Steve Smith Tuition: Physics Notes

The Distribution of Energies of Particles in a Gas

Contents

Prerequisites

There are a number of things that you should be aware of before you read on. They are:

- the idea of thermal equilibrium;
- elastic collisions;
- curve fitting to data (regression);
- summation notation;
- geometric series;
- probability distribution functions, such as the normal distribution;
- and the difference between discrete and continuous probability distributions.

That's all. Urgh. This is going to be tough, eh?

Notes

None.

Document History

Date	Version	Comments
6th December 2017	1.0	Initial creation of the document.

1 The Game

In order to get a handle on how energy is distributed amongst the particles of a gas, I'm going to create a (relatively) simple model of the gas. And to do that we're going to play a game...

1.1 The Pieces

First, the pieces in the game are:

(1) We have a container with a large number of particles in it. And when I say large, I mean *large*. These will be the particles in our "gas".

(2) Each of the particles in the container has an energy, and the energy a particle can have can only be a multiple of some small energy, which I will call δE. So the only possible energies a particle can have are 0, δE, 2 δE, 3 δE, etc. Initially, let's assume that all the particles have the same energy, which I will call E_{av}, because that's the average energy of the particles in the gas.

1.2 The Rules

Now we know about the pieces, here are the rules of the game:

(1) No energy flows into or out of the container, so that the total energy of all the particles added together remains constant. This means that our container is in *thermal equilibrium*.

(2) As time goes by, the particles in the container collide with each other. For any given collision, which only occurs between *two* randomly chosen particles, one of the two particles (which is also chosen randomly) gives δE of energy to the other (unless its energy is zero, of course). This models, in a simple way, an *elastic* collision: one where kinetic energy of the colliding particles is conserved.

(3) Particles don't gain or lose energy when they collide with the walls of the container.

1.3 Playing the Game : 1

So, let's see how this goes, by picking a simple system, and working through a few collisions. Let's choose a system with five particles in it, and we'll give each particle three units of energy to begin with.

Energy will come in clumps of 1 unit (so $\delta E = 1$), so you can't have any energies other than 0, 1, 2, 3, etc., units.

Before any collisions have taken place, the system could be summarised by Table 1, where I have called the five particles the names of A, B, C, D, and E, and given them 3 units of energy each, and Figure 1, where I have drawn a graph of the numbers of particles with the different energies possible.

Particle	**A**	**B**	**C**	**D**	**E**
Energy	3	3	3	3	3

Table 1: Particle Energies : 0 Collisions

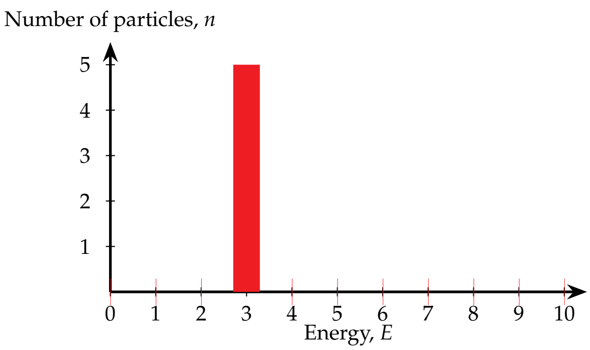


Figure 1: Energy Distribution: 5 Particles; 3 Units of Energy Each, Initially; 0 Collisions

At present, all the particles have three units of energy, so there is a single bar on the graph that corresponds to there being five particles with three units of energy, and no particles with any other energy.

The First Collision Right. So let's have our first collision. I choose two particles at random: let's say they are *B* and *C*. The collision involves an exchange of energy, and the rules of the game say that *B* has to give one unit of energy to *C*. The situation is now shown in Table 2 and Figure 2.

Particle	A	B	C	D	E
Energy	3	2	4	3	3

Table 2: Particle Energies : 1 Collision

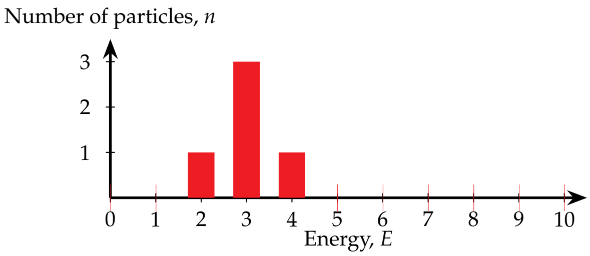


Figure 2: Energy Distribution: 5 Particles; 3 Units of Energy Each, Initially; 1 Collision

Now there is one particle with two units of energy, three particles with three units of energy, and one particle with four units of energy.

The Second Collision And let's have our next collision. I choose two particles at random: let's say they are *C* and *E*. So *C* has to give one unit of energy to *E*. The situation is now shown in Table 3 and Figure 3.

Particle	A	B	C	D	E
Energy	3	2	3	3	4

Table 3: Particle Energies : 2 Collisions

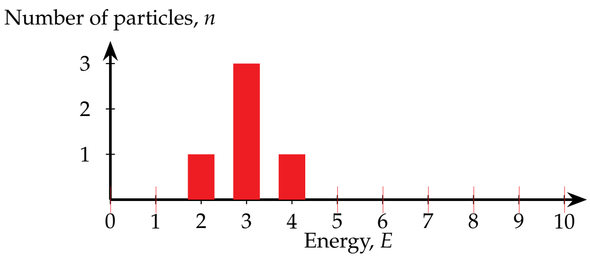


Figure 3: Energy Distribution: 5 Particles; 3 Units of Energy Each, Initially; 2 Collisions

That's interesting! Even though the way that energy is distributed amongst the particles has changed, the graph hasn't!

