A simulation experiment with a canonical ensemble

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***Abstract*—In trying to get a better understanding of statistical mechanics, I tried a simulation experiment to see how probabilities in a canonical ensemble work. The findings show that at low temperatures, the lower energy states have a higher probability of being filled, with the only the lowest near absolute zero, and that at sufficiently high temperatures, the probability approaches a purely random system.**

I. Defining the System

I started with a system defined by 6 levels of potential energy and 6 levels of kinetic energy. I came up with the idea by thinking of 2 6-sided dice, 1 white representing the potential energy state, and 1 red representing the kinetic energy state. (This is like a dice throw in the game, *craps*, so I will call it that here.) The total energy of the system would be the Hamiltonian defined by the sum of the 2 dice.

I considered a closed system to calculate a *canonical ensemble*. Let the energy levels be represented by the number showing on each die multiplied by a quantized energy, u, so the potential energy and kinetic energy can take on values of u, $2u$, $3u$, $4u$, $5u$, $6u$. Thus, the Hamiltonian (sum of potential & kinetic energy) can have values of $2u$, $3u$, ... , $11u$, $12u$. Based on the possible combinations of craps throw, certain energy levels in the Hamiltonian are redundant (degenerate), e.g., $5u$ has a redundancy (degeneracy) of 4, as it can be formed 4 ways with the 2 dice.

II. The Partition Function

Next, I decided to calculate the *partition function* of this system:

$$Z = \sum_{n=2}^{12} e^{-\beta H_n} \tag{1}$$

where $-\beta = \frac{1}{k_B T}$ and H_n is the Hamiltonian for the sum of the dice, n, e.g., $H_8 = 8u$. Applying all the energy levels, we get:

$$Z = e^{-\beta 2u} + 2\left(e^{-\beta 3u} + e^{-\beta 11u}\right) + 3\left(e^{-\beta 4u} + e^{-\beta 10u}\right) + \cdots$$

$$\cdots + 4\left(e^{-\beta 5u} + e^{-\beta 9u}\right) + 5\left(e^{-\beta 6u} + e^{-\beta 8u}\right) + 6e^{-\beta 7u} + e^{-\beta 12u}$$

This can be rewritten as:

$$Z = 2e^{-\beta 7u}\left[\cosh(5\beta u) + 2\cosh(4\beta u) + \cdots\right.$$

$$\left.\cdots + 3\cosh(3\beta u) + 4\cosh(2\beta u) + \cosh(5\beta u) + 3\right] \tag{2}$$

Now we can calculate the probability of each energy state with:

$$P_n = \frac{g e^{-n\beta u}}{Z} \tag{3}$$

where g is the redundancy (degeneracy) of the n^{th} energy state.

III. Simulations

A. Room Temperature (300 K)

In this initial example, I let T = 300 K ("room temperature") and $u = k_B T$. Using these values, we get a probability mass function (PMF) for the energy states that looks like Figure 1:

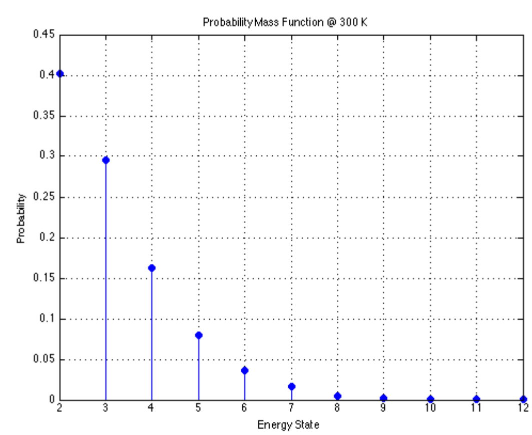

Figure 1. PMF of the system at 300 K

This looks a lot like an exponential decay, as we might see in a Maxwell-Boltzmann probability distribution. However, as a check, plotting $\ln(P_n)$ against the energy states, we get a plot that is not linear, as in Figure 2, so it is not really a pure exponential relation.

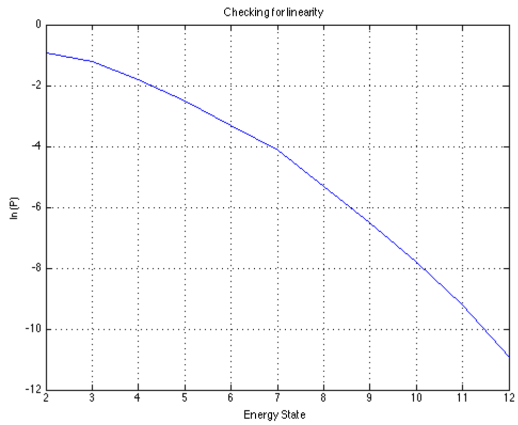

Figure 2. Check for linearity in $\ln\left(P_n\right)$ vs. n

B. 100 K

Keeping the same defined energy levels, I decided to examine the effects of a change in temperature. Figure 3 shows the PMF of the system at 100 K compared to 300 K:

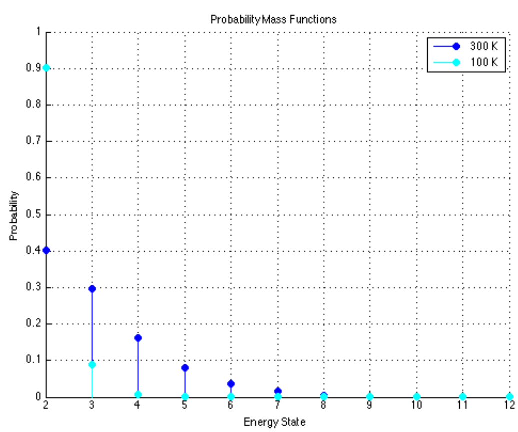

Figure 3. PMF of the system at 300 K & 100 K

There is a marked shift of the probability of energy states toward the lower end, which is expected with the lower temperature.

