) = -\sum_{k=1}^N \mu H s_k = -\mu H \sum_{k=1}^N s_k, \quad (36)$$

where $\{s_k\}$ denotes a particular microstate. Therefore, the probability to be in a spin microstate defined by $\{s_k\}$ is

$$p(\{s_k\}) = \exp \left(\beta \mu H \sum_{k=1}^N s_k \right) \left(\frac{1}{Z} \right), \quad (37)$$

²This assumption is a pretty good one because in many materials, magnetism arises from electrons all of which do indeed have the same magnetic moment.

where Z is the partition function given by

$$Z = \sum_{\{s_k = \pm 1\}} \exp \beta \mu H \sum_{k=1}^N s_k \quad (38)$$

where $\sum_{\{s_k = \pm 1\}}$ denotes the fact that we are summing over all possible values of s_k for $k = 1, \dots, N$. We can go further and simplify the partition function. The summation in Eq.(38) is over all possible spin microstates of the system. Given that each spin can take on the value -1 or $+1$, we can write this summation in expanded form as

$$\sum_{\{s_k = \pm 1\}} \left(= \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} \cdots \sum_{s_N = \pm 1} \right), \quad (39)$$

where

$$\sum_{s_1 = \pm 1} f(s_1) = f(1) + f(-1). \quad (40)$$

Next, with the multiplication property of exponentials, we have

$$\exp \beta \mu H \sum_{k=1}^N s_k \left(= \prod_{k=1}^N e^{\beta \mu H s_k}. \quad (41)$$

With these calculations, Eq.(38) becomes

$$\begin{aligned} Z &= \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} \left(\cdots \sum_{s_N = \pm 1} \prod_{k=1}^N e^{\beta \mu H s_k} \right. \\ &= \sum_{s_1 = \pm 1} e^{\beta \mu H s_1} \sum_{s_2 = \pm 1} \left(e^{\beta \mu H s_2} \cdots \sum_{s_N = \pm 1} e^{\beta \mu H s_N} \right. \\ &= \prod_{k=1}^N \sum_{s_k = \pm 1} e^{\beta \mu H s_k}. \end{aligned} \quad (42)$$

From here, we are close to the end. By Eq.(40), we have

$$\sum_{s_k = \pm 1} e^{\beta \mu H s_k} = e^{\beta \mu H} + e^{-\beta \mu H} = 2 \cosh(\beta \mu H), \quad (43)$$

where we used the definition of the hyperbolic cosine function $\cosh(x) = (e^x + e^{-x})/2$. Returning to Eq.(42), we obtain

$$Z = \prod_{k=1}^N 2 \cosh(\beta \mu H) = 2^N \cosh^N(\beta \mu H), \quad (44)$$

therefore the probability Eq.(37) to be in a particular microstate is

$$p(\{s_k\}) = \frac{\exp \left(\beta \mu H \sum_{k=1}^N s_k \right)}{2^N \cosh^N(\beta \mu H)}. \quad (45)$$

We conclude, by asking one final question: As a function of H and T , what is the average spin of the system? We define the average spin as

$$\langle s \rangle \equiv \frac{1}{N} \sum_{i=1}^N \langle s_i \rangle. \quad (46)$$

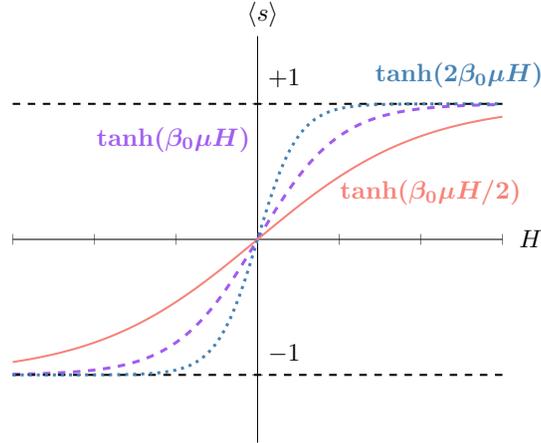


Figure 3: Plot of $\langle s \rangle$ as a function of H for various temperatures. We see that as we increase temperature T or lower β , the average magnetization $\langle s \rangle$ approaches ± 1 for lower values of H .

