

PREVIOUSLY ON

...*Thermodynamics*

Clausius Inequality

Existence of a definite integral $\int \frac{dq}{T}$

Entropy - a state variable

Second Law stated as principle of increasing entropy

Entropy changes in system and the surroundings

The Principle of Increasing Entropy

Isolated system, or **System** plus **Surroundings** enclosed by an adiabatic wall, or entire universe.

$$d\dot{q} = 0 \Rightarrow \Delta S \geq 0.$$

The entropy of a thermally isolated ensemble can never decrease.

This defines a direction of time. The Second Law is the **ONLY** fundamental equation in physics which violates CPT Symmetry.

Boltzmann argued that its validity was not based on the inherent laws of nature but rather on the choice of extremely improbable initial conditions.

The Central Equation of Thermodynamics

Combine the first and second laws.

$$dU = \delta Q + \delta W \quad \rightarrow \quad \boxed{dU = TdS - PdV}$$

- Derived for **infinitesimal reversible** processes in differential form.
- This equation involves **only state variables**.
- Can be integrated to relate changes of state variables *independent of the path of integration*.
- Integration of equation can be applied to irreversible processes.
- Can be written $TdS = dU + PdV$, relating entropy to more easily measurable quantities.
- U and V are extensive quantities, so S must also be extensive.

Caveat:

PdV implies mechanical work compressing a fluid.

In general dW should include all forms of work. e.g.

- For electric charge (Z) and emf \mathcal{E} , $dU = TdS - PdV + \mathcal{E}dZ$.
- For a rubber band length L under tension \mathcal{F} , $dU = TdS + \mathcal{F}dL$.

Entropy of an ideal gas

For an Ideal gas $U = U(T)$, so $dU = C_v dT$.

The central equation for dS , then gives:

$$dS = C_v \frac{dT}{T} + nR \frac{dV}{V}; \quad dS = C_v \frac{dT}{T} + Nk_B \frac{dV}{V}; \quad ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

For n moles or N molecules or the molar entropy s .

Integrating the above expression gives:

$$s = c_v \ln T + R \ln v + s_0$$

with s_0 the constant of integration.

Note that according to this, as $T \rightarrow 0$, $s \rightarrow -\infty$.

Kinetic theory and ideal gas equation break down at low T .

We'll see later that entropy is positive, it is about counting things.

Heat must come in countable lumps. **Quanta**.

Entropy change on Joule expansion

- By definition, in free expansion of an ideal gas, $dW = 0$; $dQ = 0$.
- Hence $dU = 0$, U does not change,
- For ideal gas $U = U(T)$, so T doesn't change.
- But volume v changes, so entropy s changes.
- integrate $ds = c_v \frac{dT}{T} + R \frac{dv}{v}$
the change in entropy in free expansion is:

$$s_f - s_i = c_v \ln T_f + R \ln v_f + s_0 - (c_v \ln T_i + R \ln v_i + s_0) = R \ln \frac{v_f}{v_i}$$

- or $v_f = v_i \exp[(s_f - s_i)/R]$

note the way logs are creeping in.

Meanwhile, in Vienna Ludwig Boltzmann, 1844-1906

Hanged himself. Famous tombstone erected in 1930



Maxwell-Boltzmann distribution. $S = k_B \ln W$

W is for *Wahrscheinlichkeit*, mistranslated ways published by Maxwell in 1860 and Boltzmann in 1866), at a time when most physicists (esp. Mach) didn't believe in atoms (chemists did...)

An example, “heating water on a stove”

Calculate the change in entropy of water heated from 20° C to 100° C on a stove.

method 1 (lecture 6): Create equivalent reversible process.

$$\Delta S = \int_{T_i}^{T_f} \frac{dq_R}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

The change of entropy of the water is the same as in the irreversible process that actually occurs since entropy is a state function and the initial and final equilibrium states match.

