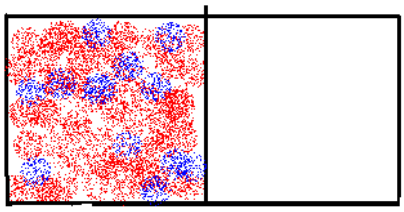
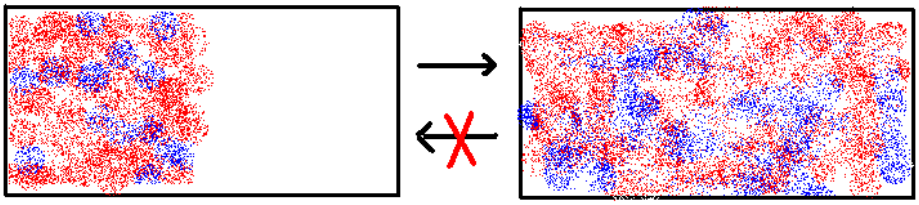
The Reduction of Thermodynamics to Mechanics

Thermodynamics	Mechanics (Kinetic Theory of Gases)
Temperature	Average kinetic energy
Pressure	Average force per unit area
Volume	volume

What about entropy?



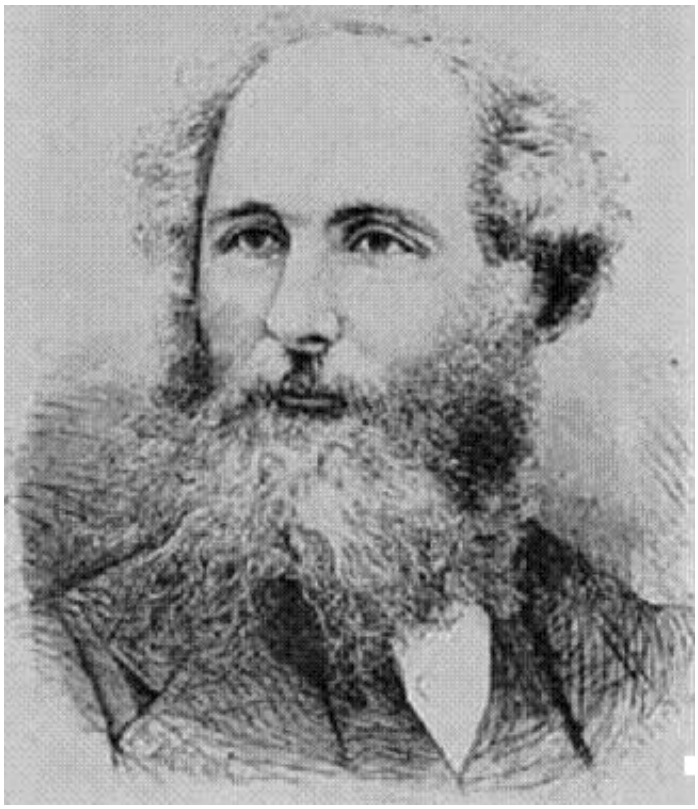


The **PROBABILITY** of going from left to right is overwhelming and the probability of going the other way around is diminishing

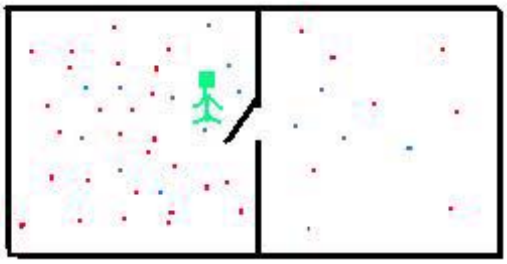
But what is this **probability**?

NOTE , the application of probabilistic notions is inevitable. It cannot be the case that processes ALWAYS go only one way.

To show that J.C. Maxwell



invented his famous demon



And what did Maxwell had to say about PROBABILITY?

From: The Life of J.C. Maxwell – L. Campbell and W. Garnett, London: Macmilian and Co., 1882

