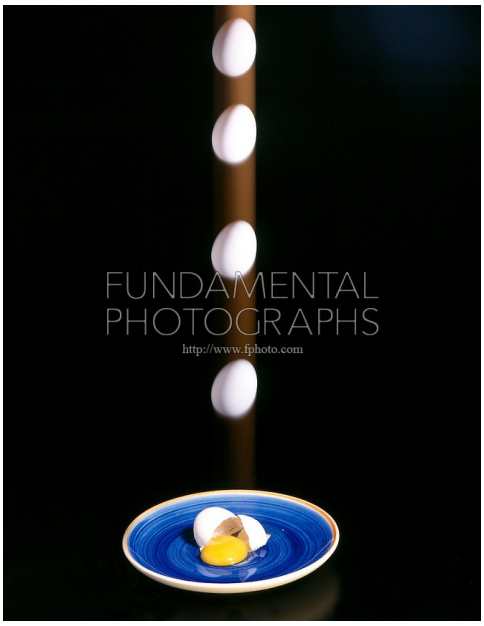
Introduction

- *Every* physical process obeys the law of **conservation of energy**.
- But it's easy to imagine processes that obey this law that **don't** actually happen.
- **E.g.:** the expanding sound waves of the egg cracking could reverse, and travel backwards, converging on the egg, and the smashed egg could reform and fly up off the plate. This wouldn't violate conservation of energy, but it never happens. **Why not?**
- What is the origin of this apparent **time asymmetry** in the way nature works?



There is time asymetry with how energy works. For instance dropping an egg can only go one direction.

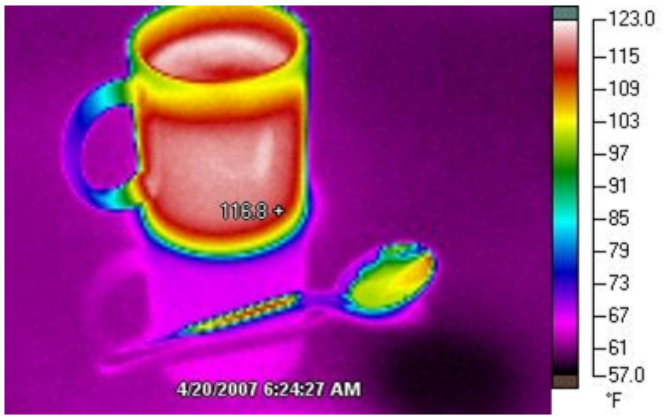
1.1 blub

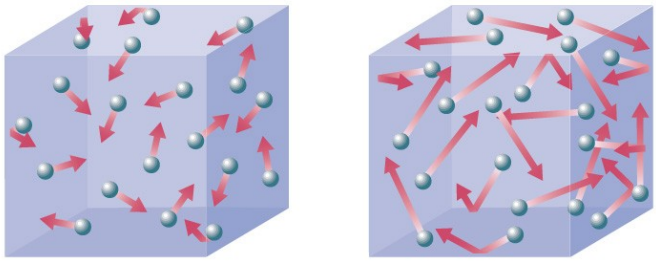
Introduction

- **Simpler example:** When a hot cup of coffee cools to room temperature, thermal energy flows from the coffee molecules to the air molecules, in a way that **conserves total energy**.

- The **reverse** process also conserves total energy, but **never happens**. The energy *could* flow back into the coffee, but it never does. Why not? Why does energy spontaneously flow from hot to cold, but **not from cold to hot**?

- There must be *another* law at work, beyond conservation of energy. This other law seems to involve the **direction of flow** of energy, or how energy tends to **distribute** itself.





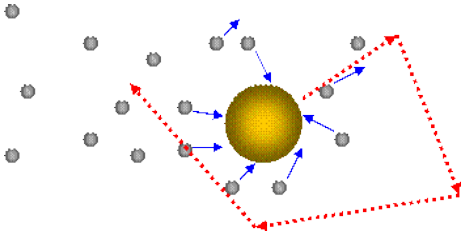
Longer arrows mean higher average speed.

