Time Reversal Balances and the Effect of Flux in Statistical and Quantum Mechanics

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In a previous note (1), we argued that the Maxwell-Boltzmann (MB) distribution exp(-p*p/2mT) and similar forms such as exp(-e1/T) and exp(-V(x)/T) were based on reactions of the form P(p1)P(p3)=P(p2)P(p4) or P(p1)V(1 to 2) = P(p2)V(2 to 1) ((1)) where p1, momentum, is being scattered into p2. Taking the natural log of this expression and comparing it to a conservation of kinetic energy (or energy levels in other cases) leads to the form exp(-p*p/2mT). This approach was applied to static statistical mechanics with a potential V(x), statistical mechanics with time independent flow, quantum mechanics with a temperature and fixed energy levels and the T=0 ground state quantum oscillator. It was argued that the MB type distribution breaks down for other bound state cases because there are two velocities in such cases. The first is the vrms(x) velocity where .5mvrms(x)*vrms(x) is the classical kinetic energy and u(x)=(1/W(x)) d/dx W(x) where W(x) is the bound state wavefunction. In this note, we try to give a specific calculation involving velocity (or flux) for the statistical mechanical case to show how it complements a reaction balance ((1)) as long as the flux velocity obeys Newtonian mechanics. For the ground state quantum oscillator, this is the case for the flux 1/W d/dx W, but not for other levels or potentials. Thus, this lack of Newton's law in the flux 1/W d/dx W (which is responsible for d/dx d(x), where d(x) is the spatial density) seems to lead to the breakdown of the reaction balance ((1)) and the MB distribution in quantum mechanical bound states, leading to a new kind of statistical requirement for quantum bound states.

Classical Statistical Mechanics

Consider the case of a classical gas with no potential V(x). Then one may argue that two particle scattering dominates this example i.e.

p1 + p2 = p3 + p4 ((2))

Here pi are momentum vectors and elastic scattering is assumed so:

p1*p1/2m + p2*p2/2m = p3*p3/2m + p4*p4/2m ((3))

If one applies "and" probability, then:

P(p1)P(p2) = P(p3)P(4) ((4))

This implies independence of reactions and time reversal to ensure that P(pi) does not change in time.

A question now arises as to what happens when one introduces a potential V(x). It seems the above arguments should hold at a point x, but the particles change their momenta as they move from point to another i.e.:

$p(xa)*p(xa)/2m + V(xa) = p(xb)*p(xb)/2m + V(xb)$ ((5))

This suggests a distribution of $P(p,x) = C \exp(-p*p/2mT) \exp(-V(x)/T)$ ((6))

This was already presented in (1). Here we wish to argue that one may look at this problem in the following way. Consider P(p,x) at a fixed point x. Then, this probability may change in two ways:

1. The momentum p at x may scatter into another momentum p1 or another momentum p1 may scatter into p at x. This is the reaction balance represented by ((4)). The balance of the reaction is an assumption.
2. A particle with p1 at x-dx may convert to p at x under V(x) or a particle with p2 at x+dx may convert to p at x under V(x). This is another type of reaction based on acceleration by the potential. Also, particles with p and -p at x will be leaving the region x.

The requirement for equilibrium is that both processes (1) and (2) lead to a P(p,x) that does not change in time. If one assumes that ((4)) holds, and that the velocity of a nonscattering particle v(x) follows Newton's law (which is does), one may investigate whether process (2) is automatically in balance. If it is, the assumption of ((4)), i.e. a time reversal balance of the reaction process seems to hold, and one may have a Maxwell-Boltzmann type distribution. If (2) does not result in a balance, then one cannot have the time-reversal balance of ((4)), and the Maxwell-Boltzmann type of distribution will not hold. (These ideas will later be applied to bound state quantum mechanics.)

A. Consider a particle at x-dx with velocity v1 which moves to point x, under F(x)=dV/dx, and arrives with a velocity v. It is assumed that P(v,x)=MB(v)P(x) where MB(v) is the Maxwell-Boltzmann distribution for v. We are assuming that this holds and will see the effects of a potential. Newton's law is also assumed. Assume the force F(x) is pointing to the right, i.e. accelerating to the right. We wish to write P(v1,x-dx) in terms of v i.e. v= v1 + F(x-dx)/m dx/v1 approx = v1 + F(x)/m dx/v to first order.

