

Factorial Counting in Ensembles and Statistical Mechanics

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In statistical mechanics, microcanonical factorial counting applied to systems in an ensemble is approximated by a canonical distribution with a weight of $\exp(-E/T)$ (where E is the energy of the fixed N particle system). Such an approach is even applied to a “hot” nucleus with $E = \sum_i e_i$. In such a case, however, no mention is made of the number of particles in a system, implying such a statistical approach should apply to very small numbers of particles. It is only when the canonical distribution $\exp(-E/T)$ is approximated by the grand canonical $\exp(-(E-uN)/T)$ where N is the number of particles in a system that one finds that $\langle N^2 \rangle - \langle N \rangle^2$ approaches zero for large N . Then, restrictions to large numbers of particles are made. In previous notes, we have argued one may describe a statistical system in terms of reaction balance and have tried to map such a balance into a factorial scheme, thus linking it to traditional statistical mechanics. Thus, we argued there is no a priori reason for the counting of different arrangements to have meaning unless it maps into reaction balance. In this note, we wish to examine more closely equilibrium with a small number of particles to see if there is a simple map between factorial counting (arrangements of an ensemble) and reaction balance. We try to argue that there is not and that reaction balance alone applies to such cases.

Scattering and Energy Conservation

We argue physical reactions occur in a system and are governed by conservation of energy in equilibrium as well as by probabilities for the reaction to occur. A reaction does not necessarily require two objects (as in two body scattering), but the energy of a particle must change, thus the change in energy must be transferred to a second entity. Therefore, the time reversed reaction does involve at least two entities. If one considers “and” probability, then multiple entities in a reaction lead to a product of probabilities, one factor per entity. Taking the \ln of such an expression leads to a conservation law which one may try to equate to conservation of energy. Thus,

$$\ln(\text{probability to react}(e)) = -(e-u)/T \quad ((1))$$

where u and T are constants. In other words, the probability for an entity with e to react (not exist) in an equilibrium system is related to the energy itself, in fact the relationship is of the form of ((1)). Furthermore, it is often argued that:

$$\text{Probability to react}(e) = g(f(e)) \text{ where } f(e) \text{ is the number of particles with energy } e \quad ((2))$$

One has to be careful with ((2)), however. ((1)) applies to each kind of reaction, but a particle with energy e may be involved in many reactions or even the same reaction within different configurations (e.g. electrons in an excited atom). Later, a system with two electrons and three

energy levels is examined using reaction balance. ((1)) is still used, but writing $g(f(e))$ may only apply for large particle numbers where one may approximate results by the use averages. It is also good to consider issues associated with energy. Consider a system which has N particles and only two allowable reactions e_1+e_2 to e_3+e_4 and the reverse. Imagine there is a wall at temperature T and that the system is in equilibrium. Next, add N_2 extra e_1 particles. Then, a readjustment would be needed such that the fractions related to N_2 change from 100% of e_1 particles to $N_2 C \exp(-e_i/T)$.

We suggest in this note, that one may develop mathematical schemes which lead to ((1)). It seems one maps the scheme to ((1)) and so the scheme may have some physical meaning, but only if it maps to the reaction balance approach. We argue the scheme itself should not be taken as a fundamental principle, rather reaction balance is the principle. A scheme that may lead to ((1)) is:

Imagine one wishes to map reaction probabilities $g(f(e))$ in space to a line. Then, one might try to use various factorial schemes to obtain such an arrangement e.g.

$M! / (m_1! m_2! \dots)$ ((3a)) where m_1 is the number of particles with energy e_1 .