That's actually something I wasn't expecting: that there is more than one way of distributing the total energy amongst the particles that would lead to the same $n - E$ graph. This idea is fundamental to the way that these systems have to be analysed. We have to consider the numbers of ways of doing things. That means...oh dear, oh dear...statistics!! Urgh.

The Third Collision Anyway, getting back to our game, let's have our next collision. I choose two particles at random: let's say they are A and E. So A has to give one unit of energy to E. The situation is now shown in Table 4 and Figure 4.

Particle	A	B	C	D	E
Energy	2	2	3	3	5

Table 4: Particle Energies : 3 Collisions

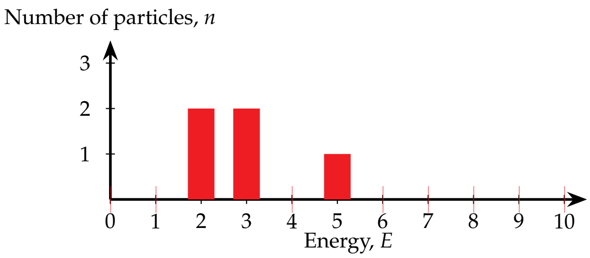


Figure 4: Energy Distribution: 5 Particles; 3 Units of Energy Each, Initially; 3 Collisions

Get the idea?

1.4 Playing the Game : 2

So...the question is: what happens to the distribution of energies of all the particles as time goes by? Especially if you have a much larger number of particles, and a much larger number of collisions?

Well, this strikes me as the ideal time to use a computer program. Because the rules of this game are so relatively simple, and we just have to do the same thing (pick two random particles and get them to exchange energy through a collision) over and over again, a computer is ideally suited to this task.

I have written a computer program to play this game.

For one particular run of the program, I used 10,000 particles, and gave them each 25 units of energy. During each collision, one of the particles (picked at random) gave the other one unit of energy (unless it didn't have any). I then ran the program through 1 *billion* collisions. And the results are quite interesting!

To get a grasp on the results, check out Table 5. I have drawn graphs of the numbers of particles, n, for each energy from 0 to 150 (that's 6 times the average). The graphs correspond to the distribution of energies of the particles after a given number of collisions. There is a lot to take in here!

Graph (a) shows the situation after 1000 collisions. Just over 8000 particles still have their energy at 25 units, but there are some particles now with energies slightly higher and some particles with energies slightly lower than 25 units (as you might expect, if you think about it a bit!).

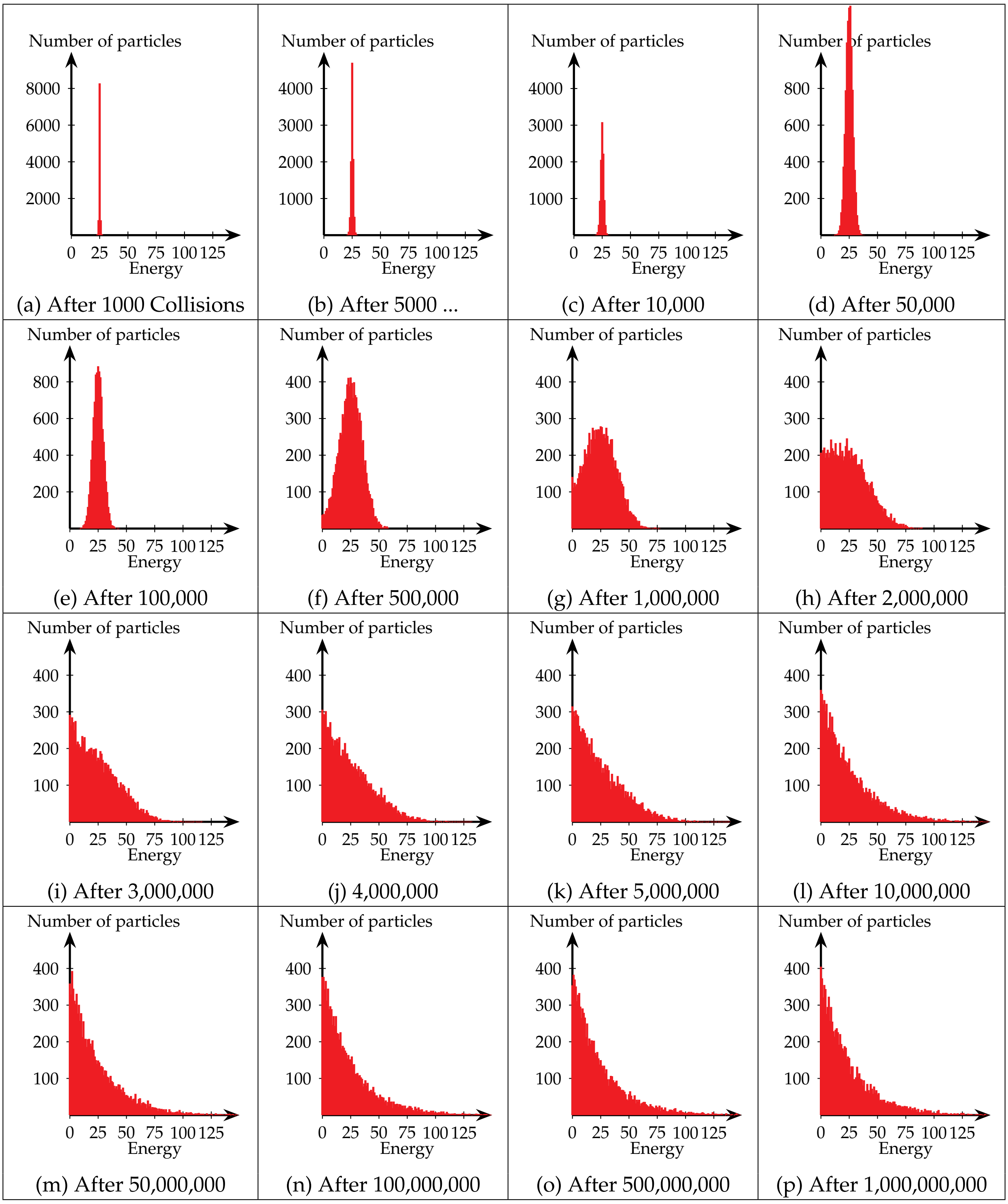
After 5000 collisions, graph (b), the spike at $E = 25$ is coming down rapidly (just look at the scales on the vertical axes of these graphs), and the range of particle energies is spreading slowly.