From Eq.(36), we see that the average energy is related to the average spin through

$$\langle E \rangle = -N\mu H \langle s \rangle. \quad (47)$$

Also, we previously related the average energy of our system to the partition function in Eq.(34). Therefore, we have

$$\begin{aligned} \langle s \rangle &= \frac{1}{N\mu H} \frac{\partial}{\partial \beta} \ln Z \\ &= \frac{1}{N\mu H} \frac{\partial}{\partial \beta} \ln \left[2^N \cosh^N(\beta\mu H) \right] \left(\right. \\ &= \frac{1}{\mu H} \frac{\partial}{\partial \beta} \ln \cosh(\beta\mu H), \end{aligned} \quad (48)$$

which leaves us with

$$\langle s \rangle = \tanh(\beta\mu H). \quad (49)$$

In the first problem of Assignment # 4, we analyzed the identical problem from the perspective of macrostates. Taking $m = \sum_{i=1}^N s_i / N$ to define the macrostate, we found that the value of m which gives us a free energy minimum is given by

$$\mu H = \frac{k_B T}{2} \ln \frac{1+m}{1-m}, \quad (50)$$

which when solved for m , yields

$$m = \frac{e^{2\beta\mu H} - 1}{e^{2\beta\mu H} + 1} = \frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}} = \tanh(\beta\mu H). \quad (51)$$

Therefore, Eq.(49) matches the result we found when we analyzed the system in terms of microstates. A plot of Eq.(49) is shown in Fig. 3. From the plot we see that lower values of temperature (i.e., higher values of β) result in $\langle s \rangle$ approaching ± 1 more quickly for lower values of H . In general, this system exemplifies a paramagnetic system in which $\langle s \rangle$, the average spin of single spin, is only nonzero if the external magnetic field H is non-zero.

Finally, if we consider this system in the limit of high temperature T , we can Taylor expand the hyperbolic

tangent in Eq.(49). By the expansion $\tanh(x) = x + \mathcal{O}(x^3)$, we have

$$\langle s \rangle = \frac{\mu H}{k_B T} + \mathcal{O}(\mu^3 H^3 / k_B^3 T^3) \quad (52)$$

Defining the **total magnetization** of this spin system as $M \equiv \mu N \langle s \rangle$, Eq.(52) indicates that at high temperatures the total magnetization has the form

$$M = \frac{N \mu^2 H}{k_B T} + \mathcal{O}(\mu^3 H^3 / k_B^3 T^3) \quad (53)$$

Eq.(53) is called the **Curie law for magnetism**. It states that for paramagnetic fields at high temperature and/or weak external field, the total magnetization M of the material is linearly proportional to the external field H and inversely proportional to the temperature T . The effect is named after its discoverer Pierre Curie, the husband of the Marie Curie.

7 Recap

At this point we are able to fill in the other side of Fig. 1.

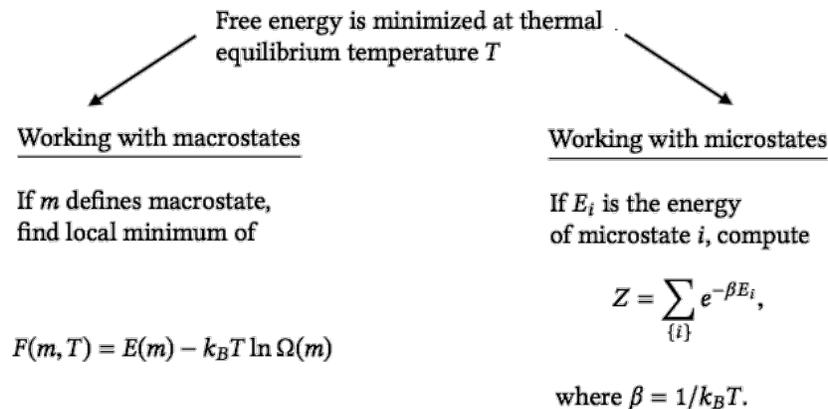


Figure 4: To study a thermal system in terms of the macrostate, we compute the minimum of the free energy written as a function of the macrostate. In terms of microstates, the minimum of the free energy is given by $F = -k_B T \ln Z$, where $Z = \sum_{\{i\}} e^{-\beta E_i}$ with E_i the energy of microstate i .

When trying to analyze the properties of the thermal equilibrium of a system, we can either consider the macrostates of the system and try to determine the macrostate associated the local minimum of the free energy function. Alternatively, we can study the system in terms of microstates and compute the partition function for the system. This latter procedure does not require any additional minimization because the Boltzmann distribution used to compute the partition function was already derived from constraining the free energy to be at a local minimum.

Because it automatically defines the equilibrium of a system, the partition function is foundational to equilibrium statistical physics. Consequently, for the next few lectures we will be exploring how to apply the right branch in Fig. 4 to some common (and not so common) systems of interest.

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