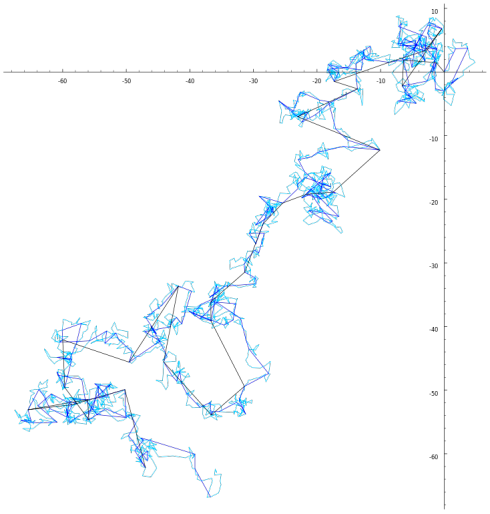
We start with a hot up of coffee with lots of thermal energy. We leave it to sit for a while and it starts passing its thermal energy to the air around it. So we have concentrated energy spontaneously disperse, but we never see the opposite happen. This is called entropy.

1.2 blub

Brownian Motion

- **Brownian motion** is a "*random walk*" of a larger particle resulting from its collisions with smaller, surrounding atoms or molecules that are in random thermal motion.

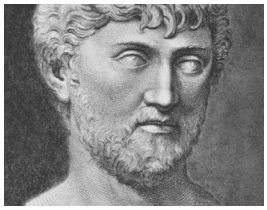




1.3 blub

Brownian Motion

History:



- **Lucretius** (c. 60 BC), *On the Nature of Things* (listen to CBC podcast): Used the random motion of dust motes in a shaft of sunlight as evidence for Democritus' idea of atoms (essentially *right*!).

- Named after the botanist **Robert Brown** who, in 1827, observed similar random motion of pollen grains in water.

- Mathematical descriptions began in the late 1800s; **Einstein** (1905) made a detailed **quantitative** analysis of Brownian motion that provided definitive confirmation that atoms and molecules actually exist.

- **Diffusion:** $\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$

Brownian motion was used as proof fro democratus's ideas.

1.4 blub

Diffusion

- **Diffusion** is the net migration of particles from a region of **high** concentration to a region of **low** concentration.

Diffusion is the migration of particles from high concentration to a region of low concentration. This happens randomly without outside influence.

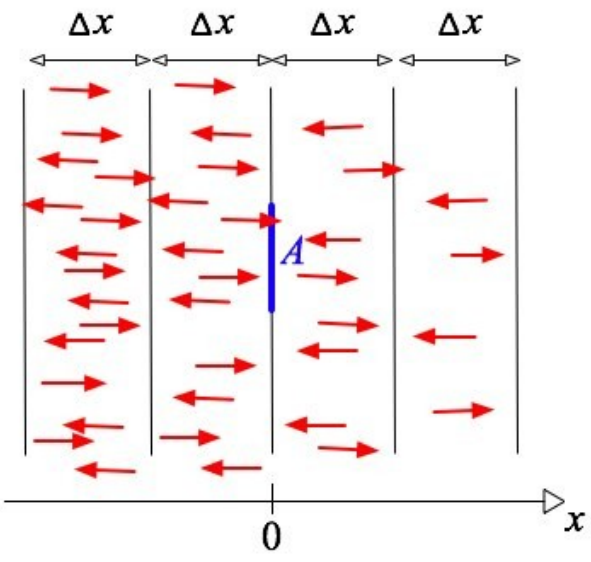
1.5 blub

Diffusion

- **Diffusion** is the net migration of particles from a region of **high** concentration to a region of **low** concentration.

- Diffusion is similar to Brownian motion: Each particle moves **independently** of the others, in **purely random** thermal motion. *So why is there a **net migration** from higher to lower concentration?*

- **Diagram:** Particles in any one layer are equally likely to move left as right. There is a **net** motion to the right simply because there are *more particles to the left of area A* (about half of which move right), *than particles to the right of A* (about half of which move left).



