

ENTROPY & STATISTICS

PROBABILITY ENTERS PHYSICS

↳ strict determinism leaves.

RE-VISIT THE FREE-EXPANSION EXAMPLE...



SUPPOSE... just after the partition is lifted



unusual situation, right?

From the V_B situation, what's the probability for



that molecule to end up in the original V_A ?

prob: $W_A = \frac{V_A}{V}$ where V is some arbitrary, larger volume

How about for N molecules? they are independent,

$$W_A = \left(\frac{V_A}{V}\right)^N$$

How about from $V \rightarrow V_B$? $W_B = \left(\frac{V_B}{V}\right)^N$

Take ratio:

$$\frac{W_B}{W_A} = \frac{\left(\frac{V_B}{V}\right)^N}{\left(\frac{V_A}{V}\right)^N} = \left(\frac{V_B}{V_A}\right)^N$$

take log and $\times k$:

$$k \ln \frac{W_B}{W_A} = \underset{\substack{\uparrow \\ nN_A}}{N} k \ln \left(\frac{V_B}{V_A}\right)$$

$$k \ln \frac{W_B}{W_A} = nN_A k \ln \left(\frac{V_B}{V_A}\right)$$

$$k \ln \frac{W_B}{W_A} = nR \ln \left(\frac{V_B}{V_A}\right)$$

Thermodynamically, we found that

$$\Delta S = nR \ln \left(\frac{V_B}{V_A}\right) = S_B - S_A$$

SO: we can interpret

$$k \ln W_B - k \ln W_A = S_B - S_A$$

or, generally

$$S = k \ln W$$

Very famous result.

called a "free expansion" → different from our piston where work was involved

BUT: well-defined states at beginning & end... can use any reversible situation to calculate ENTROPY...

Like a piston which does work... in an isothermal transition:

$$\Delta W = \Delta Q = nRT \ln V_f/V_i$$

So:


$$\Delta S = \frac{\Delta Q}{T} = nR \ln(V_f/V_i)$$

for this IRREVERSIBLE transition

Notice: $V_f > V_i$ so, $\Delta S > 0$

Entropy is a measure of the **PROBABILITY** of a state.

It says something else:

one thing about V_A 
relative to V_B 

The locations of the molecules are
MORE ORDERED

in V_A than V_B

and

$$S_A < S_B$$

The irreversible system spontaneously & naturally evolved from V_A to V_B

from the ordered to the disordered
state.

Disorder is preferred. Entropy tells you how much.

Ans -

Had this been a piston - reversible - Then

ΔW could have been done in going

from $T_i V_i \rightarrow T_f V_f$.

HERE -- there is energy ^{originally} ~~change~~ which is





UNAVAILABLE for work. afterwards

$$W = nRT \ln V_f/V_i \quad \text{available --}$$

but lost

$$E_{\text{unavailable}} = T \Delta S$$

Remember!

T_H			?
T_C			T_M
	i	f	

a) what is the final temperature, T_M --

b) what is the change of entropy of the H object?

• what is the change of entropy of the C object?

c) what is the total ΔS for the system

a) Heat lost by one, gained by the other--

$$Q_H = -Q_C$$

$$m_1 c_1 \Delta T_H = -m_2 c_2 \Delta T_C$$

$$m_1 c_1 (T_M - T_H) = -m_2 c_2 (T_M - T_C)$$

same material -- same mass

$$(T_M - T_H) = -(T_M - T_C)$$

$$T_M = \frac{1}{2} (T_H + T_C) \quad \text{average}$$

b) not inherently ~~an~~ reversible process...

but can imagine an ∞ number of reservoirs, each infinitesimally cooler than, say T_H , taking the hot guy toward T_M infinitesimally--

-- so can integrate this system

$$\Delta S = \Delta S_H + \Delta S_C \quad \leftarrow \text{system entropy.}$$

$$\begin{aligned} \Delta S &= \int_H \frac{dQ_H}{T} + \int_C \frac{dQ_C}{T} \\ &= \int_{T_H}^{T_M} mc \frac{dT}{T} + \int_{T_C}^{T_M} mc \frac{dT}{T} \end{aligned}$$

$$\Delta S = mc \left[\ln \frac{T_M}{T_H} + \ln \left(\frac{T_M}{T_C} \right) \right]$$

$$\text{since } T_M = \frac{1}{2} (T_C + T_H)$$

$$\ln \frac{1}{2} \left(\frac{T_C}{T_H} + 1 \right) < 0 \quad \ln \frac{1}{2} \left(\frac{T_H}{T_C} + 1 \right) > 0$$

continuing-- algebra
...

$$\Delta S = mc \ln \left[\frac{(T_H + T_C)^2}{4T_H T_C} \right]$$

which is POSITIVE

The system's entropy increased.

