Thermal Physics

Easy Parts of Statistical Mechanics

*according to*

Jess Brewer

Let's start with a simple question:

*You have almost certainly heard of something called "**entropy**".*

What is it?

"A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me.   It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts."

– Albert Einstein
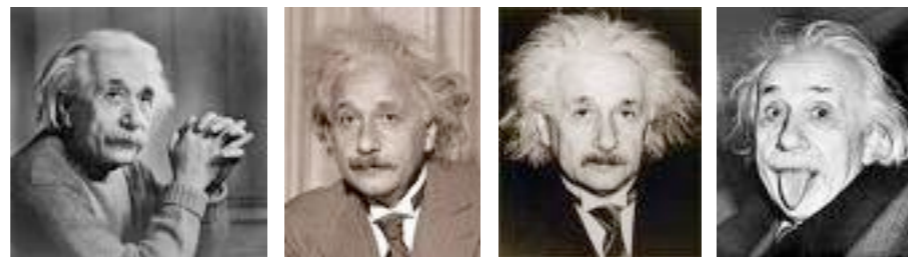
"But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics."
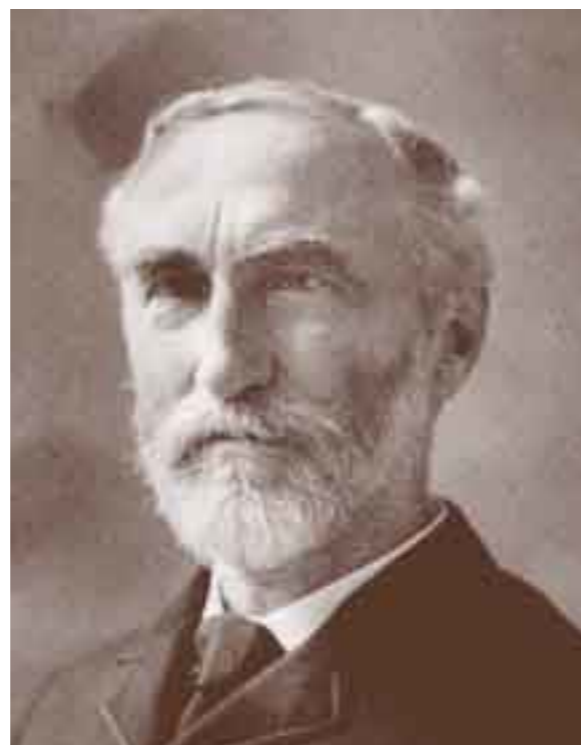
– Josiah Willard Gibbs

1839-1903

$$S = k \log W$$

LVDWIG
BOLTZMANN
1844–1906

Dr PHIL. PAULA
BOLTZMANN
GEB. CHIARI
1891–1977
ARTHUR
BOLTZMANN
DIPL.ING. Dr PHIL. HOFRAT
1881–1952
LVDWIG
BOLTZMANN
1925–1943
SEINER MÄNNLICHER NACHKOMME.
GEFALLEN BEI SMOLENSK

HENRIETTE
BOLTZMANN
GEB. EDLE von AIGENTLER
1854–1938

$$S = k \log W$$

? *?*

Entropy!

