

# PROBABILITY IN STATISTICAL MECHANICS REINTERPRETED

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Examined is a consequence of using the probability to calculate both the entropy of a system and as a measure of the likelihood of the system being found in a specific microstate. Using three simple examples, it is found in each case that a contradiction exists. The contradiction arises if we require that the entropy of a microstate in which the system can be found must equal that of the systems entropy as calculated using quantum statistical mechanical theory. It is argued that the contradiction can be resolved by retaining the usual equations of statistical mechanics, but interpreting the meaning of the probabilities so that they no longer provide a measure of the system being found in a specific microstate.

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Probability in statistical mechanics is used in two different ways. The entropy of the system is computed using the probabilities as is the chance that the system will be found in a particular microstate. We look at two particularly simple systems to show that the usual meanings ascribed to the probability lead to a contradiction. In order to resolve the contradiction we offer an alternate interpretation.

Consider a simple system consisting of a 50/50 mixture of “red” and “green” atoms arranged on a line. The system is isolated and at equilibrium. We ignore fluctuations and vibrations.

For a system consisting of  $n$  atoms, the atoms can be arranged in  $M$  unique configurations or microstates, where

$$M = \frac{n!}{\left(\frac{n}{2}\right)!\left(\frac{n}{2}\right)!} \quad (1)$$

We denote the ket corresponding to microstate  $i$  by  $|\psi_i\rangle$ .

The ket corresponding to the state of the system,  $|\Psi\rangle$ ,

$$|\Psi\rangle = \sum_{i=1}^M c_i |\psi_i\rangle \quad (2)$$

The quantity  $p_i$  is given by

$$p_i = c_i^* c_i \quad (3)$$

At equilibrium

$$p_i = 1/M \text{ for all } i. \quad (4)$$

We arbitrarily pick one possible microstate of the system, say,

...R, G, G, G, R, G, R, R, G, ...

This microstate has a symmetric microstate

...G, R, R, R, G, R, G, G, R, ...

More generally, for every possible configuration of red and green balls there is a symmetric configuration such that there is a red ball on a site in one configuration and a green ball on the same site in the symmetric configuration.

Summing over all microstates the probability of finding a red ball on site  $k$ ,  $q_k^r$ , is

$$q_k^r = \frac{1}{2} \sum_{i=1}^M p_i, \quad (5)$$

or as  $\sum_{i=1}^M p_i = 1$ ,

$$q_k^r = \frac{1}{2} \text{ for all } k. \quad (6)$$

When there is a 50/50 chance of finding a red ball at each location on the line, the distribution is random [1]. We have the not surprising result that the equilibrium state of this system consists of a random arrangement of red and green balls on the line.

Following this line of reasoning, the requirement that equilibrium state is random means that non-random microstates such as

...R, G, R, G, R, G, R, G, R, G, ...

and

...R, R, R, R, R, G, G, G, G, G, ...

can never occur, though they entered into the calculation of the chance of finding a red ball on a site.

We have a contradiction. On one hand, the  $p_i$ 's, corresponding to both equilibrium and non-equilibrium microstates are all equal and each of them contribute via Eq's (2) and (3) to the

description of the state of the system  $|\Psi\rangle$  as a function of the  $|\psi_i\rangle$  kets. On the other hand the same  $p_i$ 's lead to the conclusion that the system must be in a random microstate. This implies that non-random microstates cannot occur. We resolve the contradiction by retaining the above equations, including the definition of  $p_i$  in Eq. (3), but we no longer use the “probability”  $p_i$  as a measure of the chance that the system will be in a particular microstate.

A second way of looking at this contradiction is to examine the entropy of the system defined by the state ket  $|\Psi\rangle$  and compare it to that of a microstate, both at equilibrium.

The entropy for the system,  $S^{\text{sys}}$ , is given by

$$S^{\text{sys}} = -k \sum_{i=1}^M p_i \ln p_i \quad (7)$$

At equilibrium we can substitute  $p_i$  from Eq. (4) to give

$$S^{\text{sys}} = k \ln M . \quad (8)$$

Substituting  $M$  from Eq. (1) and using Sterling's approximation yields

$$S^{\text{sys}} = kn \ln 2 . \quad (9)$$

The entropy of a single random microstate in the above equilibrium system can be found using information theory [2, 3]. The uncertainty, or entropy on one site  $k$ , in thermodynamically consistent units is

$$s_k = -k(q_k^r \ln q_k^r + q_k^g \ln q_k^g), \quad (10)$$

where the superscripts  $r$  and  $g$  stand for red and green, respectively. As both  $q_k^r$  and  $q_k^g$  are  $1/2$ ,

