Maxwell-Boltzmann Gas from an Average Single Particle Viewpoint

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A Maxwell-Boltzmann gas is composed of many molecules which give rise to average bulk properties such as temperature, pressure, density etc. which are measurable. A single particle collides with other particles and when it is not colliding it moves as a Newtonian particle subject to -dV/dx. The gas is characterized by a probability distribution (the Maxwell-Boltzmann MB distribution) P((ei+V(x)) / T) where ei is kinetic energy and V(x) the potential. T is usually described as a parameter which is fixed by: Sum over i ei exp(-ei/T)/Z = E average where Z= Sum over i ei exp(-ei/T). P(ei/T) may be obtained by maximizing Shannon's entropy subject to the average energy constraint. P(x) may be obtained from a bulk balance of pressure and -dV/dx density(x).

In this note, we wish to consider a single particle view. In that case, P(ei/T) is the probability for the particle to have kinetic energy ei and exp(-V/T)/Normalization is the probability for it to be at x. Instead of maximizing Shannon's entropy, we consider the idea that P(e1+V(xa)) P(e2+V(xa) = P(e1+e2+V(xa). This is equivalent to considering two body elastic scattering with time reversal balance. If one assumes there is no extra information in the problem than conservation of energy and equal distribution of kinetic energy, then P(1)P(2)=P(3) leads to the MB distribution for a single particle. One could fix T again by considering the average energy a single particle has i.e. E average / N where N is the number of particles.

We are, however, interested in the dynamics of the average single particle. The average particle is very different from a single physical particle in one member of an ensemble i.e. a particle which collides and when it is not colliding moves under the influence of -dV/dx. For equilibrium the average particle does not accelerate, but balances the force -dV/dx. One may see this by consider the derivative d/dx acting on P i.e. d/dx P = -dV/dx P. What does d/dx P imply? We argue that -dV/dx is a cause and its action is on a particle which represents an effect.

A particle with kinetic energy ei, however, may be a cause of force because ei is proportional to its pressure, but also a recipient. Thus interacting gas particles are both causes of force and recipients (effects). Pressure is not treated in the same way as -dV/dx which simply multiplies P because P inside a little box is the effect. To be consistent, one requires the pressure outside the box to also be a cause, but it differs at each surface of the box (1-dimensional box). As a result, the so-called parameter T is really the average pressure of a single particle. On average this single particle does not accelerate in equilibrium so there is a balance with -dV/dx. If one considers N particles in a box, this balance scales to create the notion of a macroscopic density and a macroscopic pressure balance.

The P1P2=P3 probability balance, however, is at the single particle level so in this note we wish to examine why exp(-V/T) should be obtainable via macroscopic balance using the ideal gas law Pressure= density RT and -dV/dx. We argue this follows from considering an average single particle (which behaves differently from a single particle in a member of an ensemble.

We further argue that some of these ideas may apply to a single particle bound quantum state.

Many-Particle View of a Maxwell-Boltzmann Gas

In general, one may consider a Maxwell-Boltzmann gas in terms of many particles. If no potential is present, one may consider distributing a total energy (roughly equal to an average energy) to N particles such that each distribution arrangement carries the same weight. Then ln of the number of arrangements is:

ln(N!/ Product over i n(ei)!) ((1))   Using Stirling's approximation: ln(N!) approx= Nln(N) ((2))

and maximizing subject to the constraint: Sum over i ei P(ei) yields the MB distribution:

P(ei/T) = C(T) exp(-ei/T) ((3))

where T is a parameter which may be fixed through the average energy definition. Thus the notion of pressure does not explicitly appear, even though ((3)) does create a particular pressure which is proportional to average energy. In fact: pressure is given by the ideal gas law:

Pressure = density(x) RT ((4))

If a potential V(x) is added, one may use a macroscopic pressure balance argument considering a little one dimensional box such that the difference of pressures on the box sides matches -dV/dx density inside. If pressure and -dV/dx are both forces, why does one act on the density inside the box i.e. on the center-of-mass and the other on the ends of the box?

Force and Cause and Effect

A force -dV/dx is external and acts on all particles in a gas. The gas particles thus feel its effects. Pressure on the other hand is internal - it is created by the particles themselves through collisions. A particle, which has momentum, is both a cause of force when it strikes another particle, but also a recipient or effect of the force (impulse) delivered by another particle. Newtonian mechanics states that one should consider external forces (causes) acting on a body. Thus some gas particles must be designated as the "body" upon which other forces act. -dV/dx acts on all particles within a little one dimensional box as a cause, but only particles external to the box i.e. pressure external to the box act as a cause. Thus one must consider the pressure at both ends of the box while -dV/dx applies to the center-of-mass of the box. One sees an asymmetry in dealing with force within an MB gas:

{Pressure(x+dx) - Pressure(x)} A = -dV/dx density(x) Adx

RT d/dx density = -dV/dx density   ((4))

((4)) yields P(x) = normalization exp(-V/T) ((5)).