Boltzmann's constant
$(1.38 \times 10^{-23} \text{ J/K})$

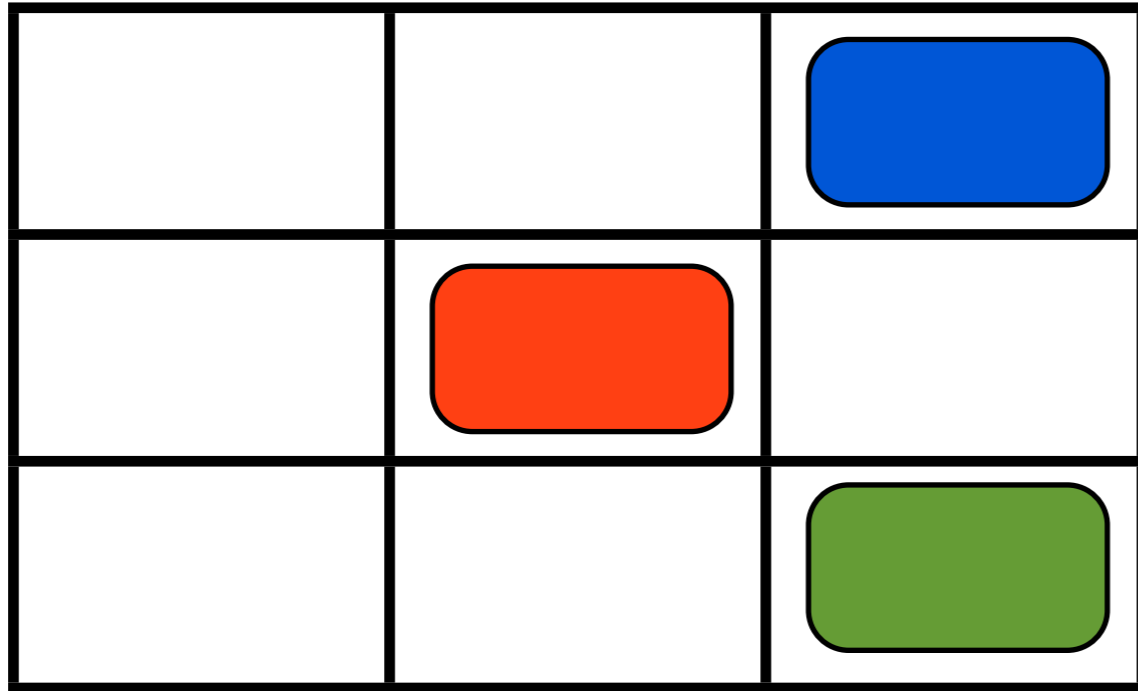*The number of different ways that the **total energy** of the system (U) can be distributed among all its microscopic degrees of freedom. Also known as the "Multiplicity function" because W is a function of U.*

Sometimes denoted Ω.

Parking Lot Analogy

The owner of a parking lot with $N = 9$ spaces gets \$1 for each car parked.

How many different ways can the owner get \$$n$?

The **first car** has N choices.

The **second car** has $(N-1)$ choices.

The **third car** has $(N-2)$ choices...

When the nth car comes in, the total # of possible choices will be $N(N-1)(N-2)\cdots(N-n+1)$

Factorials

$$N(N-1)(N-2)\cdots 3\cdot 2\cdot 1 \equiv N!$$

$$\therefore\ N(N-1)(N-2)\cdots(N-n+1) =$$

$$\frac{N!}{(N-n)(N-n-1)(N-n-2)\cdots 3\cdot 2\cdot 1}\ .$$

Is this $\Omega(n,N)$?   Not quite.   We have overcounted by the number of different ways the same n cars can be rearranged among the same n parking spaces, namely $n!$ (The lot owner doesn't care which car is in which space.)