$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$

"Law from lawlessness"
"Law from lawlessness"

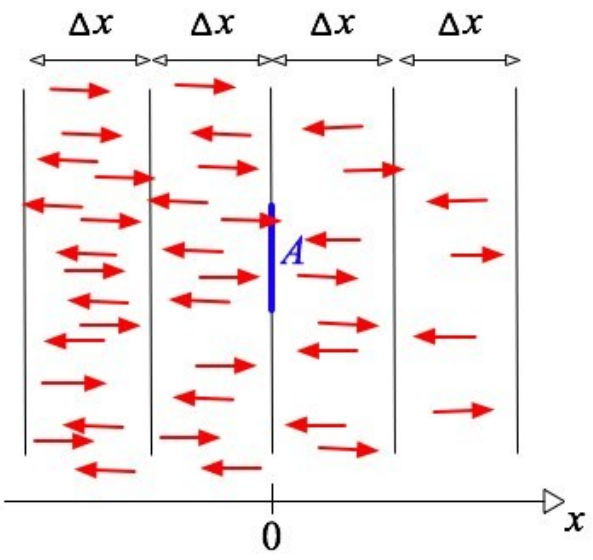
All motion is random. So we look at the average particles. Say we divide some water into cross sections. We can say that on average half of the particles in one section will move right and half will move left. This results in this diffusion of particles from high to low concentration. From this we can derive a law which is boss.

1.6 blub

Diffusion

- Diffusion continues until there is an **equal** concentration of particles in all layers ⇒ **equal** number randomly moving right or left through any area A.

- Called **dynamic equilibrium** (vs. static): Particles continue their incessant “random walking”, but on average the concentration remains uniform.



$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$

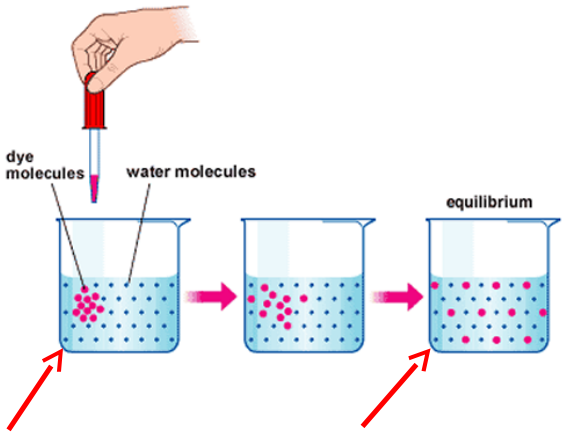
“Law from lawlessness”
“Law from lawlessness”

The end result of diffusion is a dynamic equilibrium because shits still moving but a balance has been reached.

1.7 blub

Diffusion

- Nature has **no inherent preference** for one state over another. There are simply ***many more*** ways for the particles to be spread out, than localized.
- Even a tiny amount of spreading opens up a **vast increase** in the number of nearby states like this, compared to the less spread out state it came from.
- The system **could** go back, but by the "law of large numbers" it will spend **virtually all** of its time "lost" in the huge new space of nearby, slightly more spread out states.
- This continues until **equilibrium**. There are **stupendously** more uniform-like states than even the slightly less uniform-like states a moment before. The system inexorably **ratchets** towards equilibrium.



Few **micro**scopic states look like this **macro**scopically

Many **micro**scopic states look like this **macro**scopically

Nature does not prefer an spread out of dye molcules in water. It really doesn't care. Its basically just a probabilty thing. There are way more possibilities that have more spread out particles rather than clumps.

1.8 blub

Diffusion

- Nature has **no inherent preference** for one state over another. There are simply ***many more*** ways for the particles to be spread out, than localized.
- Even a tiny amount of spreading opens up a **vast increase** in the number of nearby states like this, compared to the less spread out state it came from.
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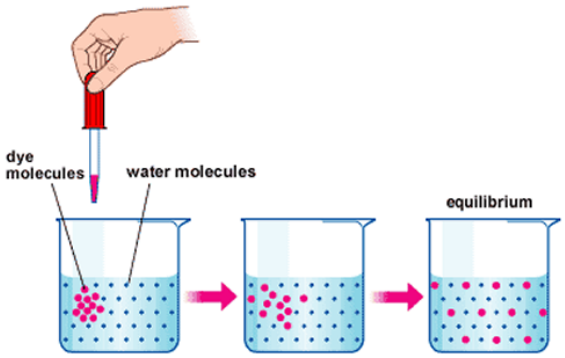


There's **no reason** system can't go back to the original state. It's merely **stupendously unlikely**.

Process is **irreversible** just by the **"law of large numbers".**

There si random jiggling of water molecules which is held over from the big band theory. These water molecules collide with the dye molecules. These move things around. Statistically speaking it is nearly guarenteed that the mixture will end up looking homogeneous.

Our body is very good at extracting order from the things we consume. So basically we are reversing the diffusion process.