$$s_k = k \ln 2 . \quad (11)$$

There are  $n$  sites and as the probabilities for each site are independent we obtain for the entropy of the microstate,  $S^{\text{ms}}$ ,

$$S^{\text{ms}} = kn \ln 2 . \quad (12)$$

Thus

$$S^{\text{sys}} = S^{\text{ms}} . \quad (13)$$

At equilibrium the entropy of the system  $|\Psi\rangle$  is a function of all the  $p_i$ 's; the entropy of a microstate is a function only of the arrangement of atoms in that microstate. We make the fundamental assumption that the entropy of the system in state  $|\Psi\rangle$  at equilibrium must be the same as the entropy of the microstate in which we find the system. This implies that as non-random microstates do not have the same entropy as that of the system, they can never occur. The  $p_i$ 's should not be interpreted as the probability that the system will be in a particular microstate.

We now consider a more general case of an isolated system at equilibrium, consisting as before of a line of  $n$  atoms. Each atom on a site can take on a quantized range of values, such as momentum. Again we calculate the entropy.

We denote by  $q_{kj}$  the probability of an atom on site  $k$  taking on a specific value with an index  $j$ . At equilibrium, in order for the entropy of the system to be a maximum, atoms with property  $j$  must be randomly arranged on the line. Or equivalently,  $q_{kj} = q_{lj}$  for all  $k$  and  $l$ . As  $q_{kj}$  is independent of  $k$ , we use  $q_j$  in the following.

For each site

$$\sum_{j=1}^r q_j = 1, \quad (14)$$

where the property can take on  $r$  values. The total number of particles with property  $j$ ,  $b_j$ , is

$$b_j = q_j n. \quad (15)$$

The number of ways,  $M$ , the  $b_j$  particles can be arranged on the line is

$$M = \frac{n!}{\prod_{j=1}^r b_j!}. \quad (16)$$

Substituting  $M$  into Eq. (8), using Sterling's approximation and Eqs. (14) and (15) yields for the entropy of the system,  $S^{\text{sys}}$ ,

$$S^{\text{sys}} = -nk \sum_{j=1}^r q_j \ln q_j. \quad (17)$$

Using the information theory approach, the entropy for a single site,  $s_k$ , in an equilibrium microstate is

$$s_k = -k \sum_{j=1}^r q_j \ln q_j . \quad (18)$$

Multiplying the RHS of Eq. (18) by  $n$ , as there are  $n$  sites, yields for the entropy of the microstate,  $S^{ms}$ ,

$$S^{ms} = -nk \sum_{j=1}^r q_j \ln q_j . \quad (19)$$

At equilibrium the entropy of the system is equal to the entropy of an equilibrium microstate, again satisfying Eq. (13).

As in the first example, the  $p_i$ 's associated with all the  $M$  microstates, equilibrium and non-equilibrium, are needed for the calculation of the entropy of system  $|\Psi\rangle$ . But, as there, we expect that the system can only be in a microstate that has the same entropy as  $|\Psi\rangle$ .

Microstates that have lower entropy than that of a system at equilibrium are not accesable. This is accord with the second law of thermodynamics, where an isolated system cannot spontaneously take on a microstate with lower entropy.

We now consider the general case where our viewpoint is inspired by the above.

Consider an isolated thermodynamic system. The system need not be in equilibrium.

The state of the system  $|\Psi\rangle$  is given by Eq. (2) and the quantities  $p_i$  are given by Eq. (3). The entropy of the system is given by Eq. (7). As  $|\Psi\rangle$  evolves its entropy  $S^{sys}$  evolves as given by Eq. (2), (3) and (7).

The microstate that the system is in evolves so that its entropy remains equal to that of the entropy of the system. Microstates that do not have the same entropy as the system can never be accessed.

## Summary

We described the state of a isolated thermodynamic system two ways. The first is the quantum mechanical description given by the state ket. The second is in terms of the properties of the atoms in a microstate. Standard quantum and statistical mechanical theory calls for the system at equilibrium to be equally likely in any microstate, irrespective of whether or not that microstate has the same entropy as the state ket. We asserted that the entropy of a microstate must be the same as that of the state ket. Microstates with other entropies cannot be observed irrespective of the value of their associated probabilities.

## References

1. E. Beltrami, *What is Random?*, (Copernicus, Springer-Verlag, New York, 1999) Kindle Edition Location 235 (approximately)
2. A. I. Khinchin, *Mathematical Foundations of Information Theory*, (Dover, New York, 1957) P. 3
3. E. T. Jaynes, "Information Theory and Statistical Mechanics," *Phys. Rev.*, **106**, (1957), 620

*What is Random...* Location 235

"...the quintessential example of a random process...: The succession of zeros and ones is independent and uniformly distributed with each digit having an equal chance of occurring."