A letter from Maxwell to Campbell probably from June 1850

"… I was thinking to-day of the duties of (the) cognitive faculty. It is universally admitted that duties are voluntary, and that the will governs understanding by giving or withholding Attention. They say that Understanding ought to work by the rules of right reason. These rules are, or ought to be contained in Logic; but the actual science of Logic is conversant at present only with thing either certain, impossible of *entirely* doubted, none of which (fortunately) we have to reason on. Therefore the true Logic for this world is the Calculus of Probabilities, which takes account of the magnitude of the probability (which is, or which ought to be in a reasonable man's mind). This branch of Math., which is generally thought to favour gambling, dicing, and wagering, and therefore highly immoral, is the only "Mathematics for Practical Men," as we ought to be. Now, as human knowledge comes by the sense in such a way that the existence of things external is only inferred from the harmonious (not similar) testimony of the different sense, Understanding, acting by the laws of the right reason, will assign to different truth (or facts, or testimonies, or what shall I call them) different degrees of probability. Now, as the sense give new testimonies continually, and as no man ever detected in them any real inconsistency, it follows that the probability and *credibility* of their testimony is increasing day by day, and the more a man uses them the more he believes them. He believes them. What is believing? When the probability (there is no better word found) in a man's mind of a certain proposition being true is greater than that of its being false, he believes it with a proportion of faith corresponding to the probability, and this probability may be increased or diminished by new facts. This is faith in general. When a man think he has enough of evidence for some notion of his he refuses to listen to any additional evidence *pro* or *con*, saying, "It is settled question, *probatis probata*; it needs no evidence; it is certain." This is knowledge ad distinguished from faith. He says, "I do not believe; I know". "If any man thinketh that he knoweth, he knoweth yet nothing as he ought to know". This knowledge is a shutting off one's ears to all arguments, and is the same as "Implicit faith" in one of its meanings. "Childlike faith", confounded with it, is not credulity, for children are not credulous, but find out sooner than some think that many men are liars."

In Maxwell's view, therefore, probability is in our heads ("in a reasonable man's mind", as Maxwell puts it). The closest view is what we now call "degree of rational belief". Indeed, part of what determines the probability for a rational person is data about the relative frequency of events (so that rare events are normally assigned small probability, and frequent events high probability).

However, in this view

PROBABILITY $\neq$ RELATIVE FREQUENCY

But look what happened to our reduction. Instead of

THERMODYNAMICS ————→ MECHANICS

We have

THERMODYNAMICS ————→ MECHANICS + PROBABILITY

Where the central component of the theory, the probability distribution, is 'in our head' and is not a part of the physical world.

PHYSICISTS DON'T LIKE THAT

Here is one such person Ludwig Boltzmann

Boltzmann believed that

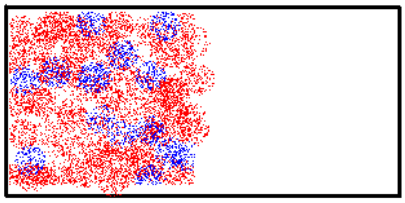
PROBABILITY = RELATIVE FREQUENCY

and that we can complete the reduction

THERMODYNAMICS ————→ MECHANICS

To accomplish this feat he wanted to prove:

HYPOTHESIS: The laws of (classical) dynamics dictate that the molecules in a closed insulated container of gas will be found very rarely in a state



with all the molecules on the left hand side, while typically, and most of the time, they will be spread equally everywhere.

We know from experience that the gas molecules NEVER spontaneously arrange themselves on one side. This is the reason why we assign this state of affairs a low degree of belief. Boltzmann's idea is to show that our experience follows necessarily from the laws of mechanics. If his program is successful he can claim that the concept probability only expresses the relative frequency dictated by Newtonian mechanics.

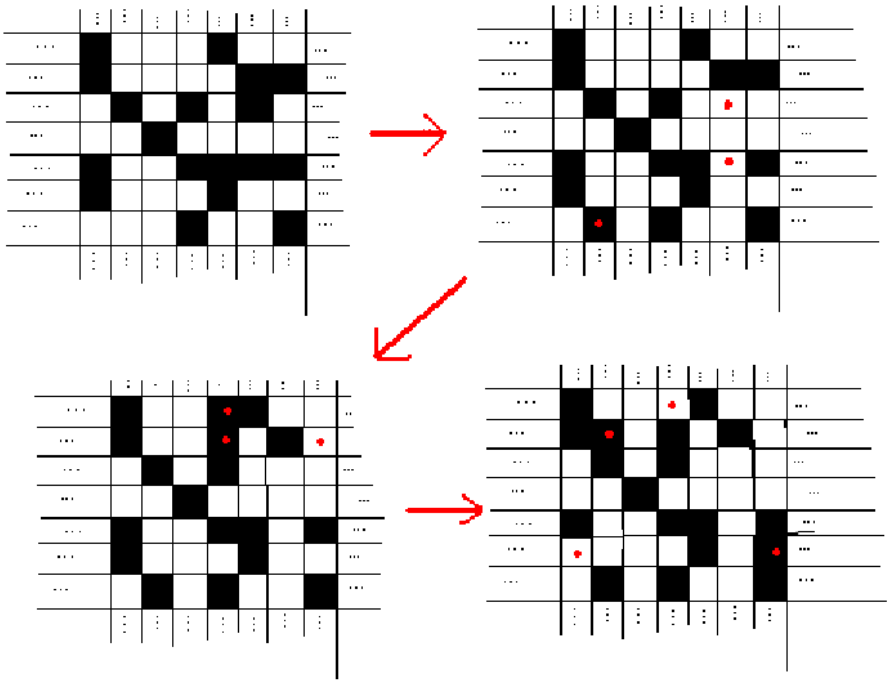
To explain his idea we shall consider first a dynamic system with finitely many possible states. Not of system made of particles but a system of pixels in a picture. Consider a square array of 1000x1000 pixels, each pixel can be black or white. Any possible arrangement of black and white pixels in our 1000x1000 square we shall call a PICTURE. We shall use the name REAL PICTURE to denote an arrangement of pixels that makes sense to us as representing something. There are $2^{1,000,000}$ possible PICTURES (more than $10^{300,000}$) but much fewer REAL PICTURES.