In general, one may maximize \ln of ((3a)) by changing m_i subject to $\sum \text{over } i \ m_i = M$ ((3b)) and $\sum \text{over } i \ e_i m_i = E$ and ((3c)). A question arises, however, as to why one should maximize \ln of ((3)) and not ((3)) itself. For large m_i values, one may argue there is a math approximation, Stirling's approximation. Thus, the argument is that one uses \ln simply because of Stirling's approximation. It should be pointed out, however, that this approach converts ((3a)) into the form:

$\sum \text{over } i \ q(m_i)$ ((4))

This leads to independent equations for m_i if one maximizes with respect to m_i and adds constraints. Thus, each of these independent m_i terms is set to 0 or:

$\ln(q(m_i) + b_1 + b_2 e_i) = 0$ ((5))

This maps directly back into ideas used for reactions and conservation of energy. One may try to assign physical meaning to the arrangements in ((3a)), but one may argue this is a little forced. In any event, the physical meaning attached does not necessarily represent a fundamental principle of nature, as one can devise other mathematical schemes which yield the same result ((5)).

This may perhaps be seen more clearly if one considers low m_i values. In such a case, there is no use of Stirling's approximation and so no justification in taking the \ln of ((3a)) unless by using \ln one really wants to map to the reaction approach ((1)). What is interesting is that for small m_i , ((3a)) yields almost the same results as Stirling's approximation:

$$Q = \ln(M!/[m_1! m_2! \dots]) = \ln(M!) - \sum_i \ln(m_i!) \quad ((6))$$

$$Q(m_1+1) - Q(m_1) = \ln[(m_1+1)/m_1] \quad ((7))$$

Linking ((7)) to the constraint $\sum_i m_i + \sum_i e_i m_i$ and setting to zero yields:

$$\ln[(m_1+1)/m_1] = (e_1 - u)/T \text{ where } u \text{ and } T \text{ are constants}$$

$$\text{This yields } m_1+1 = m_1 \exp((e_1 - u)/T) \text{ or } m_1 = 1 / [1 - \exp((e_1 - u)/T)] \quad ((8))$$

This is not that same as ((1)). If there are not too many e_i levels and N is of the order of 10 or so, ((8)) may be very similar to the Maxwell-Boltzmann factor.

We argue that in the case of low number so particles, the factorial approach does not match the simple reaction balance case ((1)) exactly. Thus, the idea of counting system arrangements in an ensemble is an approximation at best.

More complicated scenarios than ((1))

((1)) yields a reaction balance for a particular reaction. In a system, however, many reactions may occur and it is possible that for small numbers, these reactions are not decoupled. Thus, ((1)), a reaction balance, may apply to each and one may possibly add in effects such as Pauli blocking and boson enhancement if photons or phonons are being absorbed or emitted. In (1), an example of the following three energy level, 2 electron system is given:

N1 cases of: 1 e1 0 e2 1 e3
 N2 cases of: 0 e1 1 e2 1 e3
 N3 cases of: 1 e1 1 e2 0 e3

By explicitly considering reactions which do not violate Pauli blocking, it was found that:

$$N_1 = x \quad N_2 = x [n(n+2) + n^2(2n+1)] / [n^*n + n^2(2n+1)] \quad N_3 = N_2 (2n+1)/n - x(n+1)/n \quad ((9))$$

where $n = 1/[1 - \exp(-e/T)]$ and $n_2 = 1/[1 - \exp(-2e/T)]$ where e is the interlevel spacing energy

If one considers the low temperature case, where $e \gg T$, then $n \approx \exp(-e/T)$ and $n_2 \approx \exp(-2e/T)$, then one would expect N_3 to be the largest, followed by N_2 and then N_1 . Carrying out this approximation yields $N_3 = 1/(n^*n)$, $N_2 = 1/n$ and $N_1 = 1$. Here $1/n$ is large.

The above problem may be solved in an alternative way. In the method used above, it is assumed that if an electron in a scenario N_1 , N_2 or N_3 occupied a state, this electron blocks the other electron from moving into the state. We now consider a transformation from the N_1 state

to the N3 state and balance it with the time reversal reaction and consider probabilities for both electrons at the same time.

