Maximum Entropy, Bias Removal, Conserved Quantity and Second Law of Thermodynamics

Francesco R. Ruggeri Hanwell, N.B. July 12, 2023

Given an unbiased die, the probability is ⅙ for a result. This probability value may be obtained directly by imposing the condition of a lack of bias and noting there are six possible results. Alternatively, one may maximize Shannon's entropy subject to the constraint Sum over i p(i)=1 where i runs from 1 to 6. Maximization of Shannon's entropy seems to remove as much bias as possible with the constraint indicating what bias remains. For the die case the constraint has no bias, but for an average energy constraint Sum over i ei p(i) there is, namely ei.

In previous notes we have argued that the constraint used in the maximization of entropy is "special". Here we argue that it represents a conserved quantity if interactions occur. Thus there may be many constraints in a system, but choosing a conserved quantity in an interaction is rarer, but seems to be linked with equilibration. Finally, we suggest that maximization of entropy subject to a conserved quantity constraint removes as much bias as possible and it is this maximized entropy-probability which is subject to the second law of thermodynamics.

It is possible, however, to have probabilities and to create entropies which are not based on maximization of entropy. For example, Shannon's entropy may be applied to the spatial density of various n-slit interactions for a particle with constant momentum p. In this case, even though there is no maximization of entropy, the emerging particle has the same p magnitude (hence same uncertainty within a wavelength), but there is the added uncertainty of its direction. As a result, it seems that entropy increases in accordance with the second law.

A free particle with momentum p, however, has a two dimensional probability distribution in space exp(ipx) characterized by a wavelength hbar/p. This may be taken as related to the entropy of the free particle, but a free particle may undergo spontaneous interactions which either increase or decrease p, hence increase or decrease hbar/p and entropy. In other words, the second law does not apply to such an entropy, but this entropy is associated with an unusual constraint. This conclusion seems to hold when one considers two body scattering. Thus we suggest that there are various kinds of entropy. Some are linked with maximization of entropy subject to a conserved quantity constraint (and are associated with equilibration) and others are not. The latter do not necessarily obey the second law of thermodynamics, we argue.

The Case of a Die

A die consists of six sides. If there is no bias, the probability for each possible result must be the same and given that probability adds to 1, p(i)=⅙. This result may alternatively be obtained by maximizing Shannon's entropy - Sum over i p(i) ln(p(i)) subject to the constraint Sum i=1 to 6 p(i) = 1. Shannon's maximum entropy approach seems to remove bias from the problem. We ask how this occurs. Consider a set of p(i) which add to 1. For a large number of trials N→ infinite, the product probability associated with a specific N trial run is:

Probability of a trial = Product i $p(i)^{Np(i)}$ = exp{ Sum over i ln(p(i)) Np(i) } ((1))

This result is the same for any trial run with N→infinite. At this point the p(i) are completely unknown except for the fact that they sum to 1. If there is no bias in the system one may suggest minimizing the probability which means maximizing the argument of the exponent subject to the constraint sum over i p(i)=1. We argue that the purpose of introducing maximization is to remove any possible bias. We also stress that for the case of a die, no physical interactions occur as in gas of colliding particles.

Gas of Colliding Particles

For the case of colliding particles one may at first ignore collisions and ask: What probability maximizes Shannon's entropy subject to the constraint Sum over i ei p(i) where ei is single particle energy. In this case, ei means each particle has a bias. One may immediately ask: Why is ei used in the constraint instead of ei*ei etc.? As we have noted before, ei is a "special" constraint and we try to explain why it is used. First, however, we wish to show that the Maxwell-Boltzmann result may be obtained without any notion of collisions by maximizing:

- Sum over i p(i) ln(p(i)) + 1/T Sum over i ei p(i) ((2))

The result p(i)=C exp(-ei/T) ((3)) follows where 1/T is a Lagrange multiplier.
In the scenario of no collisions, the maximization of ((2)) suggests a minimization of overall probability (maximization of possible outcomes or removal of as much bias as possible) subject to the constraint ei p(i) which includes bias which one cannot remove. At this point ei does not have to be a conserved quantity as there are no interactions/collisions.