For 10,000 to 100,000 collisions, (c) - (e), the number of particles with $E = 25$ falls, and the base of the distribution of energies is widening. We are increasingly seeing a symmetrical *Normal Distribution* forming. We might have expected this, too!

Now after 500,000 collisions, (f), we are starting to see significant numbers of particles with $E = 0$! That is - no energy at all! Wow. And of course, as soon as the Normal Distribution spreads so that the left-hand end of the base is at $E = 0$, then the distribution becomes un-normal-like, as symmetry can no longer be preserved. That's because a particle can't have a *negative* energy, of course.

After around 1,000,000 collisions, (g), we are starting to see an interesting change in the general shape of the distribution of particle energies. More and more particles have $E = 0$, and the distribution is spreading further to the right. Those observations mean that the center peak has to collapse to support more particles with low and high energies.

Interestingly, by 2,000,000 collisions, the peak at $E = 25$ has completely gone.



(a) After 1000 Collisions (b) After 5000 ... (c) After 10,000 (d) After 50,000

(e) After 100,000 (f) After 500,000 (g) After 1,000,000 (h) After 2,000,000

(i) After 3,000,000 (j) 4,000,000 (k) After 5,000,000 (l) After 10,000,000

(m) After 50,000,000 (n) After 100,000,000 (o) After 500,000,000 (p) After 1,000,000,000

Table 5: One Run of the Program: 10,000 Particles; 25 Units of Energy Each, Initially; 1 Billion Collisions

Between 2,000,000 and 10,000,000 collisions, (h) - (l), the distribution shape is becoming more like a decreasing exponential (like we see in radioactivity and capacitor discharge).

And after around 50,000,000 collisions, shown in graphs (m) - (p), the distribution seems to be stabilising in that characteristic exponential-decay-looking way.

Once a kind of steady-state is reached, the particles are said to be in *statistical equilibrium*.

I have expanded the graph (p) in Figure 5.

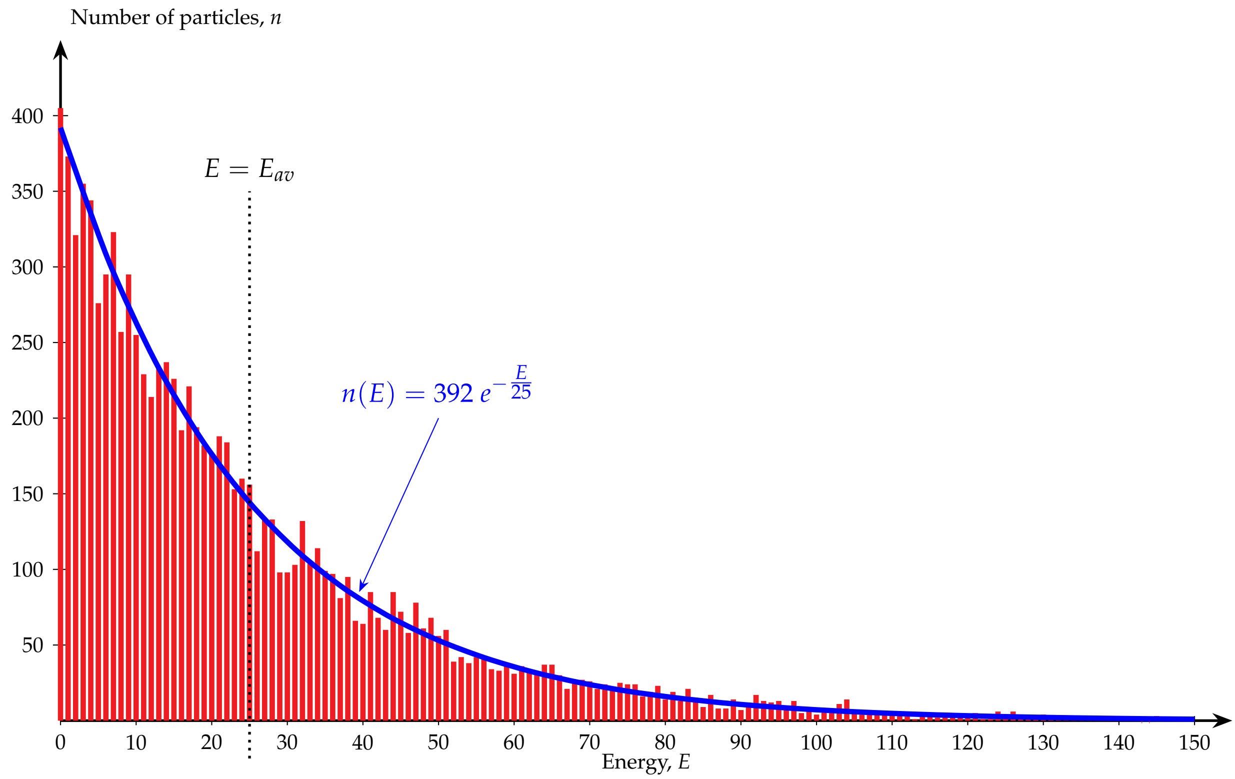


Figure 5: Energy Distribution: 10,000 Particles; 25 Units of Energy Each, Initially; 1 Billion Collisions