2^{nd}_3 : The entropy of a closed system can never decrease

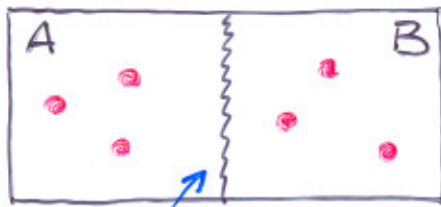
2^{nd}_4 : The entropy of the universe can never decrease.

2^{nd}_5 : Heat tends to flow from hot to colder bodies.

THE ARROW OF TIME
IS PICKED OUT BY
ENTROPY

NEW SYSTEM..

... new point to wake...



3 molecules in
each side

a membrane which will not pass
molecules.. but like a trampoline,
will transfer kinetic energy



call: U_A -- the internal energy of A
 U_B -- " " B } mix

subject to: $U_S = U_A + U_B$

remember that $U = \frac{3}{2} NkT$

so $T \propto \frac{U}{N}$ --- forget about $\frac{3}{2}k$ for now.

we'll say $T = \frac{U}{N}$ okay?

$$T_A = \frac{U_A}{3}$$

$$T_B = \frac{U_B}{3}$$

Further, we'll say that $U_S = 11$ units of energy.

$$11 = U_A + U_B$$

New terminology

microstate

configurations ("macrostates" sometimes)

define by example...

2 die... what's the probability of rolling 7?

Brute force...

Die A	Die B	roll
1	1	2
1	2	3
1	3	4
1	4	5
1	5	6
1	6	7

etc... (next page)

each ~~pair~~^{pair} is a microstate

die A	die B	roll
1	1	2
1	2	3
1	3	4
1	4	5
1	5	6
1	6	7
2	1	3
2	2	4
2	3	5
2	4	6
2	5	7
2	6	8
3	1	4
3	2	5
3	3	6
3	4	7
3	5	8
3	6	9
4	1	5
4	2	6
4	3	7
4	4	8
4	5	9
4	6	10
5	1	6
5	2	7
5	3	8
5	4	9
5	5	10
5	6	11
6	1	7
6	2	8
6	3	9
6	4	10
6	5	11
6	6	12



total number
of possibilities

36

6 ways
to make "7"

The probability of making 7 is $\frac{6}{36}$

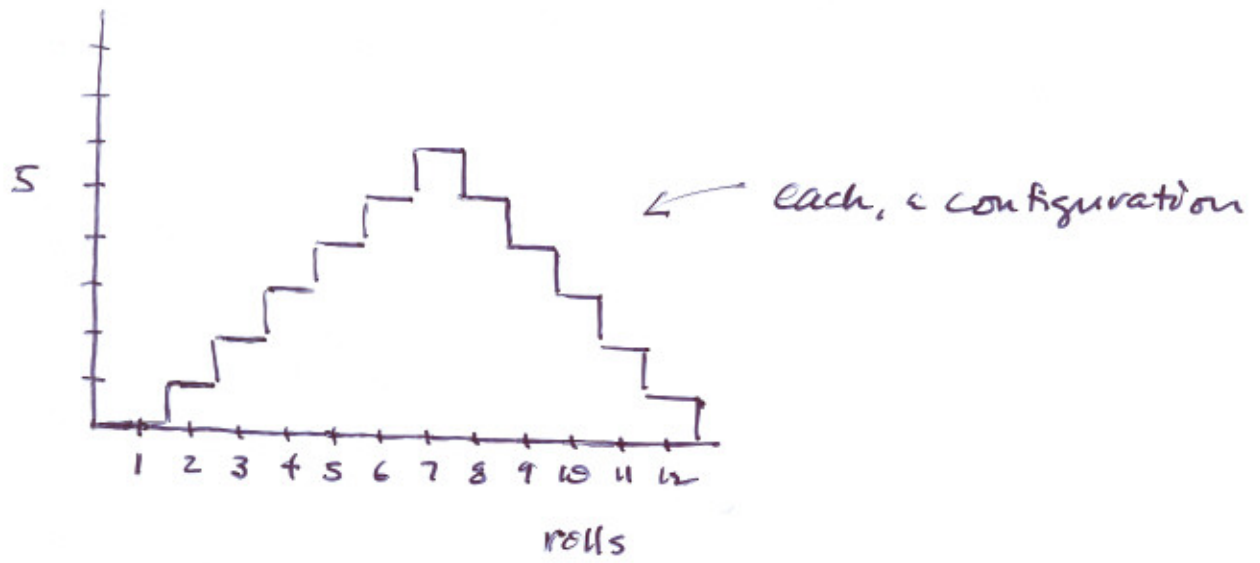
Each pair of ~~config~~ dice is a ^{MICRO} STATE... each corresponds to a roll, some of which are the same