Next consider the reality of physical interactions i.e. two body collisions. This means that for a gas with N->infinite particles, there are Np(i) particles with energy ei. It is possible for a collision to occur for particles with ei and ej. In the above discussion, ei and ej are simply parameters associated with the particles such that they have a fixed average value i.e. the constraint in the maximization problem. If ei and ej interact, then n(i)-->n(i)-1 and n(j)-->n(j)-1 and one ei and one ej disappear. Assume that i and j become k and l leading to an extra ek and el in the system. Next assume that ei+ej not= ek+el. If one assumes that at the same time a k and l become an i and j, globally everything is balanced and there is no need to assume that ei+ej=ek+el. Locally, however, this would mean that energy could disappear from one local region and instantaneously appear at another quite a distance away. We rule this out on physical grounds and so suggest that:

ei+ej = ek+el ((4))

As a result, the constraint associated with a maximization of Shannon's entropy problem is special, it must represent a conserved quantity in an interaction. In such a case, maximizing subject to this constraint removes all possible bias except that carried by the constraint.

Second Law of Thermodynamics

The second law of thermodynamics suggests that entropy remains constant or increases in a spontaneous interaction i.e. without work being done. We suggest that this law applies to entropies based on probabilities associated with maximization of entropy subject to a conserved quantity constraint. In such a case, the maximization process suggests that as much bias as possible is removed i.e. as many single particle possibilities are included subject to the bias of the conserved quantity constraint. In other words, a system will not spontaneously introduce bias in order to reduce single particle degrees of freedom when the probabilities themselves follow from a maximization of entropy subject to a constraint process. In other words, we argue that maximization of entropy subject to a constraint and the second law of thermodynamics are complementary.

N-Slit Diffraction-Interference

For the case of a free particle with wavefunction exp(ipx) passing through an n-slit system, there is originally the uncertainty (entropy) associated with the wavelength. After passing through the system, p magnitude is the same, so the wavelength and its uncertainty is the same. There is, however, an added uncertainty in the direction of the p vector from the point of view of someone viewing the process. Thus one may argue that in this case, even though there is no maximization of entropy subject to a constraint, the process increases the entropy by maintaining the uncertainty due to the wavelength and adding more uncertainty due to the direction of p.

Probabilities which Violate the Second Law of Thermodynamics

Shannon's entropy may be constructed using probabilities not associated with maximization of entropy subject to a conserved quantity constraint. Consider the case of a gas. Each particle has a momentum p and a nonrelativistic energy E=pp/2m. According to quantum mechanics, there exists a period hbar/E and a two dimensional probability in time, exp(-iEt)/sqrt(t1), and a wavelength hbar/p and a probability in space exp(ipx)/sqrt(L). One may consider the wavelength and the period as relevant pieces of information, but these are not conserved quantities. Furthermore, one may introduce temporal and spatial entropy using:

P(t) = C1 |cos(hbar t/E)| ((5a)) and P(x) = C2 |cos(hbar x/p)| ((5b))

For P(t) and P(x) to be normalized to 1, C1 goes as 1/E and C2 as 1/p. This suggests that Shannon's entropy in time goes as: C3+ln(E) ((6a)) and in space as: C5 + ln(p) ((6b)).

Spontaneously, interactions occur for which p,E increase or decrease. This means the entropy of ((6)) may spontaneously increase or decrease. { Note: One may consider an elastic two body collision. In such a case, momentum and energy are conserved, but the wavelength or period is not. If uncertainty (i.e entropy) is associated with these, it seems that overall there may be an increase or decrease in system entropy as both the forward and backwards reaction may spontaneously occur. It does not seem that the entropies of the two colliding particles equals that of the final result.}This does not seem to be a problem, however, because this entropy is associated with probabilities which are not maximized subject to a conserved quantity constraint which serves as the information in the problem.