First of all, let's just take this in. What Figure 5 is telling us is that once statistical equilibrium has been reached in our "gas", there are a lot of particles with low energy - much lower than the average of $E_{av} = 25$ units. And there are also quite a lot of particles that have an energy *much* greater than the average.

Superimposed on the data (in red, showing the number of particles with each energy from 0 to 150 units) is the function

$$n(E) = 392\, e^{-\frac{E}{25}}$$

which is a pretty good fit to the data. So this leads us to believe that the distribution *does* turn into an exponential-decay-type thing, if you wait for enough collisions!

I didn't just pick those numbers, the 392 and the 25 at random, by the way. I used *OpenOffice Calc* (a free alternative to *Microsoft Excel*) to do an exponential *regression* of the data. That just means fitting the best exponential curve to the data. And those were the numbers that *Calc* came up with (well, rounded a bit!).

Interestingly, the 25 (that came out of the regression analysis) is the same as the number of units of energy that was given to each particle initially! This leads us to an interesting conjecture: that for this "gas", given the initial conditions, and given the rules of the collisions, then eventually the distribution of energies of the particles of the gas follows this relationship:

$$n(E) = A\, e^{-\frac{E}{E_{av}}} \tag{1}$$

where again, E_{av} is the average amount of energy of the particles during the process, and A is some constant.

What about the 392? Where could that come from? Well, you'll have to have a look at Appendix A for that! Beware though - it's tricky!

And you get this same equation, even if you used a different initial average energy, or start with a random distribution of initial energies amongst the particles. Eventually, you would get the same exponential decay distribution, so long as you have enough collisions. The value of A changes, depending on how many particles you start with, and their initial average energy. But for a given system, it is always a constant.

And so we can talk about this energy-distribution-amongst-the-particles later, I'm going to call this exponential decay of energies from *my* game and *my* rules, given by Equation (1), the *Stevo Distribution*.

1.5 Energies of Particular Particles

Another thing I did with this program was to look at the ranges of energies that particular particles had during the course of all the collisions.

In the case where I started off with 10,000 particles, each with an energy of 25 units, and then carried out all of the billion collisions, I found something interesting about the spread of energies that particular individual particles had during the run. I've summarised this information in Table 6:

Particle	Range of Energies
A	0-150
B	0-113
C	0-147
D	0-124
E	0-106
F	0-150
G	0-150
H	0-111
I	0-107
J	0-121

Table 6: The Range of Energies of Particular Particles

I picked 10 particles at random from the 10,000, and gave them the names A, B, C, D, E, F, G, H, I and J. Then I kept track of all the energies that these ten particles had during the course of the billion collisions.

I should point out here that I only looked for energies in the range 0-150 units. So it is very likely that particles A, F and G had energies of greater than 150 units at some point during the billion collisions.

Now if you think about it, if there are a billion collisions, and 10,000 particles, then the number of collisions that a particular particle would expect to be involved in is

$$\frac{1,000,000,000}{10,000} \times 2 = 200,000$$

[The $\times 2$ comes in because every collision involves *two* particles!]

So what Table 6 tells you is that in as few as 200,000 collisions, particular particles go through an enormous range of energies, from 0 all the way up to beyond 6 times the average. And I say *as few as* 200,000 collisions because each individual particle in a real gas goes through *millions, if not billions of collisions each second*.

So that means that although the energy distribution across all particles will follow Figure 5, a particular single particle will be flitting about in this distribution going through all of the energies up to some energy that's way higher than the average, dropping down to lower energies, going back up to high energies... How high its maximum energy gets will be down to the luck of the collisions it has.

2 The Boltzmann Factor

The quantity

$$e^{-\frac{E}{E_{av}}}$$

that turned up from our game in Section 1.4, and featured in Equation (1), is known as the *Boltzmann Factor*. In this section, we are going to explore two uses of it.

2.1 The Probability of a Particle Having High Energy

The first use is to determine the probability of a given particle having an energy greater than or equal to some cut-off energy, E_c. From Appendix A I have shown that, for the Stevo Distribution, this will be

$$p(E \geq E_c) = e^{-\frac{E_c}{E_{av}}} \tag{2}$$

which is the Boltzmann Factor directly!!

2.1.1 An Example

As an example, let's use the Stevo Distribution, with average particle energy of $E_{av} = 25$ units, and see if we can work out the probability of a randomly chosen particle having energy greater than or equal to 50 units. Well, that's easy: using (2),

$$\begin{aligned} p(E \geq 50) &= e^{-\frac{50}{25}} \\ &\approx 0.1353... \end{aligned}$$

That means that there would be roughly a 13.5% chance of finding that a randomly chosen particle had *twice* the average energy (*or more*) of all the particles.