N1 to N3 balance

Let $C = N1 + N2 + N3$ (normalization constant)

$$N1/C (n2+1) [1 - N1/C (n+1)] + [N1/C (n+1)]^2 = N3/C n2 [1 - n N3/C] + (nN3/C)^2$$

In the low T limit, $n = \exp(-e/T)$, $n2 = \exp(-2e/T)$ and $N3 > N2 > (N1=1)$ so one may approximate $C = N3$. Then, the above yield $N3 = 1/(n*n)$.

Next, consider N1 to N2:

$$nN1/C [1 - (1+n2)N1/C] + (nN1/C)^2 = nN2/C [1 - (n+1)N2/C] + [(n+1)N2/C]^2$$

Again, assuming $C \approx C3$, $N1=1$, $n = \exp(-e/T)$ and $n2 = \exp(-2e/T)$ gives $N2 = 1/n$. These are the results of the previous method.

Consider the example of a particle in state e3. There are two scenarios for this. In N1 cases, e3 may decay to eg while in N2 cases it may decay to e1. Thus, due to Pauli blocking, one cannot simply argue the probability for e3 to decay is proportional to $f(e3)$ or a modified $f(e3)/(1-f(e3))$ in this case of small particle numbers. It seems only in the case of large particle numbers that one may use this approximation. Thus, previous notes as well as the work of Kaniadakis (2) which argue for:

$$\ln(g(f(e))) = -(e-u)/T \quad ((10))$$

really apply to large particle numbers.

It is these large particle scenarios which may be easily mapped into factorial schemes. For example, ((10)) has been argued in previous notes to map into a $M! / (m1! m2! \dots)$ scheme.

For the small number case considered above, with N1, N2 and N3, if one applies the "arrangement of systems in an ensemble" approach which appears in textbooks, one would again use:

$$M! / (N1! N2! N3!) \quad ((10)) \quad \text{with } N1 + N2 + N3 = M$$

it seems. This, however, does not match the results ((9)). Thus, for small particle number equilibrium based on reaction balance, it does not seem there is a simple mappable system arrangement scheme. This, we argue, it seems one should use caution when taking factorial arrangement schemes very seriously or from considering them as representing fundamental

physical principles. On the other hand, we argue reaction balance is a physically based approach. In addition, in obtaining ((9)), one considers specific electron level pictures yielding N_1 , N_2 and N_3 and so purely statistical arguments are not being used even though every reaction itself is treated using ((1)). Furthermore, ((1)) is based on energy conservation more than statistics, it seems.

It should be noted that in obtaining ((9)), a Bose-Einstein distribution is assumed for the photons. In (3), it is shown that the BE distribution may be obtained directly from a two level reaction balance scheme.

Conclusion

In conclusion, we argue that reaction balance is a physical approach to establish equilibrium results. In the case of large numbers, one may use $\ln(g(f(e))) = -(e-u)/T$ where g is a function related to the physics of the reaction, for example $g=f/(1+f)$ for bosons and $g=f/(1-f)$ for fermions. In such a case, one is dealing with large numbers and using “average values”. Thus, for fermions a level is blocked on average by $f(e_i)$, i.e. the average presence of a particle in level e_i . One may then map this approach into a factorial scheme as well as link to Kaniadakis entropy density $\int df \ln(g(f))$ which in turn links to the grand canonical partition function. We argue that reaction balance also pertains to small numbers of particles. One does not need to consider factorial arrangements of systems in an ensemble in such a case, but one cannot use average schemes like $f/(1-f)$ for fermions. One must consider different allowable reactions and balance them. In such a case, even without fermions $f(e)$ is not the probability for a particle with energy e to react because there may be two scenarios, with different weights N_1 and N_2 associated with different reactions. In other words, reactions are not decoupled. One applies a balance to each. The results, which we have tried to show above, do not map into a factorial arrangement of systems in an ensemble. Thus, we argue one should be cautious when assigning physical principles (e.g. maximization of arrangements) to equilibrium problems. We try to argue that reaction balance is the principle to use.

References

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