IV. Applying S = k ln W : Physics & Applications

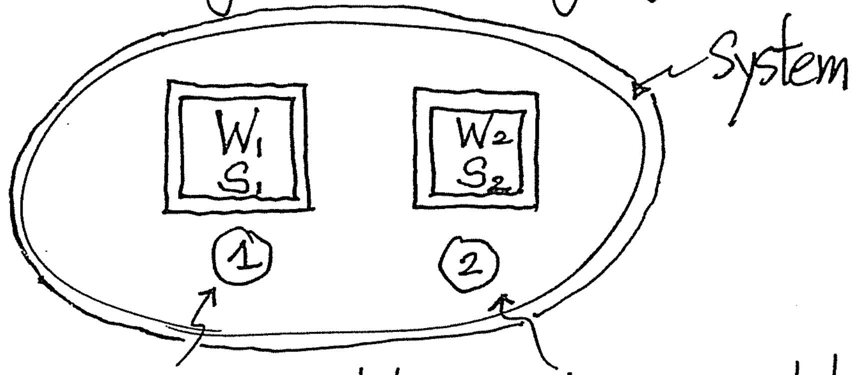
[Seeing (how S = k ln W works) is believing!]

Main Points

- $S = k \ln W$ gives results consistent with what we know from thermodynamics. For example:
  - Relaxing a constraint allows more microstates to become accessible [Relaxing a constraint leads to irreversible (spontaneous) process and entropy increases]
  - Two systems at equilibrium have something in common $[(\frac{\partial S}{\partial E})]$ [temperature]
- Large Systems: "All microstates are equally probable" leads to "irreversibility" and thus "an arrow of time"
- Standard Problems
  - Two-level systems (defects in solid; paramagnetism)
  - Collection of harmonic oscillators (heat capacity of solid)
  - Classical ideal gas

A. Numbers of Microstates Multiply and Entropies Add

Consider a system consisting of two subsystems



Microscopic: W_1: # microstates subsystem ① W_2: # microstates subsystem ②

Macroscopic: S_1: Entropy S_2: Entropy

- S is an Extensive variable
- Consider them as one big system, we want to have:

$$W = \underbrace{W_1 \cdot W_2}_{\text{\# microstates multiply!}}$$

∵ Each microstate in ① can go with a microstate in ② to become a microstate of the composite system

and

$$S = \underbrace{S_1 + S_2}_{\text{entropies add}} \qquad \text{(extensive)}$$

- $S = k \ln W$ works this way!

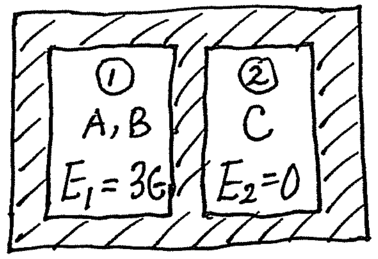
$$S = k \ln W = k \ln (W_1 \cdot W_2)$$
$$= k \ln W_1 + k \ln W_2$$
$$= S_1 + S_2 \quad \text{as needed!}$$

$\therefore$ $S = k \ln W$ makes good sense!

B. From Non-equilibrium towards equilibrium, System has access to more microstates

We considered an example of $E = 3\varepsilon$ among $N = 3$ distinguishable particles, and counted $W = 10$.

Now, let's impose an additional constraint (add an insulating rigid wall) that A & B particles form a subsystem ① and C particle forms subsystem ②



Let's put all 3ε energy into ①

① is an isolated system

② is an isolated system

$\boxed{①+②}$ is an isolated system

Subsystem ①

$W_1 = 4$ microstates

$\therefore$

A	B
3ϵ	0
0	3ϵ
2ε	ε
ϵ	2ε

$N_1 = 2$, $E_1 = 3\epsilon$

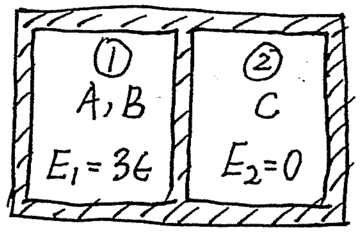
Subsystem ②

$W_2 = 1$ microstate

$N_2 = 1$, $E_2 = 0 \Rightarrow$ Particle C has zero energy (1 microstate)

$$W_{1+2} = W_1 \cdot W_2 = 4$$

What is going on?