Multiplicity

$$\Omega(n, N) = \frac{N!}{(N-n)!\ n!}$$

is the number of *significantly* different ways
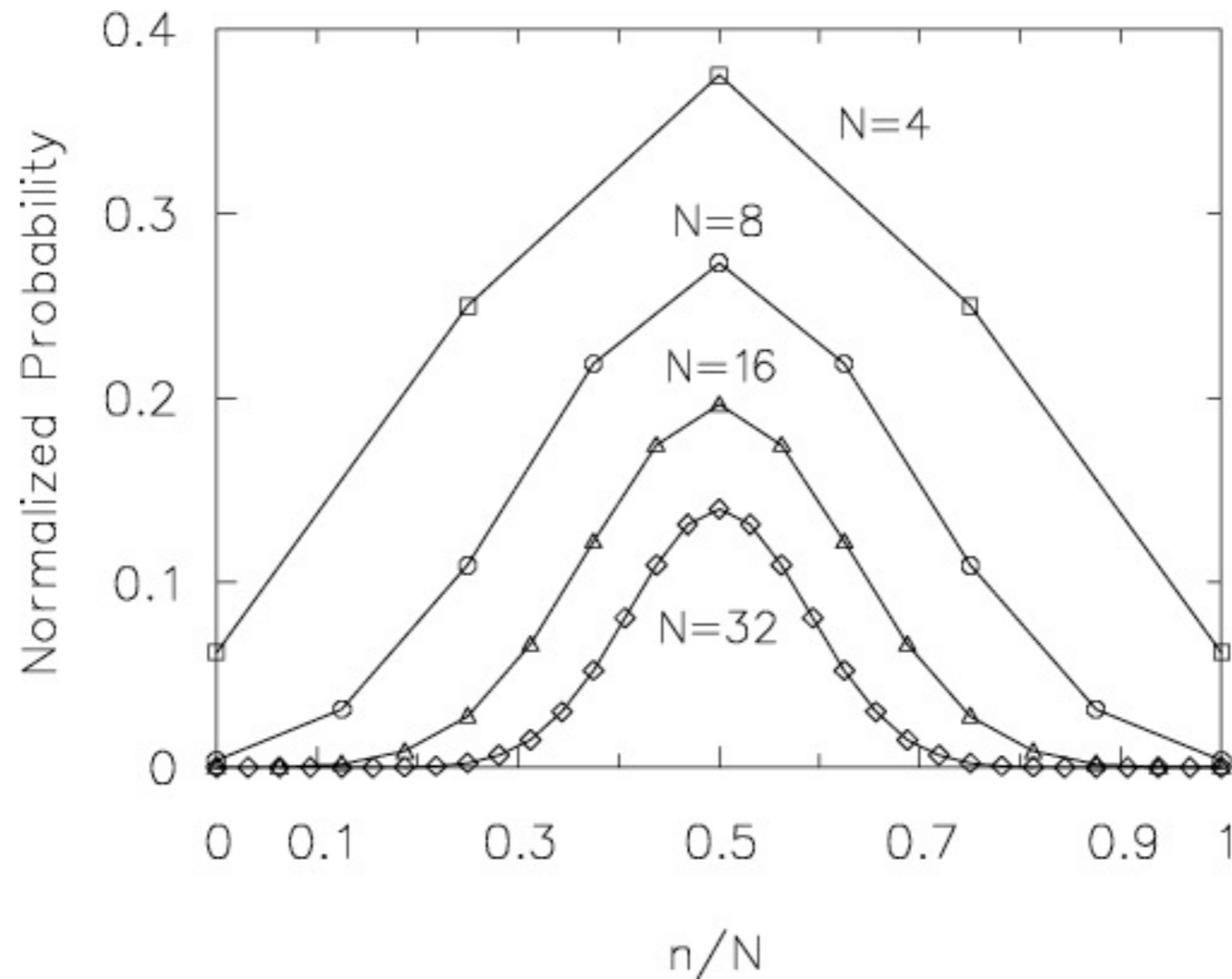that the owner of an N-car parking lot
can accommodate n cars.

What does this have to do with Thermal Physics?

Well, the owner gets $\$n$ for this situation, and in
Physics the "coin of the realm" is Energy U.

Like U, money is conserved: if someone gets extra,
someone else has to give it up.   Hold that thought.