1.9 blub

Diffusion

No "physical law" governs this process. It is driven one way (and not the other) by purely **random**, **purposeless** thermal motion. Of all possible next states (of which nature *prefers none*), the **vast majority** are more spread out, so chances are the next state will be more spread out.

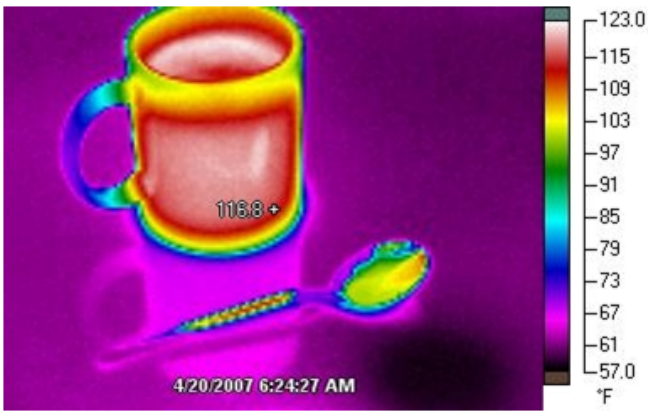
The diffusion process defined above also applies to the energy in a coffee cup. We call this law of diffusion the second law of thermal dynamics.

1.10 blub

Diffusion of Thermal Energy

- It's the same for the cup of coffee: There are simply **stupendously** more ways for the thermal energy to be spread uniformly throughout the [coffee + room air] than to be spread throughout the [coffee alone].

- There is nothing preventing the thermal energy flowing from the warmed air back into the room-temperature coffee, it's just **stupendously unlikely**.



- This **lawless/purposeless** tendency for particles or energy to spread out (disperse/diffuse) is called the **Second Law of Thermodynamics**. "Law from lawlessness".

Basically the second law of thermal dynamics is that energy tends to spread out. Entropy is kind of a measure of disorder. It is possible to have places in the universe where entropy is decreasing, but you will always have a net positive growth of entropy.

What animates us is random thermal motion left over from the big bang which our body extracts order from and uses to move.

1.11 blub

Second Law

- **Second Law of Thermodynamics:** The entropy of an isolated system never decreases

  This is perhaps the most potent statement in all of science, rivaled only by the first law of thermodynamics: the law of conservation of energy.

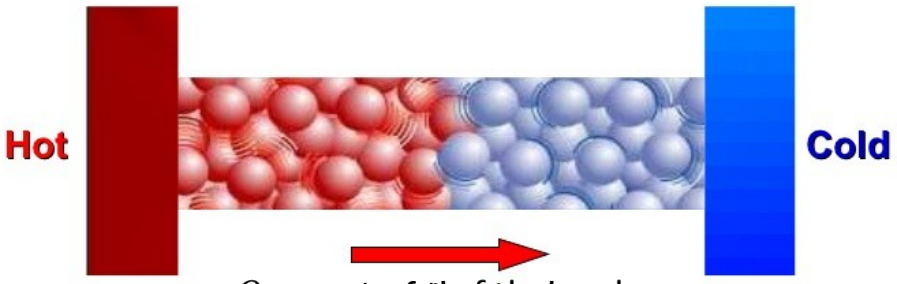
- Roughly speaking, **"entropy" is a measure of "disorder"**. The natural diffusion (or dispersion) of energy (or particles) increases the disorder in the universe. Disorder can decrease ***locally*** (e.g., life), but at the expense of ***greater increase*** in disorder **elsewhere**, so that the universe **as a whole** (or any isolated system within the universe) inexorably **ratchets towards greater disorder**, or higher entropy.

- While energy is **conserved** (and thus eternal), it is continually being **degraded** into a lower quality (more spread out) form. (Recall "heat death" of the universe.) While this might sound bleak, it is precisely this lawless, purposeless process that is responsible for virtually **all change** in the world, and (as we shall see) it is the very ***engine of life itself***! It's not energy, but **degradation of energy**, that "makes the world go round".