Another way of saying this, of course, is that on average, around 13.5% of all particles have an energy that is at least twice the average.

2.1.2 Another Example

As another example, let's use the Stevo Distribution, with average particle energy of E_{av} units, and see if we can work out the probability of a randomly chosen particle having energy greater than or equal to $15E_{av}$ units. Well, that's easy: using (2),

$$\begin{aligned} p(E \geq 15E_{av}) &= e^{-\frac{15E_{av}}{E_{av}}} \\ &= e^{-15} \\ &\approx 3.06 \times 10^{-7} \end{aligned}$$

That means that there would be roughly a 0.00003% chance of finding that a randomly chosen particle had *fifteen* times the average energy (*or more*) of all the particles.

Another way of saying this, of course, is that on average, around 0.00003% of all particles have an energy that is at least fifteen times the average. Now that doesn't sound like a lot, does it? But if we were able to apply the same idea to one mole of a gas, which has 6.02×10^{23} particles in it, then that corresponds to 1.84×10^{17} particles!! That's a *huge* number of particles.

Why is this significant? Well, if you had a liquid, where the distribution of energies followed the Stevo Distribution with the average energy of the particles being E_{av}, and let's say that the energy required for a particle to escape the liquid (by evaporation) was $15E_{av}$ (or more), then what this tells us is that an enormous number of particles in the liquid would have this energy of $15E_{av}$ (or more).

So, as there are billions of collisions each second for a given particle(!!), then evaporation would occur at a considerable rate. And since these high energy particles leave the liquid, the liquid will cool quite rapidly, as the escaping particles are taking their high energy with them, out of the liquid.

2.2 Comparing the Numbers of Particles at Two Different Energies

From Appendix C the Boltzmann Factor in the form

$$e^{-\frac{\Delta E}{E_{av}}}$$

gives you the ratio of the numbers of particles in energy states ΔE apart (the higher energy state having fewer particles, of course).

2.2.1 An Example

As an example, let's take our system, where the average energy of the particles is $E_{av} = 25$. If we were now interested in energies $E_1 = 10$, and $E_2 = 20$, then

$$\begin{aligned} \frac{n(E_1)}{n(E_2)} &= e^{-\frac{(E_1 - E_2)}{E_{av}}} \\ \Longrightarrow \frac{n(E=10)}{n(E=20)} &= e^{-\frac{(10-20)}{25}} \\ &= e^{-\frac{(10-20)}{25}} \\ &\approx 1.49 \end{aligned}$$

This means that there is almost 50% more particles with energy $E = 10$ than there are with energy $E = 20$.

3 The Boltzmann Distribution

There is no such thing as the *Stevo Distribution*, of course. But there *is* such a thing as the *Boltzmann Distribution*.

Intriguingly, there is more than one Boltzmann Distribution. It turns out that the Boltzmann Distribution is a kind of general thing, and whenever you want to apply it to a specific situation, then you have to tailor it accordingly.

So actually, I should call the version that applies to my game the *Stevo-Boltzmann* Distribution.

3.1 The Stevo-Boltzmann Distribution

The simplest version you can have of the Boltzmann Distribution for the distribution of energies of particles in a system gives the formula for the probability density function as:

$$\mathrm{PDF}_B(E) = \frac{1}{kT}\, e^{-\frac{E}{kT}} \tag{3}$$

where k is the Boltzmann constant, and T is the absolute temperature of the system. [The subscript $_B$ signifying it's the PDF of the Boltzmann Distribution.]

Now compare this with the probability density function that I obtained from looking at the continuous version of what I'm now calling the Stevo-Boltzmann Distribution (see Appendix B.1):

$$\mathrm{PDF}_S(E) = \frac{1}{E_{av}} e^{-\frac{E}{E_{av}}}$$

[The subscript $_S$ signifying it's the PDF of the Stevo-Boltzmann Distribution.] These look pretty similar!! And hey - they are the same if

$$E_{av} = kT$$

which is (almost!) what we get from the Kinetic Theory, where we discovered that the average kinetic energy of particles in a gas is $\frac{3}{2}kT$!

The Kinetic Theory outlined at A-Level makes lots and lots of simplifying assumptions, so it shouldn't be any surprise if the details don't work out to precisely compare with reality. But what we *can* say from it would be that the average kinetic energy of the particles in a gas is *roughly* equal to kT.

This is kind of cool. Our simple game in Section 1.4 led us to an important probability distribution that underpins all of statistical mechanics and statistical thermodynamics. Not bad.

3.2 The Maxwell-Boltzmann Distribution

And when you want the version of the Boltzmann Distribution that applies to the situation of a *real* gas held in a *real* container, then you want the *Maxwell-Boltzmann* Distribution.

It turns out that the probability density function for the *Maxwell-Boltzmann* Distribution of energies, the probability density function for the distribution of energies of particles in a *real* gas, is:

$$\mathrm{PDF}_M(E) = \frac{2}{\sqrt{\pi E_{av}^3}}\, \sqrt{E}\, e^{-\frac{E}{E_{av}}}$$

[The subscript $_M$ signifying it's the PDF of the Maxwell-Boltzmann Distribution.] This is a lot more complicated than that for the Stevo-Boltzmann Distribution. The derivation of this will have to wait for another day...I'll need a whole document to do that justice, not just an appendix!

The main feature that adds complexity in the Maxwell-Boltzmann Distribution is in fact the $\sqrt{E}$ bit. And if you think about it, because of the $\sqrt{E}$, this PDF goes to zero when E goes to zero. Check out Figure 6.

