Understanding systems of non-interacting particles

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Abstract

An analytic expression for the average energy as a function of temperature for a system of non-interacting particles is derived. The results obtained using this expression are compared with the values of the average energy that are computed by explicitly enumerating over all the possible microstates. The results from these two methods are shown to be the same. The two approaches are thus computing the same quantity.

1 Introduction

The properties of many materials change with temperature. For example, upon heating ice transforms to a liquid and then evaporates to form a gas. Furthermore, the volume of space that a certain number of atoms/molecules takes up increases as the temperature increases. We can understand the reasons why the properties of materials change with temperature by using the tools of statistical mechanics.

In this report, I will investigate these ideas in statistical mechanics by discussing how the average energy of a system of non-interacting particles changes with temperature. The report begins with a discussion of the system that I have chosen to study in section 2. I then discuss how the ensemble average as a function of temperature can be calculated numerically and how an analytic expression for this function can be derived in section 3. I show that these two methods produce the same results before discussing the reason why the ensemble average depends on temperature in the way that it does in section 4. The report finishes in section 5 with a discussion of the limitations of the methods that have been employed. Throughout the report I will work in a system of arbitrary units in which all fundamental constants are set equal to one.

2 System

In my model I have N independent particles. Each of these particles can have an energy of -1 or $+1$. The energy level diagram for the particles is shown in figure 1.

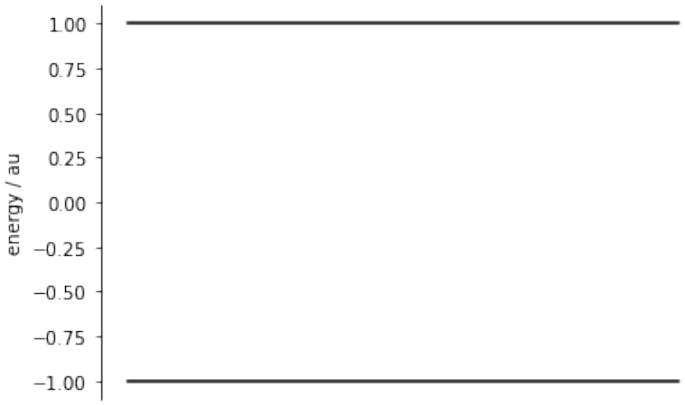

Fig. 1. The energy levels that are available to each of the particles in the system of interest.

All the particles in my system are independent. The energy for a set of N particles is thus:

$$E = \sum_{i=1}^{N} s_i$$

where s_i is -1 or $+1$ and tells us what energy level the ith particle is in.

In general, there are multiple configurations of particles that will have an energy of E. The density of states that is shown in figure 2 shows the number of states with each energy for a system of 8 particles. This density of states is calculated as:

$$\Omega(E) = \sum_{j} \delta(E_j - E)$$

In this expression the sum runs over all the of the 2^N possible microstates that the system can adopt. E_j is the energy of the jth microstate and $\delta(x)$ is a Kronecker delta that one when $x = 0$ and zero otherwise.

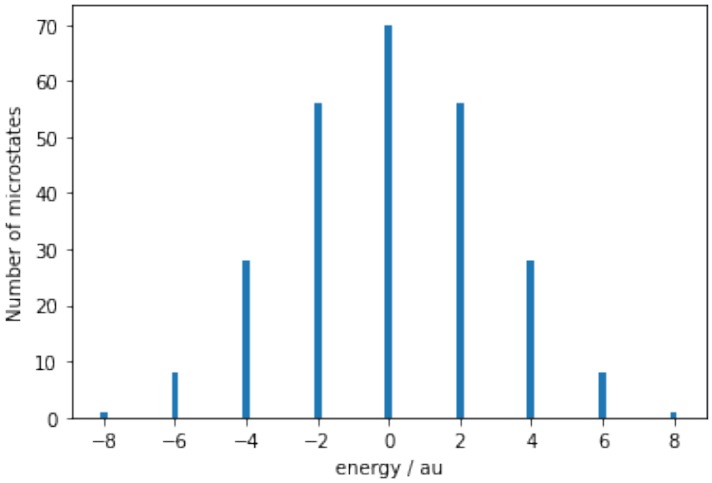

Fig. 2. The density of states for a system of 8 particles.