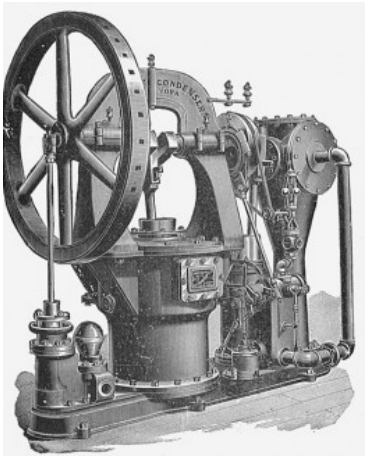
1.12 blub

Entropy

- **Entropy** (denoted by the letter S) was first understood in the context of the flow of thermal energy from a hot object to a cold object:



Q = amount of thermal energy transferred



$$\Delta S = S_f - S_i = \frac{Q}{T}$$

(T_{hot} = temperature of hot object)
(T_{cold} = temperature of cold object)

($\Delta S_{\text{hot}} = -Q/T_{\text{hot}} < 0$ (entropy of hot object **decreases**)
$\Delta S_{\text{cold}} = Q/T_{\text{cold}} > 0$ (entropy of cold object **increases**)

But $T_{\text{hot}} > T_{\text{cold}} \Rightarrow \Delta S = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} > 0$

Entropy of cold object **increases more** than entropy of hot object decreases $\Rightarrow$ **net increase**

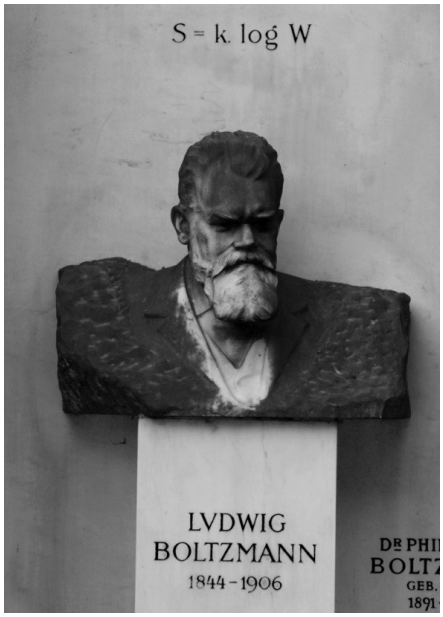
Entropy was first denoted with S. It stated around the time people wanted to make steam engines more efficient. The energy flowing from the hot object to the cold object divided by the temperature. Doing this for the hot object and the cold object are not equal (they sum to a non zero value). When you add them you get a positive value. This means that the cold object has more entropy.

This lead us to know that the amount of entropy is always increasing.

1.13 blub

Entropy

- **Entropy** was later understood much more deeply, at the *microscopic* level, by the great **Ludwig Boltzmann** (1844-1906), and summarized in his famous equation: $S = k \log W$



The equation $S = k \log W$ gives us a great understanding of entropy.

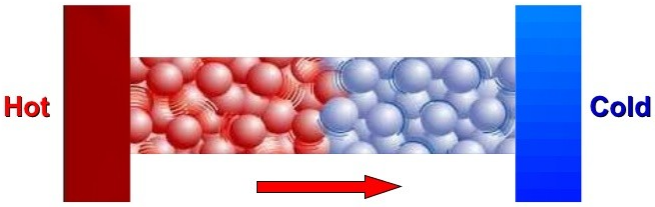
1.14 blub

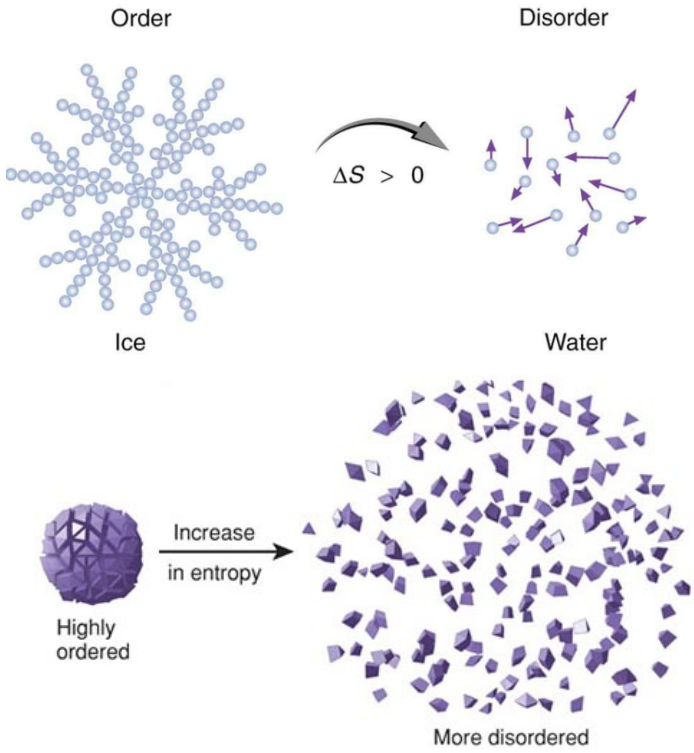
Entropy

- $S = k \log W$

- This is one of the deepest insights we have into the nature of everyday reality.