Indeed there are many REAL PICTURES - many more than all the pictures in all the (past, present and future) family albums put together + all the frames of all the movies (past present and future) - but their number is still diminishing compared with $2^{1,000,000}$.

Now assume that PICTURES are projected on a screen in front of you. Every second the PICTURE changes to another one. We do not need to specify the exact dynamic rules for changing the PICTURES, only to make two general assumptions about them.

DYN 1- *The rule that governs the change of PICTURES is deterministic; so the pattern of pixels of a given PICTURE uniquely determines the next picture (as in the game of Life).*

A fragment of PICTURE and its changes over the next 3 seconds may look like



Our second assumption concerning the dynamics is

DYN 2 - *Every PICTURE is eventually visited; If you wait long enough you will see each and every possible PICTURE.*

The two assumptions entail that the movie is periodic; after mere $2^{1,000,000}$ seconds it starts all over again. This is a “little”more than 10^{301022} years, while our universe is less than 10^{11} years old. This means that anyone who bothered to watch the movie since the big bang probably did not see any REAL PICTURE. Given our assumptions, it is perfectly reasonable to say that that the probability of REAL PICTURE appearing on the screen is very small, meaning simply that the relative frequency with which such a REAL PICTURE shows up is very nearly zero. This is not a matter of belief but the property of the dynamics.

WAIT A MINUTE

This is not an explanation which is free of human interest! After all, the distinction between REAL PICTURES and mere PICTURES depends on what grabs our attention. So even if the difficulties with probability are gone, the very choice of some events as interesting, and others (in fact most) as not very interesting is anthropocentric, or is it?

There have been attempts to distinguish mathematically between random and non-random patterns (in a way that does not involve a notion of probability, since this would be circular). There are some difficulties with this approach, and I am not convinced that this problem is completely solved. (We can discuss it in the question period).

However, the BIG problem with Boltzmann's program lies with the attempt to move from finite to infinite systems. Here we face

THE PERILS OF ∞

What is the analogy between the PICTURES and molecules in the gas?

One PICTURE is a pattern of 1000x1000 pixels; each second there is a new PICTURE and altogether $2^{1,000,000}$ possible ones.

What corresponds to a PICTURE in the movie is the STATE of the gas. At a given time the STATE is a list of the positions and velocities of all the molecules. If there are N molecules such a list consists of 6N real numbers (3 for every position + 3 for every velocity). Hence there is a continuum infinity of such possible STATES. The STATE (like the PICTURE) changes over time since the molecules are moving.

Most STATES correspond to a situation in which the molecules are randomly distributed in the container. A minority of states correspond to situations in which one side of the container has many more molecules than the other. Let's call this minority of cases INTERESTING STATES. They corresponds to REAL PICTURES in the movie. Now, the idea is to use the same reasoning and show that during the motion the system visits an INTERESTING STATE only very rarely.

However, before that we have to explain in what sense the INTERESTING STATES are a minority (after all, there is also a continuum infinity of INTERESTING STATES). The answer is that there is a natural notion of "area" defined on the set of all states, and the set of INTERESTING STATES has a very small area compared with the area of the set of all STATES.

As in the movie case, we should now make the assumptions about the dynamics which allows for Boltzmann's reasoning to go through.

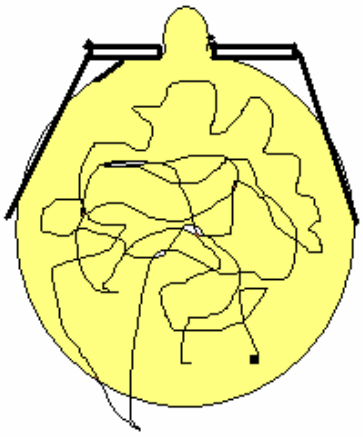
DYN 1- *The dynamics is deterministic; the state at any time t determines uniquely the state at any later time t'.*

There is no problem with this assumption since it is a characteristic of (most) Newtonian dynamics. This is precisely the sense in which classical physics is deterministic.