The density of states in figure 2 has a peak at 0. Furthermore, the binomial coefficient can be used to calculate the number of states with each energy.

For a system with a constant energy the entropy, S is given by:

$$S(E) = k_B \ln \Omega(E)$$

k_B here is a fundamental constant that we will set equal to one here. We can thus easily calculate the entropy as a function of energy for our system using the density of states in figure 2. The entropy as a function of energy is shown in 3.

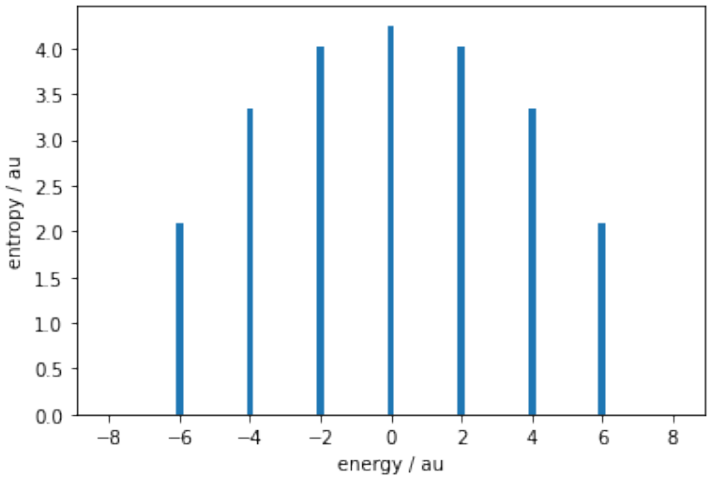

Fig. 3. The entropy as a function of energy for a system of 8 particles.

3 Results

As discussed in the introduction we wish to investigate how the average energy of our system depends on temperature. To do this we need to recall that the average energy can be calculated using:

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j e^{-\beta E_j} \qquad \text{where} \qquad Z = \sum_j e^{-\beta E_j} \tag{1}$$

In these expressions the sums run over the total number of microstates and E_j is the energy of the jth microstate. $\beta = 1/k_B T$ where T is the temperature and k_B is Boltzman's constant. The black dots in figure 4 show values that were obtained for this average by performing the sums over microstates in the expressions above explicitly.

The quantity called Z in equation 1 is known as the canonical partition function. For the systems of non-interacting particles that we have studied in this report we can derive an

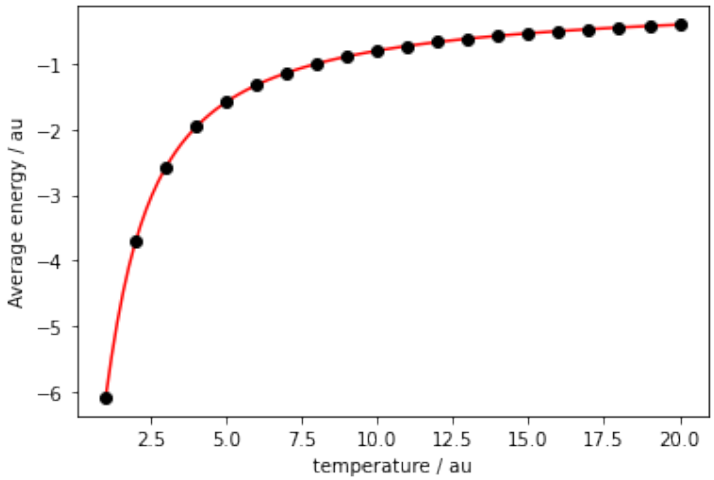

Fig. 4. The average energy as a function of temperature for a system of 8 particles. The black dots show results that were obtained by explicitly enumerating over all the microstates using equation 1. The red line is the analytic expression for the average energy that we derived and that is given in equation 3.

analytic expression for this function as follows:

$$Z = \sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_N=0}^{1}\exp\left[-\beta\left(\sum_{i=1}^{N} z(s_i)\right)\right]$$

There is one summation here for each of the particles and there are 2 values (0 or 1) for each of our N s_j terms. The function $z(s)$ returns -1 when $s = 0$ and 1 when $s = 1$.