In Figure 6 I've compared the Stevo-Boltzmann and the Maxwell-Boltzmann Distributions for the same average energy of the particles of $E_{av} = 25$ units. Obviously the main feature that distinguishes the two is that in the Stevo-Boltzmann Distribution, there is a probability that particles can have an energy of zero; whereas in the Maxwell-Boltzmann Distribution, the probability that particles can have an energy of zero is zero!

The smaller the energy, the less likely it is that you will find particles with this energy in a real gas.

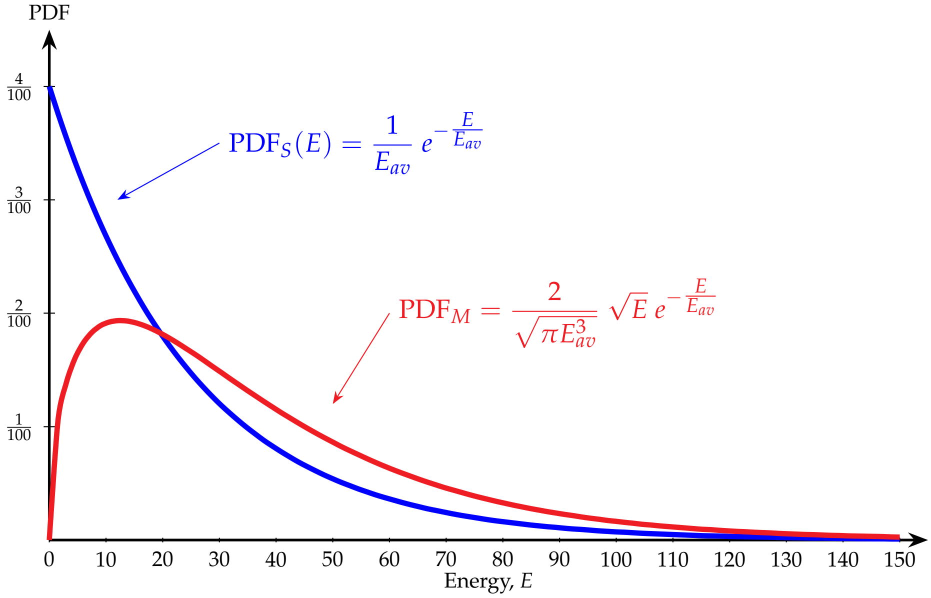


Figure 6: The Stevo-Boltzmann and Maxwell-Boltzmann PDFs: $E_{av} = 25$, Initially

So the main difference between the two distributions is found at low energies. At higher energies, the two distributions look pretty similar, because they are both dominated by the Boltzmann Factor, the

$$e^{-\frac{E}{E_{av}}}$$

term, although the Maxwell-Boltzmann curve is always slightly higher than the Stevo-Boltzmann curve.

So, for particles in a real gas, and for energies that are much higher than the average, we could approximate the Maxwell-Boltzmann Distribution of energies by the much simpler Stevo-Boltzmann Distribution of energies.

And as the Stevo-Boltzmann Distribution is dominated by the Boltzmann Factor, then that's the reason why the Boltzmann Factor is so important.

A The Discrete Stevo Probability Distribution Function

In this Appendix, I am interested in trying to answer questions like:

- what is the number of particles in our system with an energy greater than some cut-off energy E_c?
- what is the probability of finding a particle with an energy greater than or equal to E_c?
- what is the probability of finding a particle with an energy equal to E_c?

assuming that the Stevo Distribution is *discrete*.

[Remember that a discrete probability distribution is one where the outcomes of the "experiment" are discrete values[1]. And a discrete probability distribution function is the thing that tells you how the total probability (of 1) is distributed amongst all the possible discrete values that the random variable can take.]

In the game outlined in Section 1.4 we have a discrete random variable situation: the energies that particles can have are only: 0, 1, 2, 3, ..., etc.

A.1 The Number of Particles with an Energy Greater than E_c

For a discrete Stevo Distribution, the number of particles with an energy greater than or equal to E_c will be:

$$n(E \geq E_c) = \sum_{E=E_c}^{E=\infty} Ae^{-\frac{E}{E_{av}}}$$

We can write out the first few terms of this sum to get an idea of what's going on:

$$n(E \geq E_c) = Ae^{-\frac{E_c}{E_{av}}} + Ae^{-\frac{E_c+1}{E_{av}}} + Ae^{-\frac{E_c+2}{E_{av}}} + Ae^{-\frac{E_c+3}{E_{av}}} + ...$$

Now we can use the index rules to simplify this a bit:

$$n(E \geq E_c) = Ae^{-\frac{E_c}{E_{av}}} + Ae^{-\frac{E_c}{E_{av}}}e^{-\frac{1}{E_{av}}} + Ae^{-\frac{E_c}{E_{av}}}e^{-\frac{2}{E_{av}}} + Ae^{-\frac{E_c}{E_{av}}}e^{-\frac{3}{E_{av}}} + ...$$

Now we can factorise:

$$\begin{aligned} n(E \geq E_c) &= Ae^{-\frac{E_c}{E_{av}}}\left[1 + e^{-\frac{1}{E_{av}}} + e^{-\frac{2}{E_{av}}} + e^{-\frac{3}{E_{av}}} + ...\right] \\ &= Ae^{-\frac{E_c}{E_{av}}}\left[1 + e^{-\frac{1}{E_{av}}} + \left\{e^{-\frac{1}{E_{av}}}\right\}^2 + \left\{e^{-\frac{1}{E_{av}}}\right\}^3 + ...\right] \end{aligned}$$