P(v1,x-dx) = P(v-F(x)dx/v1, x-dx) approx equal to [P(x)- dx d/dxP] [1 - (1/2m)2v Fdx/(vT)] MB(v)

B. Consider a particle at x+dx with velocity v2 which moves to a point x and arrives with v. For such a case, the particle is moving to the left and encounters a force opposing its motion. Then: -v= -v2 +F(x+dx)/m (-dx)/(-v2) approx equal to -v2 + F(x)/m dx/v so:

$P(-v-F/m\ dx/v, \quad x+dx) = [P(x)+ dx\ d/dxP]\ [1+ (1/2m)2v\ dx\ m\ F/(Tv)]\ MB(-v)$

Now consider a balance

$P(v,x)=MB(v)P(x)=[P(x)+ dx\ d/dxP]\ [1+ (1/2m)2v\ m\ dx\ F/(Tv)]\ MB(-v)$

$0 = -MB(v)[\ P\ F/T +d/dxP]$ to first order ((7))

For Case B a similar result holds.

This leads to: $P(x)= C\exp(-V(x)/T)$ and is related to:

$.5mv*v + V(x)=$ constant.

Thus, assuming a reaction balance ((4)), together with a velocity which obeys Newton's law and P(v,x)=P1(v)P2(x) (separability), one finds that P2(x) is of the form exp(-V/T). In other words, it is consistent with the Maxwell-Boltzmann form exp(-p*p/2mT) which follows from the reaction balance ((4)) alone.

Quantum Mechanical Case

For the case of the ground state of quantum mechanical oscillator, P(p)=Cexp(-p*p/E) and P(x)=C1exp(-Ex*x) i.e. this matches the classical statistical mechanical scenario with E=T. According to the above arguments, this may imply a time reversal reaction balance and a velocity which obeys Newton's law. Do such exist for the ground state oscillator? One may imagine a p plane wave momentum scattering through V(x) into p1 under:

P(p)V(p to p1) and the time reversed situation P(p1)V(p to p1) ((8))

For a velocity, one may consider u(x) = 1/W dW/dx as it is related to d/dx (WW) i.e. the change in physical density. There is also a classical velocity based on the average of p*p namely:

[Sum over p p*p/2m fp exp(ipx)] / [Sum over p fp exp(ipx)] = .5m v(x)v(x).

For the oscillator, both of these follow Newton's law as:

C1v(x)*v(x) + C2 u(x)*u(x) = E ((9))

Thus, it seems that one may equate the two reactions in ((8)) and arrive at a Maxwell-Boltzmann type of distribution, namely exp(-p*pb) where b is a constant. This holds even in the quantum mechanical case, but only for the ground state oscillator.

For other levels or other potentials, (1/W) dW/dx no longer follows Newton's law i.e.

$$d/dx\ u = -1/(W^*W)\ (d/dxW)^2 + (1/W)\ (d/dx)^2\ W = (-1/W^*W)\ (d/dxW)^2 - m\ v^*v$$

One would expect that mu d/dx u = -d/dx V(x), but this does not seem to be the case as:

$$-d/dx\ V = (-1/2m)\ [\ -1/W^2\ (d/dxW)(d/dx\ d/dx\ W) + 1/W\ (d/dx)^3\ W\ ]$$

Thus, the flux is preventing the time reversal reaction balance equality from holding in ((8)). Due to the non-classical behaviour of the flux, the reaction equation is changed and one is led to a different statistical picture than that described by the Maxwell-Boltzmann distribution.

Conclusion

In conclusion, in a previous note (1), it was argued a Maxwell-Boltzmann type distribution arises when one is able to write a balanced time reversal reaction equation, such as P(p1)P(p2)=P(p3)P(p4) for statistical mechanics or P(p1)V(1 to 2) = P(p2)V(2 to 1) for some other cases. Taking the natural log of this equation leads to a conservation type of equation that may be compared with an energy conservation equation present in the system. In the case of a kinetic energy conservation equation for elastic scattering, this leads to ln(p*p/2m)=T p*p/2m which in turn gives the Maxwell-Boltzmann distribution. In the case of a velocity which follows Newton's law, we have tried to show in this note that the reaction type equation can still hold. For the quantum oscillator ground state, the two velocities in the problem u(x)=(1/W)d/dx W (where W is the wavefunction) and v(x) the classical velocity both follow Newton's law and a Maxwell-Boltzmann type distribution holds for both p and x. For other states and potentials it does not. We have argued that this is due to the physical average velocity flux 1/W d/dx W not following Newton's law. In such a case, the reaction type equation P(p1)V(1 to 2) = P(p2)V(2 to 1) may no longer hold and must be modified to account for the nonclassical behaviour of the flux u(x).

References

Ruggeri, Francesco R. Independence and Time Reversal in Statistical Mechanics and Quantum Bound States (preprint, zenodo, 2019)