roll	# combinations making roll	probability
2	1	$\frac{1}{36}$
3	2	$\frac{2}{36}$
4	3	$\frac{3}{36}$
5	4	$\frac{4}{36}$
6	5	$\frac{5}{36}$
7	6	$\frac{6}{36}$
8	5	$\frac{5}{36}$
9	4	$\frac{4}{36}$
10	3	$\frac{3}{36}$
11	2	$\frac{2}{36}$
12	1	$\frac{1}{36}$

A CONFIGURATION is each possible roll... here, there are 11.

so: (1,6), (2,5), (3,4), (4,3), (5,2), (6,1) is a configuration with a "weight" of 6.

back to the gas...



How many ways can the gas of 3 molecules have an internal energy of u ? ... if they are indistinguishable

$u = 0$ $(0, 0, 0)$ one way.

$u = 1$ $(1, 0, 0), (0, 1, 0), (0, 0, 1)$
BUT, indistinguishable

So $(1, 0, 0)$ counts them all one way

$u = 2$ $(2, 0, 0), (1, 1, 0)$ two ways

okay?

u	# states
0	1
1	1
2	2
3	3
4	4
5	5
6	7
7	8
8	10
9	12
10	14
11	16

use this to count the total number of system states...

u_A	u_B	T_A	T_B
0	11	0	$11/3$
1	10	$1/3$	$10/3$
2	9	$2/3$	3
3	8	1	$8/3$
4	7	$4/3$	$7/3$
5	6	$5/3$	2
6	5	2	$5/3$
7	4	$7/3$	$4/3$
8	3	$8/3$	1
9	2	3	$2/3$
10	1	$10/3$	$1/3$
11	0	$11/3$	0

# system states	prob.
$1 \times 16 = 16$	$16/302$
$1 \times 14 = 14$	$14/302$
$2 \times 12 = 24$	$24/302$
$3 \times 10 = 30$	$30/302$
$4 \times 8 = 32$	$32/302$
$5 \times 7 = 35$	$35/302$
$7 \times 5 = 35$	$35/302$
$8 \times 4 = 32$	$32/302$
$10 \times 3 = 30$	$30/302$
$12 \times 2 = 24$	$24/302$
$14 \times 1 = 14$	$14/302$
$16 \times 1 = 16$	$16/302$
	$\xrightarrow{\quad}$ 302 possible states

Note:

- The most probable configurations are those where the 2 gases have the closest temperatures. $T_1 \approx T_2$ here.
- If the system starts out with $T_A > T_B$...
and if it moves to the most probable state ...
 T_A becomes smaller
 T_B becomes higher.
or vice versa.

Heat is transferred FROM hot to cold.

Notice also ... one gas moves to lower probability,
The other gas moves to higher probability,

- such that the whole SYSTEM moves to the higher probability

THE ARROW OF TIME ...

systems move from states of lesser to greater probability

Have it said "ENTROPY" yet...

$$\Delta S = \frac{\Delta Q}{T}$$

}

Consider situation where
 $T_A > T_B$ initially.

How about A...

Heat leaves A to B...

less energy \Rightarrow fewer states

$$\hookrightarrow \Delta S_A < 0 \quad \leftarrow$$

How about B...

Heat enters B from A

more energy \Rightarrow more states

$$\hookrightarrow \Delta S_B > 0 \quad \leftarrow$$

and they do so in concert so that

How about System...

fewer states \rightarrow more states

$$\downarrow \\ \Delta S_S > 0$$

2nd
6

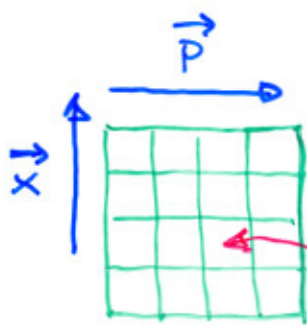
Stuff tends to get
mixed up.