However, the generalization of the second assumption to this case is much more problematic.

DYN 2- *The system visits each and every possible state in its course of motion*

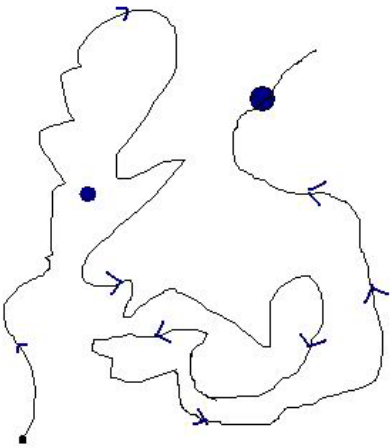
Is it true? We face here what may be called the anchorman's dilemma



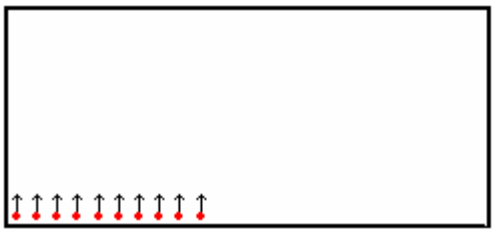
Now, it turns out that there is a solution to this dilemma, even in the limit of an infinitely thin and infinitely long hair. We can fill the whole space by a one dimensional curve, as was first shown by the mathematician Peano. This solves the anchorman's dilemma, but it does not help us! The reason is that a curve which fills up the whole space must intersect itself, and in our case this contradicts determinism. If the system returns to a previous state it must reenact the same motion all over again.

So the second assumption must be modified. A reasonable candidate:

DYN 2 *(Improved)- The system visits every neighborhood, however small, of each state.*



Unfortunately, even this cannot be true of (classical) mechanical systems. The problem is that in the infinite case we cannot require that the trajectory of the system will have that property NO MATTER WHICH STATE IT STARTED FROM. To see this consider the following situation



Now, if the system begins its motion in this way, and if there are no interaction between molecules (ideal gas) then it will certainly not reach every neighborhood of every state! So, let's call an initial state as above pathological. The most we can expect in generalizing our dynamic assumption is

DYN -2 (*further improved) ALMOST every possible state of the system is non-pathological; a system that starts from a non-pathological state goes on to visit every neighborhood of every other state.*

What does this "almost" "mean? Well, as before, it means that the "area" of the set of pathological states is zero (however, there's still an infinite continuum of them). Given this version we can finally continue the program and **claim**:

If a closed mechanical system satisfies DYN 1 and DYN 2 (further improved) then it will visit INTERESTING STATES very infrequently

It turns out that this **claim** (in a somewhat more general form) is true, but not trivial. It was proved in the 1930's, in various forms, independently by Birkhoff, von Neumann, and (a later stronger version) by Wiener. It's called the ergodic theorem. It seems that Boltzmann has prevailed and, at least for systems that satisfy **DYN 1** and **DYN 2** probability is frequency, or is it?

NO

To claim that probability IS frequency on the basis of this theorem is circular. DYN 2 is too weak to provide for a full reduction. (It is rather like trying to define probability as relative frequency on the basis of the strong law of large numbers,we can discuss this in the question period). To see why consider the following dialogue

Alice and Bob are watching a container full of gas:

-Alice: Why don't we ever see an INTERESTING STATE?

-Bob: That's because the area of the set of INTERESTING STATES is small relative to the area of the set of all states.

-Alice: What does this have to do with my question?

-Bob: By the ergodic theorem sets of small area - the set of INTERESTING STATES in particular - are rarely visited.

-Alice: But this is true only if the state from which this gas began was non-pathological!

-Bob: Yes, but the set of pathological states has a zero area.

-Alice: What does this have to do with anything...

You see, in order to prove that sets of small area are rarely visited we have to ASSUME, without a proof, that sets of zero area correspond to zero probability. Only then it is possible to associate probability with frequency. But we could have started by *defining* probability in terms of the area, and claim that it is a degree of belief which is justified on the basis of frequency. Isn't that what we do anyway?

Extra BIG trouble: Typically, closed (classical) mechanical systems do not even satisfy DYN-2 (further improved). This is by KAM theorem.

However, an ideal gas made of billiard balls like molecules, with elastic collisions, does satisfy DYN-2 (further improved). This is a theorem of Sinai