An example, "heating water on a stove"

Calculate the change in entropy of water heated from 20°C to 100°C on a stove.

method 2: Integrate the central equation:

$$\Delta S = \int_i^f \frac{dU}{T} + \int_i^f \frac{P}{T} dV$$

Need to expand dU and dV in terms of {P,T}.

$$\Delta S = \int_i^f \frac{\left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP}{T} + \int_i^f \frac{P}{T} \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right]$$

stove is open to atmosphere so P is constant and $dP = 0$.

$$\Delta S = \int_{T_i}^{T_f} \frac{\left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial(U+PV)}{\partial T}\right)_P}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial H}{\partial T}\right)_P}{T} dT$$

An example, “heating water on a stove”

Calculate the change in entropy of water heated from 20°C to 100°C on a stove.

method 3: Use enthalpy for constant pressure process:

$$dH = dU + PdV + VdP = (TdS - PdV) + PdV + VdP = TdS + VdP$$
$$\Rightarrow \boxed{dH = TdS + VdP}$$

and integrate at constant P to get

$$\int_{P=\text{const}} dS = \int_{P=\text{const}} \frac{dH}{T}$$

Writing $H = H(T, P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP.$$

Along the path $P = \text{const}$, $dP = 0$ and $dH|_P = C_p dT$

$$\Rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

as found previously.

Entropy change in the universe: a hint of the Third Law

For heating water from T to $T + \Delta T$

$$\Delta S_{water} = C_P \ln\left(\frac{T + \Delta T}{T}\right)$$

$$\Delta S_{surr} = C_P \frac{\Delta T}{T}$$

Defining $x = \frac{\Delta T}{T}$, the entropy change of the universe is:

$$\Delta S_{total} = [x - \ln(1 + x)]C_P$$

The function $f(x) = x - \ln(1 + x)$ is ALWAYS positive for $x > -1$
Entropy always increases for positive T .

Another example, “electrical work”

Consider emf \mathcal{E} driving current I through resistor R in an adiabatic box. The power delivered is $\mathcal{E}I = I^2R$. No heat or mechanical work input.

$$1^{\text{st}} \text{ law:} \quad \Delta U = I^2R\Delta t$$

Electrical work is dissipated irreversibly as heat: $\Delta U = C_V\Delta T|_V$
The change in temperature is then:

$$I^2R\Delta t = \int_{T_i}^{T_f} C_V dT = C_V\Delta T \quad \Rightarrow \quad \Delta T = I^2R\Delta t/C_V$$

What is the change of entropy?

The change in temperature:

$$\Delta T = I^2 R \Delta t / C_V$$

Use method 2 Central Equation for constant V process $dV = 0$

$$dS = dU/T \Rightarrow dS = C_V dT/T \Rightarrow \Delta S = \int_{T_i}^{T_i+\Delta T} \frac{C_V}{T} dT$$

Use method 1 Equivalent Reversible Process.

$$\Delta S = \int_{T_i}^{T_i+\Delta T} dq_R/T = \int_{T_i}^{T_i+\Delta T} C_V dT/T$$

$$\Delta S = C_V \ln \left[1 + \frac{I^2 R \Delta t}{T_i C_V} \right]$$

again, not just ideal gas, that nagging problem of infinite entropy change at $T=0$.

Romantic Poets on Entropy and Measurement

*How do I love thee? Let me count the ways.
I love thee to the depth and breadth and height*

...

Elizabeth Barrett Browning (1806 - 1861)

Probably couldn't find a rhyme for *Wahrscheinlichkeit*

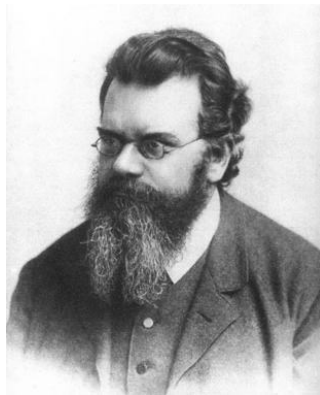


c/f Wordsworth

"I've measured it from side to side: 'Tis three feet long, and two feet wide."