Now the bit in the square brackets is a geometric series, with $a = 1$ and $r = e^{-\frac{1}{E_{av}}}$. And we want to find the sum to infinity, S_∞, of this series. That will be

$$\begin{aligned} S_\infty &= \frac{a}{1-r} \\ &= \frac{1}{1-e^{-\frac{1}{E_{av}}}} \end{aligned}$$

So,

$$n(E \geq E_c) = Ae^{-\frac{E_c}{E_{av}}} \times \frac{1}{1-e^{-\frac{1}{E_{av}}}}$$

So that, finally,

$$n(E \geq E_c) = \frac{Ae^{-\frac{E_c}{E_{av}}}}{1-e^{-\frac{1}{E_{av}}}} \quad (4)$$

[1] You probability first encountered these as *Discrete Random Variables* in a Statistics course. Simple examples would be tossing a coin, where the outcomes are just $\{H, T\}$, or rolling a die, where the outcomes are $\{1, 2, 3, 4, 5, 6\}$. In each case there is a set of outcomes, and any other outcome is impossible: getting a 3.5 when you roll the die, for example.

Now if the number of particles in the "gas" is N, then the number of particles with an energy greater than or equal to 0 will be N. We can plug that into (4):

$$\begin{aligned} N &= \frac{Ae^{-\frac{0}{E_{av}}}}{1 - e^{-\frac{1}{E_{av}}}} \\ &= \frac{A}{1 - e^{-\frac{1}{E_{av}}}} \end{aligned}$$

so that

$$A = N\left[1 - e^{-\frac{1}{E_{av}}}\right] \tag{5}$$

And plugging this into (4) gives us our final result:

$$n(E \geq E_c) = Ne^{-\frac{E_c}{E_{av}}} \tag{6}$$

So, for example, if we had 10,000 particles, and an average energy of 25 units, then the number of particles having an energy greater than 50 units will be

$$\begin{aligned} (E \geq 50) &= 10,000e^{-\frac{50}{25}} \\ &= 1353 \end{aligned}$$

rounded to the nearest particle.

Again, if we have 10,000 particles, with an average energy of 25 units, then

$$\begin{aligned} A &= 10,000\left[1 - e^{-\frac{1}{25}}\right] \\ &= 392.1056... \end{aligned}$$

which ties in with the coefficient that *OpenOffice Calc* came up with in the exponential regression from Section 1.4!!

A.2 The Probability of a Particle Having an Energy Greater Than or Equal to E_c

Now we know the number of particles that will have an energy greater than E_c (Equation (6)), we can work out the probability of finding a given particle with an energy greater than E_c. This will simply be

$$\begin{aligned} p(E \geq E_c) &= \frac{\text{the number of particles with an energy} \geq \text{E}_c}{\text{the total number of particles}} \\ &= \frac{Ne^{-\frac{E_c}{E_{av}}}}{N} \\ &= e^{-\frac{E_c}{E_{av}}} \end{aligned} \tag{7}$$

This is a very important result.

A.3 The Precise Stevo Distribution

From (5) we now know the form of the discrete Stevo Distribution for $n(E)$:

$$n(E) = N\left[1 - e^{-\frac{1}{E_{av}}}\right]e^{-\frac{E}{E_{av}}} \tag{8}$$

A.4 The Probability of a Particle Having an Energy of E_c

And from Equation (8), we know that the number of particles with energy E_c will be

$$n(E_c) = N\left[1 - e^{-\frac{1}{E_{av}}}\right] e^{-\frac{E_c}{E_{av}}}$$

and so the probability of finding a given particle with an energy equal to E_c will be

$$\begin{aligned} p(E = E_c) &= \frac{N\left[1 - e^{-\frac{1}{E_{av}}}\right] e^{-\frac{E_c}{E_{av}}}}{N} \\ &= \left[1 - e^{-\frac{1}{E_{av}}}\right] e^{-\frac{E_c}{E_{av}}} \end{aligned}$$

And so this will be the probability distribution function for the discrete Stevo Distribution:

$$\mathrm{PDF}_{DS}(E) = \left[1 - e^{-\frac{1}{E_{av}}}\right] e^{-\frac{E_c}{E_{av}}}$$

where the subscript $_{DS}$ represents <u>D</u>iscrete <u>S</u>tevo.

B The Continuous Stevo Probability Density Function

From Section 1.4, we had a hint that the discrete Stevo Distribution can be modelled by a *continuous* distribution of the form given by Equation (1).

Now could we convert this continuous function into a *probability density function*? So that we might be able to work out probabilities of particles having a range of energies? It turns out that we can. Hold on to your hat!

B.1 The Derivation

Starting with

$$N(E) = Ae^{-\frac{E}{E_{av}}} \tag{9}$$

If we wanted to turn this into a continuous probability distribution function, then the area under this graph would have to be 1. That means

$$A \int_{E=0}^{E=\infty} e^{-\frac{E}{E_{av}}}\, dE = 1$$

Doing the integration we get

$$A \left[-E_{av}\, e^{-\frac{E}{E_{av}}} \right]_{E=0}^{E=\infty} = 1$$

Plugging in the limits we get

$$A \left\{ \left[-E_{av}\, e^{-\frac{\infty}{E_{av}}} \right] - \left[-E_{av}\, e^{-\frac{0}{E_{av}}} \right] \right\} = 1$$

Now since $e^{-\frac{\infty}{E_{av}}} = 0$ and $e^{-\frac{0}{E_{av}}} = 1$, then

$$A \{E_{av}\} = 1$$

so that $A = \frac{1}{E_{av}}$. So the probability distribution function for the continuous function (9) would be

$$\text{PDF}_S(E) = \frac{1}{E_{av}} e^{-\frac{E}{E_{av}}} \tag{10}$$

B.2 An Example

So, how could we use this probability density function? Well, the way continuous PDFs are used is like this. In order to find the probability of the energy of a particle lying between E_1 and E_2, you have to find the *area* under the PDF between $E = E_1$ and $E = E_2$.