Single Particle Viewpoint

The above derivations of both exp(-ei/T) and exp(-V/T) involve many particles. Why should one consider a single particle viewpoint? Is there any different physics involved? We argue that there is. In particular, instead of considering equally weighted energy distribution over all N particles, it suffices to consider:

P(e1)P(e2)=P(e1+e2) ((6a)) or P(e1+V(x)) P(e2+V(x) = P(e1+e2+V(x)) ((6b))

This leads to the idea of information in the problem. If one takes ln of ((6b)) one obtains a conservation equation. There is also, however, the basic energy conservation equation for elastic collisions:

E1+e2 = e3 ((7))

One may ask: Does the ln of ((6b)) represent different information than ((7)) or do they represent the same information? If they represent the same information, there exists one equation i.e. ((7)) and ((6b)) are the same, up to a multiplicative constant. Taking this view leads to:

{ei+V(x)}/T = ln(P) or P= C(T) exp(- (e+V)/T) where e is kinetic energy ((8))

This yields a probability (unnormalized) exp(-ei/T) for a single particle to have energy ei and a probability exp(-V(x)/T) for it to be a x. What is T? One may fix it through an average energy per particle consideration, but we think that it is more than this. If one considers an average single particle, then P(x) = exp(-V/T) unnormalized. Taking d/dx produces:

dP/dx = (1/T) (-dV/dx) P(x) ((9))

-dV/dx is Newtonian force and P(x) is the probability for the particle to be at x. (Note: This represents an “average” particle.) Thus T dP/dx must also be a force. One may note that dP/dx / P appears in the problem so that normalization cancels. Thus T is not an arbitrary constant, but describes pressure of an average particle at x. TP(x) then represents the probabilistic pressure of an average particle at x, but one is forced to evaluate TP(x) at both sides of a little box (one dimensional) while -dV/dx acts on the center-of-mass. Why is this the case? We argue that an average particle is an unusual construct (when compared with a real single particle). The average particle contains both motion to the right and left and acts as both a cause of force and a recipient unlike -dV/dx which is only a cause acting on P(x) the recipient. In order to create a balance, one must consistently use cause and effect. If -dV/dx is a cause, then one needs the cause part of the single particle i.e. its average pressure on the walls of a little box so that the particle in the box is the recipient. This then leads to ((9)).

The average single particle scenario then scales to many particles because one has many "average" particles. In other words, P(x) for a single particle leads to NP(x) which is density for many particles. Thus we argue one may use an average single particle viewpoint.

Quantum Single Particle Bound State

A classical MB gas and a quantum single particle bound state are not the same. Both, however, may be viewed in terms of an average "single particle". Traditionally, the MB gas is not considered in terms of the "average" single particle because this construct is very different from an actual particle. Thus analysis of an average particle is not the same as analysis of a single particle in a particular member of an ensemble.

In a quantum single particle bound state, one also has an ensemble called a wavefunction i.e.

W(x) = Sum over p a(p)exp(ipx) ((10))

This represents a quantum interfering type of average particle. On the other hand, a(p)a(p) represents the probability to have a free particle with momentum p in the system. This is analogous to a single particle in a particular member of an ensemble in the MB case.

Thus the dichotomy of "average" single particle and an instance of a single particle exist both in the quantum single particle bound state and an MB gas, we argue.

Conclusion

In conclusion, we argue that although one may consider an MB gas in terms of many particles, this bypasses the notion of information in the problem, and a single particle viewpoint, which leads directly to the MB distribution exp(-ei/T)exp(-V/T). T is usually portrayed as a parameter fixed by average energy, but we argue that it is the physical pressure of a single average particle. Thus it is not a parameter. If one takes d/dx of the single particle probability exp(-V/T) one obtains: dP/dx = (1/T) -dV/dx P. -dV/dx is force from Newtonian mechanics which acts on the P(x) describing the probability of the particle to be at x. Thus one has a kind of probabilistic force term for the average single particle. What about T dP/dx? T we argue, must represent the pressure of the average particle. This particle has momentum so it may render impulses, but also receive them. An average particle contains motion in both directions. Thus in order to perform Newtonian mechanics which states that one considers external forces on a body, -dV/dx P(x) is an external probabilistic force on the average single particle at x, but TP(x) must be evaluated at two ends of a tiny box so that the recipient average particle is within the box, Then a balance may be performed for the average single particle which then scales up to the macroscopic force balance. We note that the average single particle is very different from an instance of a single particle in a particular member of an ensemble. We also note that this dichotomy exists in a quantum single particle bound state.