Entropy is Counting things

Planck, "The logarithmic connection between entropy and probability was first stated by Ludwig Boltzmann in his kinetic theory of gases"



"The calculus of probabilities teaches us precisely this: any non-uniform distribution, unlikely as it may be, is not strictly speaking impossible."

Thermodynamics and Statistical Mechanics

- Thermodynamics: total entropy of an isolated system must increase.
- Statistical Physics: transform to more probable state.
- This suggests there is a relationship between probability and entropy.

$$S = k \ln \Omega$$

(Use Ω to avoid confusion with work)

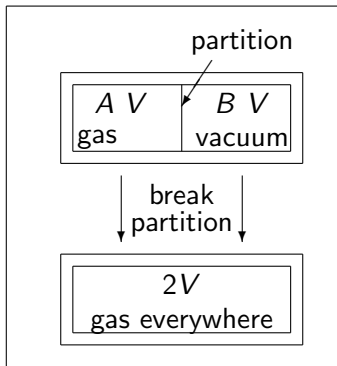
e.g. Maxwell-Boltzmann distribution,

e.g. Quantum wavefunction,

High entropy states of matter exist because of the existence of arrangements of atoms which have never, and will never occur.

Entropy, Counting, and Probability

Consider the Joule (free) expansion of N gas atoms.



When the partition is removed, all gas in A

Prob. that one atom is in A: $\frac{1}{2}$.

Prob. that all atoms are in A: $\frac{1}{2^N}$.

Prob. that 50% atoms are in A: ${}^N C_{N/2} \times \frac{1}{2^N}$.

We observe the state with most options.

We observe the state with highest entropy?

A hint of where the log comes from

Number of possible states with all particles

...

in A: $\Omega(N, V, E)$.

in A or B: $\Omega(N, 2V, E)$.

If all the accessible microstates are equally likely.

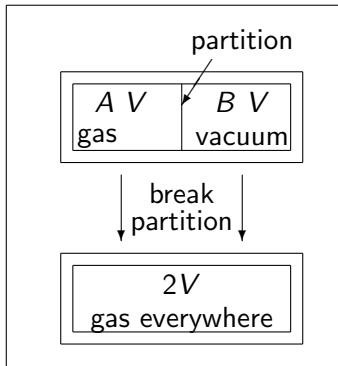
$$\frac{\Omega_A}{\Omega_{A+B}} = \frac{\Omega(N, V, E)}{\Omega(N, 2V, E)} = \left(\frac{1}{2}\right)^N$$

Suppose that there is a relationship between the entropy and Ω . $S = f(\Omega)$.

Entropy is additive $S = S_1 + S_2$, but permutations grow as product $\Omega = \Omega_1 \Omega_2$.

$$f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$$

Thus f must be a logarithm,



Definition of statistical entropy for fixed E

$$S = k_B \ln(\Omega)$$

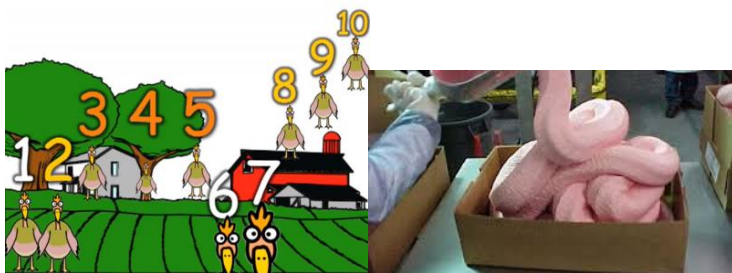
k_B , Boltzmann's Constant, relates micro- and macro- worlds.

Caveat: Lots of subtle assumptions sneaked in here: We'll do it properly in Stat.Mech..

Fewer entropy with chickens

Counting Things

You can't count a continuum.



This includes states which may never be actually realised.
This is where the ideal gas entropy breaks down

Boltzmann's entropy *requires* Quantum Mechanics.