$$\Omega(n,N) = \frac{N!}{(N-n)! \; n!}$$

*is also known as the **Binomial Distribution**:*

*The **fractional width** (in n/N) **decreases** with N.*

Stirling's Approximation

$$\log n! \approx n \log n - n + \log(2\pi n)/2$$

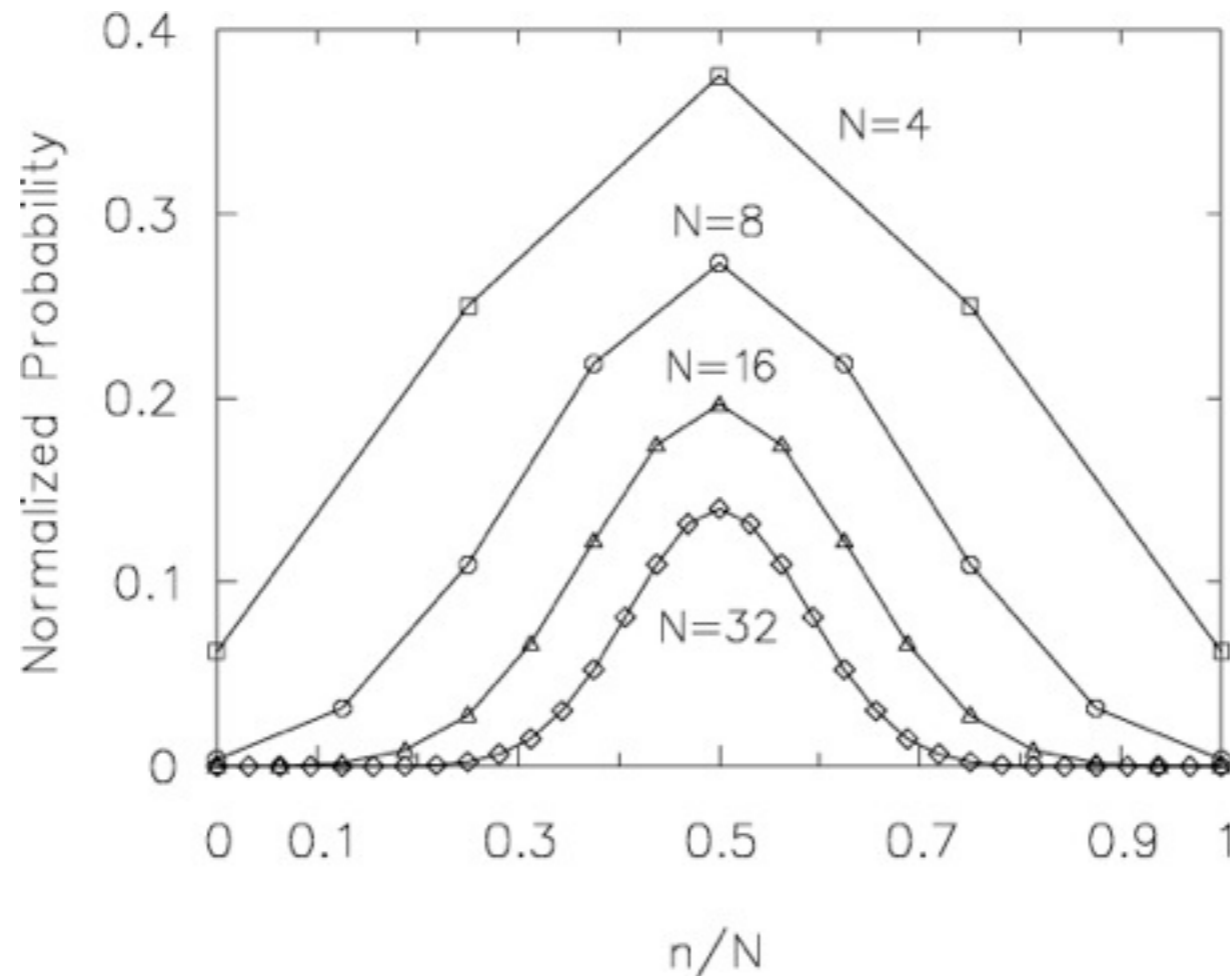can be used to show that $\Omega(n, N)$ is basically a Gaussian "bell curve" with a **mean** n of $N/2$ and a **width** proportional to $N^{1/2}$ so that the **fractional width** (width/N) is proportional to $N^{-1/2}$.

$$\Omega(n,N) = \frac{N!}{(N-n)!\ n!}$$

When N gets **big** (like 10^{22}),

$\Omega(n,N)$ gets *fantastically narrow* and

ridiculously huge, so we *take the log!*

Let's Get Vague!

Suppose we have a fixed amount of energy U_1 to distribute among all the microscopic degrees of freedom of some system S_1. We *don't care* what "microstate" S_1 is in; we are *only* interested in its **net energy** U_1 and the *number of "accessible"* microstates, $\Omega_1(U_1)$.

$$\sigma_1 = \log \Omega_1(U_1) \quad \text{is the } \textbf{entropy} \text{ of } S_1.$$

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What?!

*Wait a minute, we thought **entropy** was some mysterious thermodynamic function with weird units. This σ thing is a **pure number**, just like Ω. Also, isn't S the symbol for **entropy**?*

Solution: *multiply σ by Boltzmann's constant $k = 1.38 \times 10^{-23}$ J/K to get S.*

OK, we know what Joules are, but what's a K ?

Stay Tuned!

