History of the natural log base in statistical mechanics

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11/15/2018

I was thinking why the partition function is an exponential function with base *e* instead of another base. Is there anything special with the natural exponent?

Initially, I though this log base *e* naturally comes from the derivation of the partition function. If we use the sole function method, and consider a body A in a very large heat bath at temperature *T*. The probability of the body A in state *n* is given by

$$P_n = f\left(E_n\right) \tag{1}$$

where E_n is the energy for quantum state *n*. Similarly, for a second body B, the probability is

$$P_k = f\left(E_k\right) \tag{2}$$

In the middle step of the derivation, we'll have

$$\frac{1}{f\left(E_n\right)}\frac{\partial f\left(E_n\right)}{\partial E_n} = \frac{1}{f\left(E_k\right)}\frac{\partial f\left(E_k\right)}{\partial E_k} \tag{3}$$

On the lecture slides, we directly used the property of the natural logarithm and transformed Eq. (3) to

$$\frac{\partial \ln f\left(E_n\right)}{\partial E_n} = \frac{\partial \ln f\left(E_k\right)}{\partial E_k} \tag{4}$$

Because body A and body B are independent of each other, the right-hand side and the left-hand side must equal to a constant for Eq. (4) to hold. Thus,

$$\frac{\partial \ln f\left(E_n\right)}{\partial E_n} = \frac{\partial \ln f\left(E_k\right)}{\partial E_k} = -\beta \tag{5}$$

and we have

$$f\left(E_n\right) = Ce^{-\beta E_n} \tag{6}$$

where *C* is a constant and the natural exponential function just comes out mathematically. However, if we revisit Eq. (3) and multiply both sides by (1/ln*a*), where a is any positive constant, Eq. (3) is equivalent to

$$\frac{1}{\ln a * f\left(E_n\right)} \frac{\partial f\left(E_n\right)}{\partial E_n}=\frac{1}{\ln a * f\left(E_k\right)} \frac{\partial f\left(E_k\right)}{\partial E_k} \tag{7}$$

If we still follow the same procedure above but without cancelling out ln*a* on both sides, we will have,

$$\frac{\partial \log_a\left[f\left(E_n\right)\right]}{\partial E_n}=\frac{\partial \log_a\left[f\left(E_k\right)\right]}{\partial E_k}=-\beta \tag{8}$$

and thus, Eq. (6) becomes

$$f\left(E_n\right)=C a^{-\beta E_n} \tag{9}$$

where the probability distribution is an exponential function with log base *a*. If above argument holds, we can see that the partition function actually can be written as an exponential function with any base. Then the question turns into why we should use the natural exponent in the partition function.

To answer this question, I went back to the original paper by Ludwig Boltzmann in 1877 where he for the first time related the microscopic states with the macroscopic entropy[1]. In that 1877 paper, he didn't propose the famous entropy equation $S=k\ln W$, but twenty years later, Max Planck introduced the $S=k\ln W+const$ via citation of Boltzmann's 1877 paper[2]. The prefactor *k* was introduced by Planck, but named after Boltzmann. In Planck's paper, he directly used natural log in the entropy equation without explaining the reason. Later, J.W. Gibbs formulated the modern statistical mechanics following the fashion of Boltzmann and Planck, i.e., using natural logarithm in the math.

Therefore, the conclusion is that there is nothing special with the natural exponent used in the modern statistical mechanics, it is chosen maybe just because of its mathematical convenience. In principle, we can use the logarithm with any base in the entropy equation as long as we use the same log base throughout the whole statistical mechanics system for self-consistency. If that is the case, the Boltzmann factor will be a different number from the current SI value of 1.38*10^-23 J/K.

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[1] I luckily found a translation of Boltzmann's original paper. https://www.mdpi.com/1099-4300/17/4/1971

[2] Max Planck, "On the Law of Distribution of Energy in the Normal Spectrum", http://bourabai.kz/articles/planck/planck1901.pdf