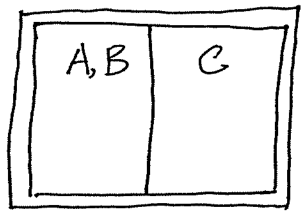


Get a sense $\underbrace{\textcircled{1}: \frac{\text{energy}}{\text{particle}} = \frac{3}{2}}_{\text{"hotter"}}$ $\underbrace{\textcircled{2}: \frac{\text{energy}}{\text{particle}} = 0}_{\text{"colder"}}$

- Subsystems ① and ② are NOT in equilibrium
- The adiabatic wall (additional constraint) keep them out of equilibrium.
- As a result, composite system can only access 4 microstates

What if we remove the additional constraint?

- Change wall so that particles A, B, C can exchange energy and wait



$N=3,\ E=3\epsilon$

Then $\underbrace{W = 10} > 4$

- ① & ② at equilibrium can access more microstates than ① & ② are kept out of equilibrium
- $dS > 0$ for irreversible processes [W increases]

- Why W increases?

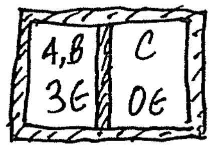
With adiabatic Wall: $E_2 = 0$ only (W=4)

Without adiabatic Wall: C particle's energy E_2 can be $0, 1\epsilon, 2\epsilon, 3\epsilon$

(W = 10)

- These 10 states include the 4 states with $E_2=0$

So (a)



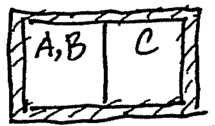
:

Labelling microstate: $\boxed{\underbrace{\#1\quad \#2\quad \#3\quad \#4}_{E_2=0}}\quad \underbrace{\#5\quad \#6\quad \#7\quad \#8\quad \#9\quad \#10}$

Non-equilibrium system can only visit this restricted set of microstates

adiabatic wall makes these skills not accessible

But (b)



All 10 microstates become accessible

$\boxed{\#1\quad \#2\quad \#3\quad \#4\quad \#5\quad \#6\quad \#7\quad \#8\quad \#9\quad \#10}$

At equilibrium (after some time), the composite system visits every microstate evenly.

From (a) to (b), $\Delta S > 0$. Thus $S = k \ln W$ makes good sense!

▪ How about Irreversible Processes?

Irreversible phenomena in macroscopic systems have a probabilistic root!

For our tiny system, $\underbrace{W=10.}$ $[N=3]$

Visit them evenly (isolated, equilibrium)

⇒ 4/10 of time we will $\underbrace{\text{see } E_2=0}$!

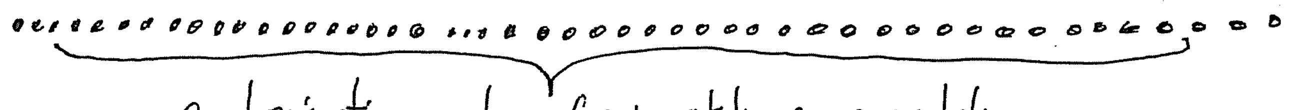
one side is colder
and one side is hotter!

[This is indeed what Statistical Mechanics predicts!]

[But we never see it happened in a metallic rod.
And we never see a pendulum at rest suddenly swings.]

The point is: For macroscopic $(N \sim 10^{25})$ systems, W is huge. The macroscopically observed situation (e.g. uniform temperature) dominates a large part of W!

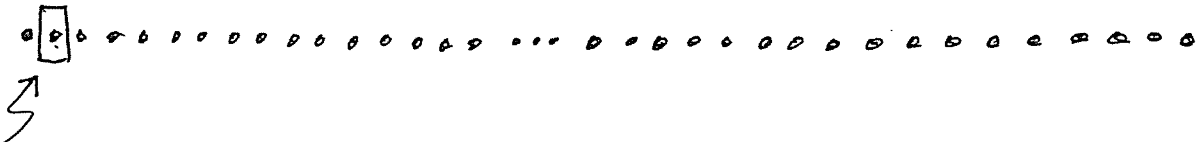
microstates
$\sim E^N$ of
them
(huge #)



a dominating number of microstates correspond to
uniform temperature in metallic rod
(you observe system in your lifetime, we see the uniform temp. situation only

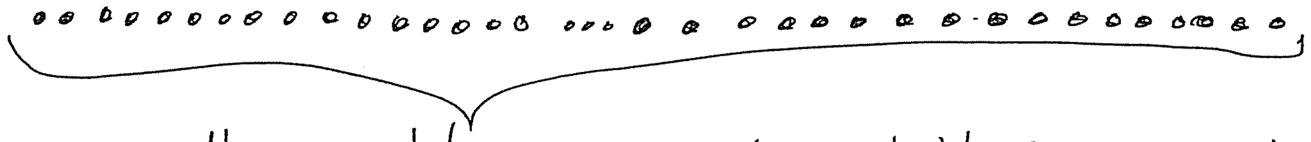
Irreversibility (seems deterministic) comes from:

Initially,



a state OR a
small group of states
corresponding to
one end being hotter

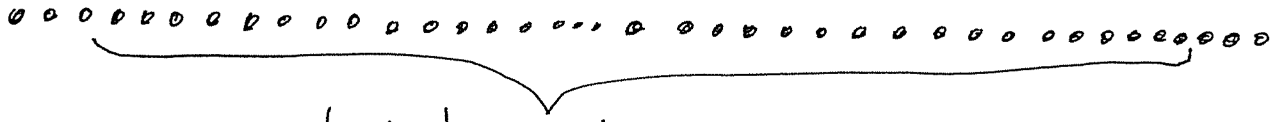
Let system evolve



all microstates are equally probable (at equilibrium)

↓

of which



a dominating number of microstates
correspond to a uniform temperature
[that's what one always sees]

Understand!?
Irreversibility and Probabilistic nature of Stat. Mech.
are compatible! (Macroscopic Systems)

Remarks

- This microscopic understanding of what we observed as irreversible/spontaneous processes is a profound idea and is one of the most important achievements in the knowledge of mankind!

  [This gives the notion of time.]
- This idea is as important as Newton's laws, Maxwell's Equations and Schrödinger Equation.
- In this Section, we gave the physical picture and discussed the key ideas using simple examples. We will paint this physical picture more mathematically in Sec. C, which leads us to the thermodynamic relations (that we know) and eventually leads us to the canonical ensemble theory (next Chapter).
- Here, let's stick to the microcanonical ensemble theory (fixed (E, V, N)) for a while.

Insert: Classical Ideal Gas as an example

[Microcanonical ensemble]

The Story: In September 1911, two separate papers were published in Annalen der Physik. They give a mathematical formula for the entropy of an ideal gas

$$S = Nk\left(\ln \frac{M^{3/2}T^{5/2}}{P} + \ln\left[\left(\frac{2\pi}{N_A h^2}\right)^{3/2} k^{5/2}\right] + \frac{5}{2} \right)$$

$\underbrace{\text{Sackur}}_{\text{31 years old}}$ - $\underbrace{\text{Tetrode}}_{\text{17 years old}}$ Equation

based on (classical) Statistical Mechanics.

1911:

- See h (Planck's constant) appears in S
- h started to appear in 1900 (Planck's black-body formula) and 1905 ($h\nu$ in photoelectric effect)
- but no Bohr's model, Schrödinger/Heisenberg Equation yet.

Let's work out $S(E, V, N)$ for classical ideal gas.

[Details given in an Appendix]

(Read History of Sackur-Tetrode Equation next page)

This Month in Physics History

September, 1911–The Sackur-Tetrode Equation: How Entropy Met Quantum Mechanics

From APS News
(August-Sept. 2009)
Vol. 18, No. 8

APS = American Physical Society

Editor's note: This month's column has been contributed by guest author Richard Williams.

Early in the twentieth century, leading physicists were struggling to get a deeper understanding of the concept of entropy. Entropy is at the heart of the all-encompassing Second Law of Thermodynamics and can be used to establish the absolute temperature scale, so it needs to be fully understood. But a troubling question remained unanswered. Could its absolute value be determined, or would it always involve an unknown additive constant?

The Sackur-Tetrode Equation

$$S = N k\{ \ln M^{3/2} T^{5/2} / P + \ln [(2 \pi / N_{Av} h^2)^{3/2} k^{5/2}] + 5/2 \}$$

Attention began to focus increasingly on Ludwig Boltzmann's ideas. His long work on the problem is summarized in the terse epitaph, $S = k \ln W$, that is carved on his tombstone in Vienna. The equation expresses entropy, S, as the logarithm of W, the number of possible states of motion available to the atoms in a system, consistent with their energy, and multiplied by the constant, k, named for Boltzmann. However, according to classical theory, there was no limit to how close to one another, in momentum and space, the neighboring states of motion could be, and, therefore, no limit to the number of states that could exist. How then could W be enumerated to give a unique result? Thus, the question about the arbitrary additive constant.

The answer would come in two separate articles in the premier German physics journal, *Annalen der Physik*, one published in September, 1911, and the other a few months later. One author was Otto Sackur, 31 years old, a rising young physical chemist at the University of Breslau. The other was Hugo Tetrode, 17 years old, the precocious son of the president of the Dutch National Bank. Both focused on how to count the number of possible distinguishable states of motion of the atoms of a monatomic gas. In similar, but not identical, analyses, they argued that the number of allowed states in a given energy range depended on how close the states of motion could get to one another–in position and momentum, for example. They considered pairs of coordinates that define the motion of atoms, either momentum and position, or energy and time. If a lower limit existed for the possible size of the elements of the space representing the pair of coordinates, this would give an upper limit to the magnitude of W, and allow a definite count to be made.