Recapitulation:

Suppose we have a fixed amount of energy U_1 to distribute among all the microscopic degrees of freedom of some system S_1. We don't care what "microstate" S_1 is in, we are only interested in its net energy U_1 and the number of "accessible" microstates, $\Omega_1(U_1)$.

$$\sigma_1 = \log \Omega_1(U_1) \quad \text{is the } \textbf{entropy} \text{ of } S_1.$$

Forget about k and K for now.

So What?

What **use** *is it to know that*

$$\sigma_1 = \log \Omega_1(U_1) \quad \text{is the } \textbf{entropy} \text{ of } S_1 \text{ ?}$$

Answer: **almost none**, *unless* S_1 *can* **exchange**

energy dU *with some other system* S_2 .

We call this "being in thermal contact".

Ω_1 *of* S_1 *is independent from* Ω_2 *of* S_2 *.*

S_1 *contains energy* U_1 *and has* $\Omega_1(U_1)$ *accessible microstates*

S_2 *contains energy* U_2 *and has* $\Omega_2(U_2)$ *accessible microstates*

$\therefore$ ***Total*** *number of accessible microstates in* ***combined*** *system is* $\Omega_{\text{tot}} = \Omega_1 \cdot \Omega_2$ *.*

Total energy $U = U_1 + U_2$ is **conserved**.

S_1 contains energy U_1 and has $\Omega_1(U_1)$ accessible microstates

S_2 contains energy U_2 and has $\Omega_2(U_2)$ accessible microstates

$$dU_1 = -dU_2$$

Changes: $d\Omega_1 = \Omega_1(U_1 + dU_1) - \Omega_1(U_1)$

$$d\Omega_2 = \Omega_2(U_2 + dU_2) - \Omega_2(U_2)$$

A Little Mathematics

$$\Omega_{\text{tot}} = \Omega_1 \cdot \Omega_2$$

$$\Longrightarrow \ d\Omega_{\text{tot}} = \Omega_2 \cdot d\Omega_1 + \Omega_1 \cdot d\Omega_2$$

$$= \Omega_2 \cdot (d\Omega_1/dU_1)dU_1 + \Omega_1 \cdot (d\Omega_2/dU_2)dU_2$$

$$= \Omega_2 \cdot (d\Omega_1/dU_1)dU_1 - \Omega_1 \cdot (d\Omega_2/dU_2)dU_1$$

Divide through by Ω_{tot} :

$$\frac{d\Omega_{\text{tot}}}{\Omega_{\text{tot}}} = \frac{(d\Omega_1/dU_1)dU_1}{\Omega_1} - \frac{(d\Omega_2/dU_2)dU_1}{\Omega_2}$$

$$d\Omega_{\text{tot}} = (d\Omega_1/dU_1)dU_1 - (d\Omega_2/dU_2)dU_1$$

$$\Omega_{\text{tot}} \qquad \Omega_1 \qquad\qquad \Omega_2$$

This is the same as saying

$$d\sigma_{\text{tot}} = (d\sigma_1/dU_1)dU_1 - (d\sigma_2/dU_2)dU_1$$

Now is the time to ask
*"**Why are we doing this?**"*

Most Probable Configuration

Remember that every possible accessible microstate is (a priori) equally likely. Thus we can never predict which microstate the system(s) will be in; we can only identify **macrostates** which comprise a larger number Ω_{tot} of microstates and therefore a larger entropy σ_{tot}. As **energy** shifts around randomly between the two systems, the **most probable** macrostate will be the one where σ_{tot} is a *maximum*. What's the <u>criterion</u> for an <u>extremum</u> of $\sigma_{\text{tot}}(U_1)$?

$$d\sigma_{\text{tot}}/dU_1 = 0$$

We have $\quad d\boldsymbol{\sigma}_{\text{tot}} = (d\boldsymbol{\sigma}_1/dU_1)dU_1 - (d\boldsymbol{\sigma}_2/dU_2)dU_1$

and we want $\quad d\boldsymbol{\sigma}_{\text{tot}}/dU_1 = 0.$

Thus $\quad d\boldsymbol{\sigma}_1/dU_1 = d\boldsymbol{\sigma}_2/dU_2$

is the criterion for the most probable configuration.