Rough description of what Boltzmann (eventually) did:

A gas could be described by the individual Newtonian equations for each of $\sim 10^{23}$ molecules

not.

Suppose you "partition" \vec{p} and \vec{x} space...6d called "phase space"

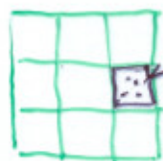


like a digital speedometer

take all molecules of gas.

presume that each (\vec{x}, \vec{p}) can be "slotted" into a finite-sized box in phase space

(\vec{x}, \vec{p}) plays the role of one die and the other



the "number" of (\vec{x}, \vec{p}) combinations in each box plays the role of the configuration

THEN...

The arrangement of the configurations of the populated boxes is a possible state of the whole gas

go from:

states of individual molecules \rightarrow states of the gas

BOLTZMANN WORKED OUT A THEORY

of the time-evolution of the various configurations of populated boxes

From strictly probabilistic considerations - not Newtonian dynamics... he found

start a configuration in phase space randomly

evolve
 \longrightarrow
in time

a particular most probable situation for $f(\vec{x}) \approx f(\vec{p})$

THE MAXWELL DISTRIBUTION OF SPEEDS...



now called

The Maxwell-Boltzmann Distribution

Probability... not deterministic, dynamical
equations of motion... determine the

most likely

outcome. Entropy fell out of his analysis...

there were issues:

Poincare: a dynamical system must eventually return to its original state.

uh oh.

if you start a cubic centimeter of gas in, say, all in a tiny corner of that cubic centimeter...then there must be a time in which the gas all returns to that corner

Boltzmann calculated that the interval of time required...would be a number of seconds counted with trillions of digits: many times the age of the universe

Boltzmann in response to a critic
(a student of Max Planck)

“

...suppose you take 1000 dice and ask about the likelihood of throwing a circumstance of all 1's?... eventually, that must happen

But, he argued his critic was “...like a dice-player who... concludes that something is wrong with his dice because such an occurrence had not yet presented itself to him.”

THIS ... changed everything.

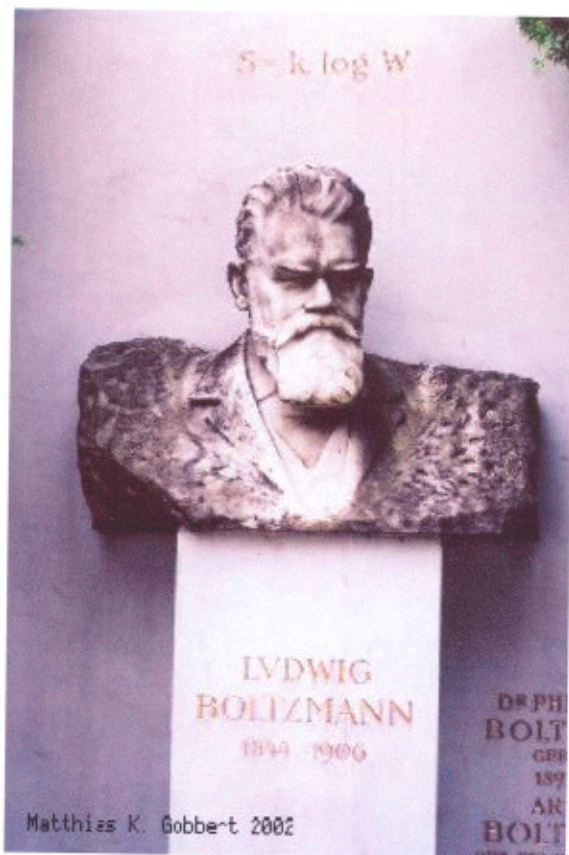
drop an egg ... its most likely configuration
is the shattered one.

Boltzmann said you have to accept the
finite chance that it could
re-assemble itself

When is tiny ... time likely for it to happen:
many times greater than the
lifetime of the universe

THIS CHANGED EVERYTHING.

1. probability as an inherent feature of reality -- not just a lazy way to do a calculation
2. the "quantization" of seemingly continuous quantities as a tractable technique



$S = k \log W$

LUDWIG
BOLTZMANN
1844 - 1906

DR PH
BOLT
1844
1906
BOLT

Matthias K. Gobbert 2002