A second example is that of a quantum bound state. The two dimensional exp(ipx) probability is used to create a linear combination called a wavefunction: Sum over p a(p)exp(ipx). This is similar to the n-slit approach, but an n-slit system utilizes a sum over different x paths and there is no further constraint. For the bound single particle, one has a sum over different p's, but no maximization of entropy is applied. Rather one calculates an average kinetic energy {Sum over p a(p) pp/2m exp(ipx) } / {Sum over p a(p)exp(ipx)} and adds it to V(x) to obtain a constant energy En which may have discrete values. One may create Shannon's entropies using W*(x)W(x) and a*(p)a(p) where W(x)=Sum over p a(p)exp(ipx), It may be noted, however, that a system in a state n may spontaneously change to level n+1 or level n-1. Thus one may have spontaneous increases or decreases in entropy as this entropy is not based on any maximization. If one considers the the photon and an infinite well potential and uses spatial uncertainty as the basis of entropy, the photon, according to ((5b)) has an entropy linked with ln(2n+1), but using W(x)W(x) as the probability for the particle, its spatial entropy is independent of n. Thus there is more spatial entropy for a state n with a photon with energy proportional to (2n+1) than for a state n+1, yet absorption occurs spontaneously and is not associated with work because no external parameter in the system changes.

In other words, it seems that there is no equilibration based on accessing all degrees of freedom except those prevented by the bias of a constraint. In the quantum bound state system there is a constraint, but the p-probabilities exp(ipx) are fixed by constant p motion. For equilibration to occur, there would need to be a balance between photons being absorbed and emitted and this scenario ignores the intrinsic entropy of a bound state.e.g. -Integral dx Wn(x)Wn(x) ln{WnWn} - Integral dp an(p)an(p) ln{an(p)an(p)}.

A Note on exp(ipx)

In the above section, we noted that considerations of the probability |cos(px)| from exp(ipx) together with the information related to hbar/p or the entropy linked with ln(p) is not linked with maximization of entropy or a conserved quantity. We have, however, argued that exp(ipx) may be obtained for a fixed x point by maximizing Shannon's entropy subject to a purely imaginary Lagrange multiplier and the conserved quantity momentum i.e.

p(k) ln(p(k)) - ix kp(k) → p(k) = exp(ikx) ((7))

For the case of motion, however, x does not remain a constant value, but takes on a range of values with exp(ipx) representing the two dimensional probability. If such an object encounters an n-slit system, then one does not maximize entropy subject to an conserved quantity constraint, but automatically considers various exp(ipx) values in an OR (add) situation, with each going through one slit. We argue that some probabilities and entropies follow from maximization associated with a conserved quantity and others do not. It seems that the second law of thermodynamics is not universal to all entropies.

An alternative to ((7)) is to maximize probability with x being the conserved quantity i.e. x1+x2=xtotal. The Lagrange multiplier is again purely imaginary to obtain a periodic result, but p is the magnitude. Then one maximizes p(x) ln(p(x)) -ip xp(x). Thus a kind of maximization appears, but does not seem to be associated with any kind of equilibration involving a distributed quantity as in the case of energy.

Conclusion

In conclusion, we first argue that the process of maximizing Shannon's entropy subject to a constraint creates a probability with all bias removed, except that in the constraint. We further argue that the constraint must be associated with a conserved quantity. Finally, we argue that a situation in which all possible bias is removed is consistent with the second law of thermodynamics.

It is possible, however, to introduce a probability which is not associated with maximization of entropy subject to a conserved constraint. Furthermore, one may consider relevant information which is not conserved. As an example, we consider the case of a free particle with two dimensional probability exp(ipx) and information linked to the wavelength hbar/p. If one defines a probability C |cos(hbar x/p)|, then Shannon's entropy is C1 + ln(p). Neither hbar/p nor ln(p) are conserved. Furthermore, collisions allow for p to either spontaneously increase or decrease, violating the second law of thermodynamics. Similarly arguments hold for exp(-iEt) and for quantum single particle bound states. Thus we argue that not all probabilities are associated with a maximization of entropy and so do not remove biases. In such cases, one may have entropy increase or decrease spontaneously.

References

1. https://en.wikipedia.org/wiki/Particle_in_a_box