That is, we are most likely to find the system in a

macrostate in which $\boldsymbol{\beta}_1 = \boldsymbol{\beta}_2$

where $\quad \boxed{\boldsymbol{\beta} \equiv d\boldsymbol{\sigma}/dU} \quad$ for each.

Most likely configuration:

$$\beta_1 = \beta_2 \quad \text{where} \quad \beta \equiv d\sigma/dU.$$

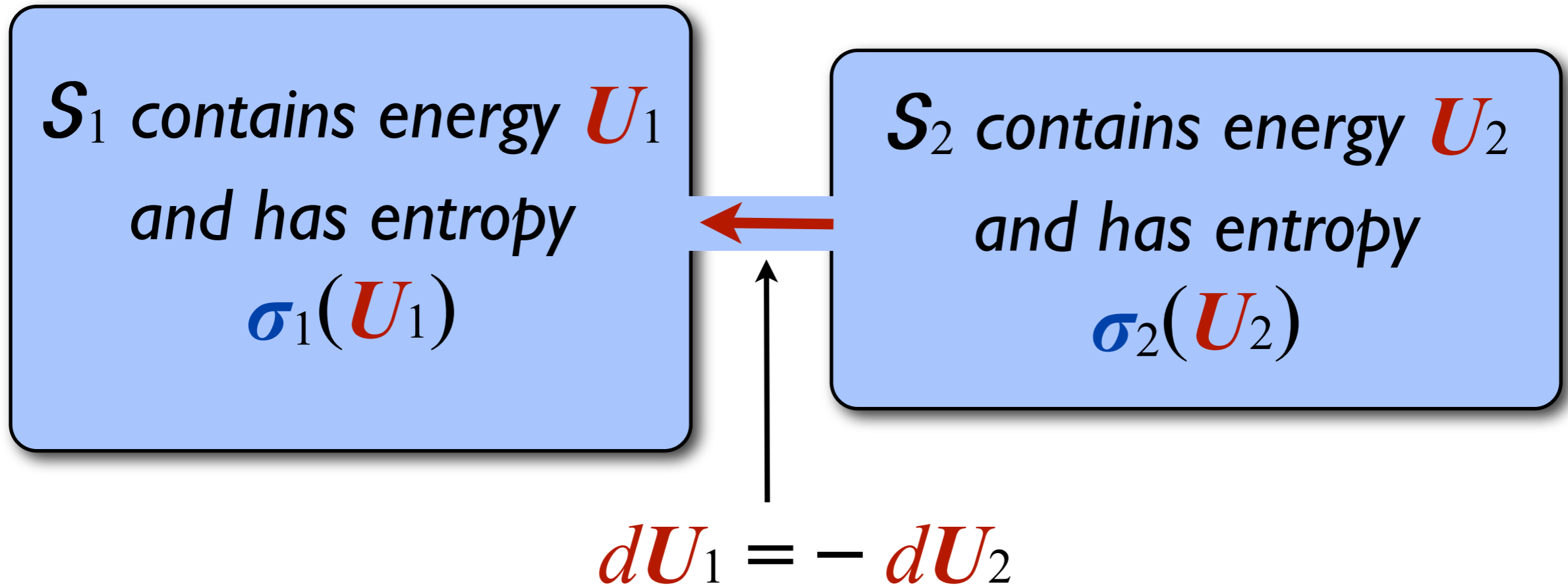Also known as "**Thermal Equilibrium**".

What does this remind you of?
What do you think β is?

To answer, let's ask ourselves **what will happen**

if (for example) $\beta_1 > \beta_2$?

$$\beta_1 > \beta_2 \quad \text{where} \quad \beta \equiv d\sigma/dU$$

S_1 contains energy U_1 and has entropy $\sigma_1(U_1)$

S_2 contains energy U_2 and has entropy $\sigma_2(U_2)$

$$dU_1 = -\,dU_2$$

*Energy U will "drift randomly" **from** S_2 **into** S_1 because σ_1 **in**creases by **more** than σ_2 **de**creases.*

$$\boldsymbol{\beta} \equiv d\boldsymbol{\sigma}/dU$$

Energy will "drift randomly"
from *a system with* **low β** *("***hot***")*

into *a region of* **high β** *("***cold***").*

This sounds a lot like **temperature**,
except "backward"!
Well, actually, "upside down".