So, if we wanted to find the probability of finding a particle with energy greater than E_c, say, then we would have to do this (see Figure 7, where I have chosen the values of 25 for E_{av} and 50 for E_c):

$$p(E > E_c) = \int_{E=E_c}^{E=\infty} \frac{1}{E_{av}} e^{-\frac{E}{E_{av}}}\, dE$$

Doing the integration we get

$$\begin{aligned} p(E > E_c) &= \left[-\frac{1}{E_{av}} E_{av}\, e^{-\frac{E}{E_{av}}} \right]_{E=E_c}^{E=\infty} \\ &= \left[-\, e^{-\frac{E}{E_{av}}} \right]_{E=E_c}^{E=\infty} \end{aligned}$$

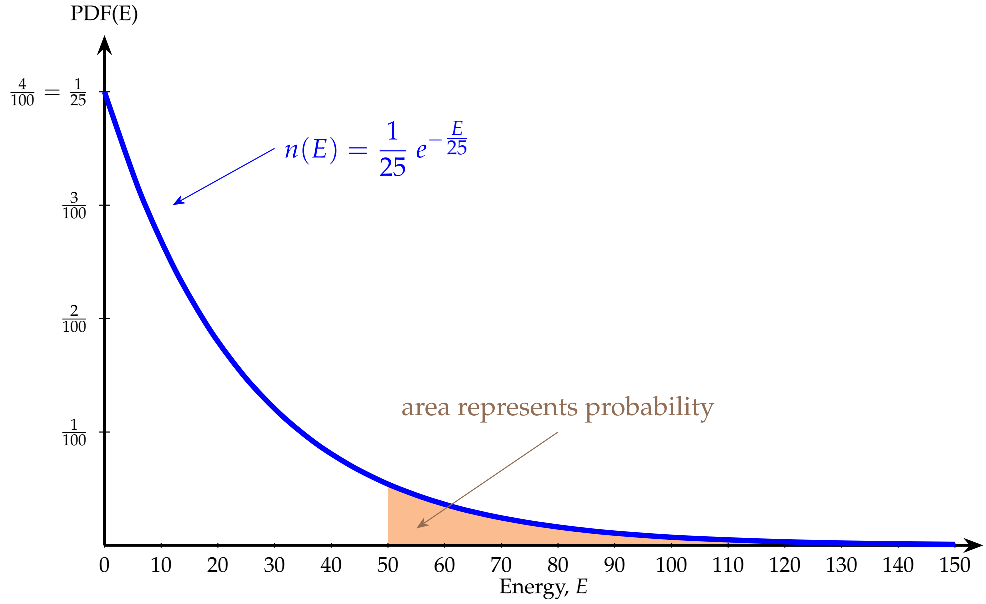


Figure 7: The Stevo PDF: 25 Units of Energy Each, Initially

Plugging in the limits we get

$$p(E > E_c) = \left\{ \left[-\, e^{-\frac{\infty}{E_{av}}} \right] - \left[-\, e^{-\frac{E_c}{E_{av}}} \right] \right\}$$

Now since $e^{-\frac{\infty}{E_{av}}} = 0$ then

$$p(E > E_c) = e^{-\frac{E_c}{E_{av}}} \tag{11}$$

And if you look back to Appendix A.2, and particularly Equation (7), you will see that this probability of a particle having an energy greater than E_c (in the continuous probability distribution) ties in wonderfully with the equation for the same thing for a discrete distribution!! So maybe we are on to something here!

C The Ratio of the Number of Particles at Two Different Energies

From Equation (1), the Stevo Distribution is given by

$$n(E) = Ae^{-\frac{E}{E_{av}}}$$

where $n(E)$ is the number of particles with energy E, and the average energy of all the particles is E_{av}.

Let's say we pick two different energies, E_1 and E_2, and we are interested in comparing the numbers of particles at those energies. Well, we know that for energy E_1,

$$n(E_1) = Ae^{-\frac{E_1}{E_{av}}} \tag{12}$$

and for energy E_2,

$$n(E_2) = Ae^{-\frac{E_2}{E_{av}}} \tag{13}$$

Now if we divide (12) by (13) we will get

$$\frac{n(E_1)}{n(E_2)} = \frac{Ae^{-\frac{E_1}{E_{av}}}}{Ae^{-\frac{E_2}{E_{av}}}}$$

But the right hand side of this equation simplifies quite a bit:

$$\begin{aligned} \frac{n(E_1)}{n(E_2)} &= \frac{e^{-\frac{E_1}{E_{av}}}}{e^{-\frac{E_2}{E_{av}}}} \\ &= e^{-\frac{E_1}{E_{av}}} \times e^{\frac{E_2}{E_{av}}} \\ &= e^{-\frac{(E_1 - E_2)}{E_{av}}} \end{aligned}$$

So the Boltzmann Factor in the form

$$e^{-\frac{\Delta E}{E_{av}}}$$

gives you the ratio of the numbers of particles in energy states ΔE apart (the higher energy state having fewer particles, of course).