Partition Function, Average Energy, and Entropy

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1 The Partition Function and the Boltzmann Distribution

The partition function is defined as the sum over all microstates of the system:

$$Z = \sum_n e^{-\beta E_n} \tag{1}$$

with the inverse temperature defined as $\beta \equiv \frac{1}{k_B T}$.

This serves as the normalization factor for the Boltzmann distribution in the canonical ensemble. The probability $p(n)$ of finding the system in a given microstate n is:

$$p(n) = \frac{e^{-\beta E_n}}{Z} \tag{2}$$

2 Averages in Statistical Mechanics

Say you want to measure a macroscopic quantity X from a system at temperature T. The expected value (or average over multiple copies of the system) is given by:

$$\langle X \rangle = \sum_n X_n p(n) = \frac{\sum_n X_n e^{-\beta E_n}}{Z} \tag{3}$$

This concept becomes perhaps most interesting when applied to the average energy of a system.

3 Average Energy

Using the formula above, the average energy $\langle E \rangle$ is:

$$\langle E \rangle = \frac{\sum_n E_n e^{-\beta E_n}}{Z} \tag{4}$$

We can express $E_n e^{-\beta E_n}$ as a derivative with respect to β:

$$\langle E \rangle = \frac{\sum_n \left(-\frac{\partial}{\partial \beta} e^{-\beta E_n}\right)}{Z} = -\frac{1}{Z}\frac{\partial}{\partial \beta}\left(\sum_n e^{-\beta E_n}\right) \tag{5}$$

Recognizing the sum as the partition function Z:

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \tag{6}$$

Using the chain rule property $\frac{d}{dx}\ln(f(x)) = \frac{1}{f(x)} f'(x)$, we arrive at the fundamental result:

$$\boxed{\langle E \rangle = -\frac{\partial}{\partial \beta}\ln(Z)} \tag{7}$$

In this way, Z acts as a moment-generating function for the system.

4 Entropy

What about the entropy? Consider W copies of a system in contact with a large reservoir at temperature T. For a large number of copies W, the number of systems sitting in a specific state $|n\rangle$ is simply:

$$W_n = p(n)W \tag{8}$$

To compute the entropy, we treat the whole collection of W systems as one large microcanonical ensemble, for which we know the Boltzmann entropy is $S_{\text{total}} = k_{\text{B}} \ln \Omega_W$.

What is Ω_W? We must figure out how many ways there are of putting W_n systems into state $|n\rangle$ for each n. This is a standard combinatorics problem (a multinomial coefficient):

$$\Omega_W = \frac{W!}{\prod_n (W_n)!} = \frac{W!}{\prod_n (p(n)W)!} \tag{9}$$

To find the entropy, we take the natural logarithm and apply Stirling's approximation ($\ln N! \approx N \ln N - N$):

$$\begin{aligned}\ln \Omega_W &= \ln(W!) - \sum_n \ln(W_n!) \\ &\approx (W \ln W - W) - \sum_n (W_n \ln W_n - W_n)\end{aligned}$$

Since the sum of the systems in each state must equal the total number of systems ($\sum_n W_n = W$), the linear terms cancel out:

$$\ln \Omega_W \approx W \ln W - \sum_n W_n \ln W_n \tag{10}$$

Substituting $W_n = p(n)W$ and recognizing that $\sum_n p(n) = 1$:

$$\begin{aligned}\ln \Omega_W &\approx W \ln W - \sum_n p(n)W \ln(p(n)W) \\ &= W \ln W - W \sum_n p(n) \left[\ln(p(n)) + \ln W\right] \\ &= W \ln W - W \ln W \sum_n p(n) - W \sum_n p(n) \ln(p(n)) \\ &= -W \sum_n p(n) \ln(p(n))\end{aligned}$$

The total entropy of the W copies is $S_{\text{total}} = -k_{\text{B}} W \sum_n p(n) \ln(p(n))$. Therefore, the entropy for **1 system** is simply:

$$\boxed{S = -k_{\text{B}} \sum_n p(n) \ln(p(n))} \tag{11}$$

(This is known as the Gibbs entropy formula).

4.1 Expressing Entropy in terms of Z

We can substitute our canonical probability $p(n) = \frac{e^{-\beta E_n}}{Z}$ into the entropy formula:

$$\ln(p(n)) = -\beta E_n - \ln Z \tag{12}$$

$$\begin{aligned} S &= -k_B \sum_n p(n) \left(-\beta E_n - \ln Z\right) \\ &= k_B \beta \sum_n E_n p(n) + k_B \ln Z \sum_n p(n) \end{aligned}$$

Since $\sum_n E_n p(n) = \langle E \rangle$ and $\sum_n p(n) = 1$, we get:

$$S = k_B \beta \langle E \rangle + k_B \ln Z \tag{13}$$

Finally, we can rewrite this strictly in terms of Z and T. Recall that $\beta = \frac{1}{k_B T}$ and $\langle E \rangle = k_B T^2 \frac{\partial \ln Z}{\partial T}$:

$$\begin{aligned} S &= \frac{\langle E \rangle}{T} + k_B \ln Z \\ &= k_B T \frac{\partial \ln Z}{\partial T} + k_B \ln Z \\ &= k_B \left(T \frac{\partial \ln Z}{\partial T} + \ln Z \right) \end{aligned}$$

By the product rule for derivatives, this simplifies neatly to:

$$\boxed{S = k_B \frac{\partial}{\partial T} (T \ln Z)} \tag{14}$$