Notice that we can replace the exponential of the sum in the expression above with a product over exponentials as follows:

$$Z = \sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_N=0}^{1}\prod_{i=1}^{N} e^{-\beta z(s_i)}$$

Further note that each term in the product depends on only one of the summation indices. This fact allows us to rewrite the above as:

$$Z = \left[\sum_{s_1=0}^{1} e^{-\beta z(s_1)}\right]\left[\sum_{s_2=0}^{1} e^{-\beta z(s_2)}\right]\cdots\left[\sum_{s_N=0}^{1} e^{-\beta z(s_N)}\right] = \left[\sum_{s_1=0}^{1} e^{-\beta z(s_1)}\right]^N$$

The last result equality here holds because all the summations are identical. By expanding out the sum we now arrive at:

$$Z = \left(e^{-\beta} + e^{\beta}\right)^N = 2^N \cosh^N(\beta) \tag{2}$$

The ensemble average of the energy is related to the partition function by:

$$\langle E \rangle = -\left(\frac{\partial \ln Z}{\partial \beta} \right)$$

Inserting equation 2 into this expression and differentiating with Sympy gives:

$$\langle E \rangle = -N \tanh(\beta) \tag{3}$$

This function is shown in red in figure 4. You can clearly see how there is a perfect match between the numeric and analytic results.

4 Discussion

We can understand why the curve in figure 4 has the shape it does by considering the probability of having each energy changes with temperature. The probability that the system has a particular energy is given by:

$$P(E) = \frac{\sum_j \delta(E_j - E) e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

In this expression the sums run over all the available microstates. E_j is the energy of the jth microstate and $\beta = 1/k_B T$. In the low temperature limit it is useful to rewrite this expression in terms of the energy, E_0 of the lowest energy microstate as follows:

$$\lim_{\beta\to\infty} P(E) = \lim_{\beta\to\infty} \frac{e^{-\beta E_0} \sum_j \delta(E_j - E) e^{-\beta(E_j - E_0)}}{e^{-\beta E_0} \sum_j e^{-\beta(E_j - E_0)}} = \lim_{\beta\to\infty} \frac{\sum_j \delta(E_j - E) e^{-\beta(E_j - E_0)}}{\sum_j e^{-\beta(E_j - E_0)}}$$

In the limit as $\beta \to \infty$ $e^{-\beta(E_j - E_0)}$ is one if $E_j = E_0$ and zero otherwise. The probability distribution above thus reduces to:

$$\lim_{\beta\to\infty} P(E) = \begin{cases} 1 & \text{if} \quad E = E_0 \\ 0 & \text{otherwise} \end{cases}$$

In other words, when the temperature is very low the system is guaranteed to be in the microstate with the lowest energy. For the system of 8 particles whose average energy as a function of temperature plot is shown in figure 4 we would thus expect the energy to decrease to a lower bound of -8 as we lower the temperature.

In the high temperature limit $P(E)$ reduces to:

$$\lim_{\beta\to 0} P(E) = \lim_{\beta\to 0} \frac{\sum_j \delta(E_j - E) e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{\sum_j \delta(E_j - E)}{N}$$

where N is the total number of microstates and the second equality holds because $e^0 = 1$. At high temperatures, the probability that the system has a particular energy is thus proportional

to the number of microstates with that energy. In figure 4 we thus see the average energy tending to a value of 0 at high temperature. The reason for this can be understood by reexamining figure 2 which shows that 70 of the 256 possible microstates have an energy of 0. More importantly, however, the distribution shown in figure 2 is symmetric around 0 so the mean for this distribution is the same as the mode.

5 Conclusions

We have shown that the energy for a system of N non-interacting spins increases monotonically with temperature. An analytic expression that relates the average energy for this system to the temperature has been derived. Furthermore, we have shown that the average energies that are obtained numerically by explicitly enumerating over all possible microstates are the same as those that can be obtained from the analytic expressions.

The assumption that particles are non-interacting is pretty severe. Many more realistic models include interactions between the various particles. This makes them more difficult to solve using the analytic techniques because it becomes there are only a relatively small number of integrals and summations can be evaluated exactly.

The alternative approach where the average energy is evaluated by explicit enumeration is also unpractical in many cases because the number of microstates we need to consider scales exponentially with the number of particles and thus quickly becomes enormous. For this reason we need to use approximate, Monte-Carlo approaches to solve many problems in statistical mechanics.