Tetrode started with an equation from the classical statistical mechanics of J. Willard Gibbs. He required the product of the elements, momentum–position, to be not smaller than Planck's constant. Sackur adhered more to the style of Max Planck's school of thermodynamics. By similar reasoning, he limited the spacing of the allowed states for the elements, energy–time. This, together with Boltzmann's Equation, gave them an expression for the absolute entropy, the Sackur-Tetrode Equation.

Their equation can be used today without modification to calculate the standard entropy for ideal monatomic gases. Knowing only the temperature, pressure, and atomic weight of the atoms, an extremely simple calculation gives the entropy value so accurately that the calculated value is preferred to experimental values in tabulations of best values of thermodynamic data, such as the *CRC Handbook of Chemistry and Physics*.

After his work on this problem, Tetrode wrote some other theoretical papers, but none achieved comparable recognition. He lapsed into scientific obscurity, little remembered even among the community of Dutch physicists. In 1932, his compatriot, the physicist H.G.B. Casimir, spent a year as an assistant to Wolfgang Pauli at the Technische Hochschule in Zurich. Once, Pauli goaded him, "You Dutch people are strange birds. You have the example of Tetrode. He has done outstanding work, but no one knows about him, and it seems that no one wants to know." Casimir realized that he, too, knew little about Tetrode's life, and he began to learn more about it. In 1984 he wrote an article summarizing Tetrode's life, entitled, "A Forgotten Genius." Tetrode's higher education was brief, obviously at 17 years of age, when he wrote his article for *Annalen*, but also, later, his education was irregular for a scientist. He spent 1912 at the University in Leipzig, but apparently attended few lectures and did not take the usual exams. He corresponded with the major Dutch physicists at times, but did not form lasting scientific relationships. Nor did he cultivate those who might advance his scientific career. At one point, Albert Einstein and Paul Ehrenfest called at his home, but the maid told them that he could not receive them. He died of tuberculosis in 1931.

Sackur's career advanced more along the normal course for a scientist. After his doctorate from the University of Breslau, he worked there with Rudolph Ladenburg, then in London with William Ramsay, and finally in Germany with Walther Nernst, whose heat theorem was at the center of efforts to resolve the concept of absolute entropy, leading eventually, with some help from the work of Sackur and Tetrode, to the Third Law of Thermodynamics. Sackur wrote well-received books on thermodynamics, and in 1914 he joined Fritz Haber's prestigious Institute in Berlin. Haber's reputation at the time was golden, after his stunning achievement of the fixation of nitrogen from the air to form ammonia. It would bring him the Nobel Prize. His reputation began to suffer when he led Germany's project to use poison gas as a weapon in World War I. He focused the Institute's work on this project, bringing in Sackur, James Franck, and others. In late 1914, Sackur was killed in a lab explosion, prematurely ending a promising career. But this was not all. Haber's wife, Clara Immerwahr, was a close personal friend of Sackur. She opposed Haber's poison gas work on moral grounds and had long protested bitterly. When she learned of Sackur's death, from what she saw as coerced work on an immoral project, she was inconsolable. Finally, distraught, she committed suicide, using her husband's service pistol, completing a tragedy of Shakespearean dimensions.

Otto Sackur and Hugo Tetrode died too young, victims of the scourges of their time, tuberculosis and war. Despite their disparate backgrounds, they, like Boltzmann, left an equation as an epitaph, one that endures and joins them together.

Recall: Statistical Mechanics is the microscopic theory of thermodynamics

- Starting Point is microscopic description of the ideal gas system [N atoms (point particles) in a Volume V]

$$H = H(\vec{r}_1, \vec{p}_1; \vec{r}_2, \vec{p}_2, \cdots, \vec{r}_N, \vec{p}_N)$$ (Hamiltonian) (formally)

$$= \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$ (symbolically)

$$= \sum_{i=1}^{N} \left(\frac{p_{ix}^2}{2m} + \frac{p_{iy}^2}{2m} + \frac{p_{iz}^2}{2m} \right)$$ (non-interacting, kinetic energy terms only)

$$= H(\{\vec{p}_i\})$$ (depends only on $\vec{p}_i$'s)

This is all we need!

- Find $W(E,V,N)$, then $S(E,V,N)$ and then the thermodynamics of an (classical) ideal gas