C. Near Absolute Zero (3 K)

To see the effect near absolute zero, I set T = 3 K, close, but avoiding underflow calculation errors in the MATLAB code I was using. Also, using $T = 0$ would result in division-by-zero errors. MATLAB treat this case as infinity, but it still throws off the calculations.

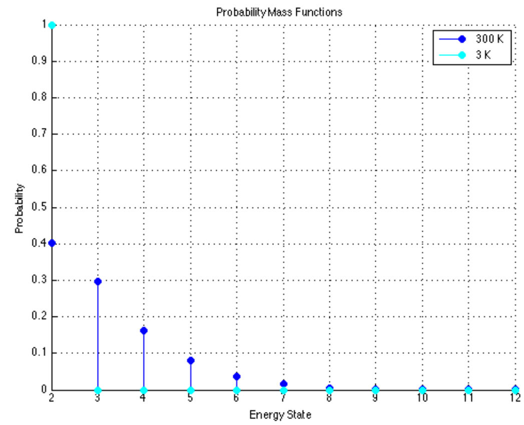

Figure 4. PMF of the system at 300 K & 3 K

In this case, the only occupied energy state is $2u$, the lowest, which is what we would expect near absolute zero. At absolute zero, only the lowest accessible energy state should be occupied, unless there are "crowding" issues, as with fermions.

D. 1,000 K

At higher temperatures, something different occurs. Trying 1,000 K, we get the PMF in Figure 5:

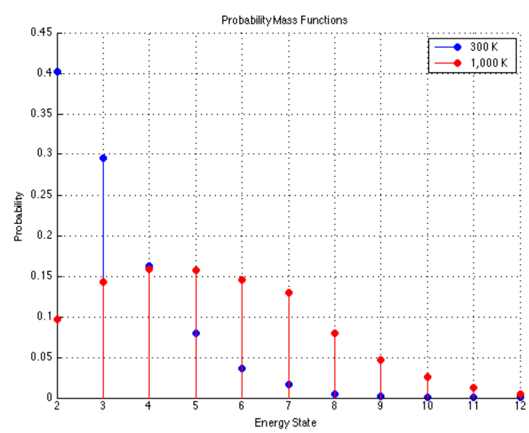

Figure 5. PMF of the system at 300 K & 1,000 K

In this case, with the higher temperature, the PMF loses its appearance to a Maxwell-Boltzmann distribution, further confirming the suspicion it was not, along with the non-linear $\ln\left(P_n\right)$ plot in Figure 2. The energy state for $2u$ is no longer the one with the highest probability. In fact, the PMF curve has shifted toward the higher energy states. This makes sense with a higher temperature.

E. 10,000 K

At 10,000 K, something interesting appears. The PMF strongly resembles that of the PMF for a craps throw, as shown in Figure 6:

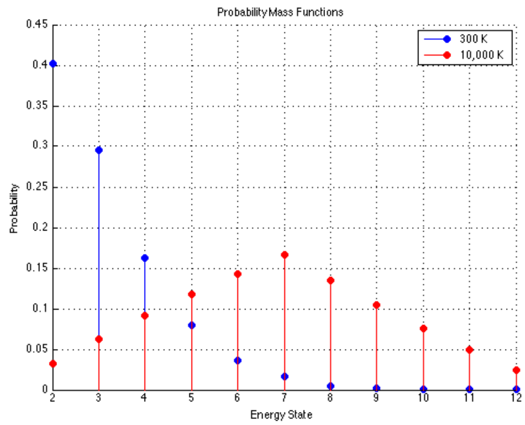

Figure 6. PMF of the system at 300 K & 10,000

The PMF is shifted further toward the higher energy states, which corresponds to the higher temperature, but it loses its "curved" appearance, taking on the triangular appearance of a craps PMF with a mode of $n = 7$. It is close, but not quite exact, which we can tell by comparing the probability values of P_3 and P_{11}. For dice, they should be exactly the same; here, $P_{11} < P_3$, which would indicate the temperature is not quite high enough for the system to favor u_{11} equally to u_3.

In a further test at 1,000,000 K, the PMF of the system is nearly identical to that for craps. This implies that as $T \to \infty$, the PMF will become that for craps.

IV. Conclusion

These simulations show an example of how a closed system defined by a canonical ensemble with arrange the probabilities of its energy states in response to temperature. At absolute zero, only the lowest energy state will be occupied. Approaching an infinite temperature, the states will have a purely random arrangement, conforming to the PMF defining it.

The PMF of the system at 300 K had that appearance only because I had defined the energy states as multiples of $u = k_B T$. For other cases, the PMF will differ naturally.