Temperature $\boldsymbol{\tau}$ *is* <u>defined</u> *as* $1/\boldsymbol{\beta}$.

Great Big Thermal Reservoir

R *at temperature* τ_R

loses entropy

$$d\sigma_R = -\,\varepsilon_\alpha/\tau_R$$

when ε_α *is supplied to* S.

Probability $P_\alpha \propto \Omega_{\text{tot}}$

$$\Omega_{\text{tot}} = 1 \cdot \Omega_R$$

$$= e^{(\sigma_R + d\sigma_R)}$$

$$= e^{\sigma_R} \cdot e^{-\varepsilon_\alpha/\tau_R}$$

$$\therefore\ P_\alpha \propto e^{-\varepsilon_\alpha/\tau_R}$$

(Boltzmann factor)

Itsy-bitsy, teenie-weenie system S *in a <u>fully</u>*

<u>specified microstate</u> α *whose energy is* ε_α

Example 1:

Isothermal Atmosphere

S = *one nitrogen molecule, mass m*

R = *the rest of the atmosphere*

τ_R = *temperature of the atmosphere*

≈ 300 K $= 4.14 \times 10^{-21}$ J

$\varepsilon_h = mgh$ = *gravitational potential energy of*

the molecule at altitude h

$$\therefore \; P(h) \propto e^{-mgh/\tau_R}$$

Mass of an N₂ Molecule

$$P(h) \propto e^{-mgh/\tau_R}$$

Empirical observation: *Pressure drops off with altitude like* $e^{-h/\lambda}$ *where* $\lambda \approx 8$ km

$$\therefore \quad mg/\tau_R \approx 1/\lambda \quad \text{or} \quad m \approx \tau_R/g\lambda \quad \text{or}$$

$$m \approx (4.14\times10^{-21}\ \text{J})/(9.8\ \text{m/s}^2)(8\times10^3\ \text{m}) \quad \text{or}$$

$$\boxed{m \approx 5.28\times10^{-26}\ \text{kg}}$$

Check: $m_{N_2} = 2\times14\ \text{AMU} = 4.65\times10^{-26}\ \text{kg}$

Example 2:

Proton Polarization

S = the **spin** of one proton

(*magnetic moment μ* = 1.41×10^{-26} J/T)

R = *your brain.* τ_R = 310 K = 4.28×10^{-21} J

$\varepsilon_{\uparrow\downarrow} = \pm \mu B = 4.23 \times 10^{-26}$ J *where* $B = 3$ T

is a typical magnetic field in an MRI scanner.

$\therefore P_{\uparrow\downarrow} \propto e^{\pm \mu B / \tau_R} = e^{\pm 4.23/428000} = e^{\pm 0.0000099}$

$$P_{\uparrow\downarrow} \propto e^{\pm 0.00001} \approx 1 \pm \varepsilon + \varepsilon^2 \pm \varepsilon^3 + \dots \text{ where } \varepsilon = 10^{-5}$$

*But "$\propto$" is not "$=$"! How do we **normalize***

so that $P_\uparrow + P_\downarrow = 1$?

*(The **sum** of probabilities of **all possible states** must be 1, duh!)*

Answer: stick in a constant, then find out what it is!

$$P_{\uparrow\downarrow} = C(1 \pm \varepsilon + \varepsilon^2) \quad \ni \quad 1 = 2C(1 + \varepsilon^2) \quad \text{or}$$

$$C = 1/[2(1 + \varepsilon^2)] = 0.499999999998 \approx 1/2 , \quad \text{so}$$

*the **polarization** of the proton spins is*

$$P_\uparrow - P_\downarrow = (1 + \varepsilon - 1 + \varepsilon)/2 = \varepsilon = 10^{-5}.$$

The protons are only polarized to 10 parts per million! This is pretty pathetic, but higher fields are expensive, and patients often object to being cooled down to a few thousandths of a Kelvin ....

*As an exercise, you might try calculating the polarization of a collection of **electrons** (with magnetic moment $\boldsymbol{\mu}_e = 0.93 \times 10^{-23}$ J/T) in the same magnetic field (3 T) at room temperature (300 K) or at the temperature of liquid helium (4.2 K). This sort of thing makes a good exam question ....*

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