- Before we explore it in more detail, let's appreciate it's profound generality:
  - ✓ Deals with spreading of thermal energy…
  - ✓ …but also changes in **order**, or **complexity** (crucial for understanding life)





A water droplet has a fairly high level of disorder (many ways to arrange them and have it look the same), but when we freeze it there is much less disorder (fewer ways for it to be arrange).

1.15 blub

Entropy

- $S = k \log W$
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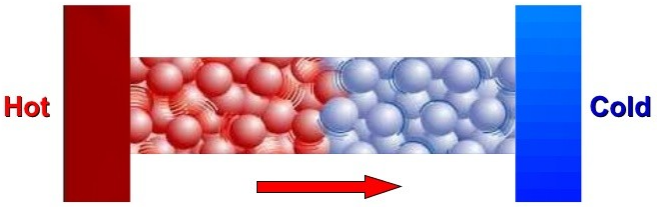
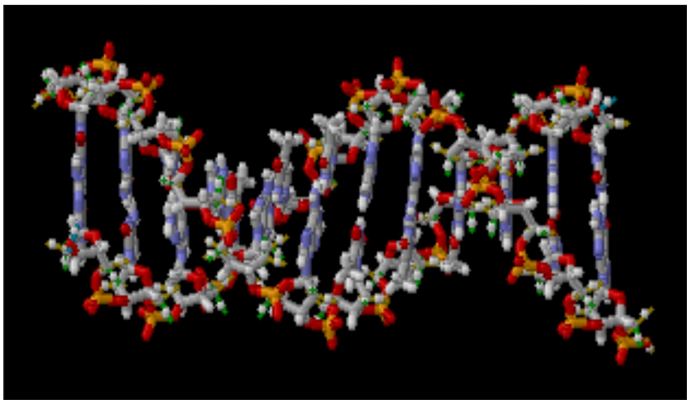


Periodic to "aperiodic" crystals: lower order/ complexity to higher order/complexity, or higher entropy to lower entropy



Crystal structures have some order, but you can rearrange them alot. But if you try to do the same with dna lots of shit changes. So we can say that dna is highly ordered.

1.16 blub

Mathematics of Boltzmann's formula $S = k \log W$

- $S = k \log W$ is used to **quantify** the amount of disorder, or entropy (S).
- k is called **Boltzmann's constant**, and has units of **energy per degree of temperature**. This tells us entropy is intimately connected with the concepts of **energy** and **temperature**, as we shall see. For simplicity we will set $k = 1$ (ignore this constant).
- $\log 100{,}000 = \log 10^5 = 5$. The log function counts how many powers of 10 in a large number. It reduces stupendously large numbers like 10^{100} (googol), often encountered in the statistics of natural systems, to more manageable numbers: $\log 10^{100} = 100$.
- The important quantity is *number of* **microstates** *compatible with a given* **macrostate**.

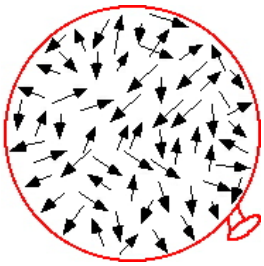
$S = k \log W$

K is Boltzmann's constant. For the sake of understanding we are just going to ignore this, its a constant, who cares. W is the number of microstates compatible with a given macrostate.

1.17 blub

Macrostates & Microstates

- The important quantity is *W = number of* **micro**states compatible with a given **macro**state.
- The important quantity is *number of* **micro**states *compatible with a given* **macro**state.
- E.g.: A balloon full of air:
  - **Macro**scopic description: Volume, pressure, temperature
  - **Micro**scopic description: Position and velocity of every air molecule
  - *W* is the stupendously large number of different possible **micro**scopic states that would be *indistinguishable* (look the same to us) from a **macro**scopic point of view.

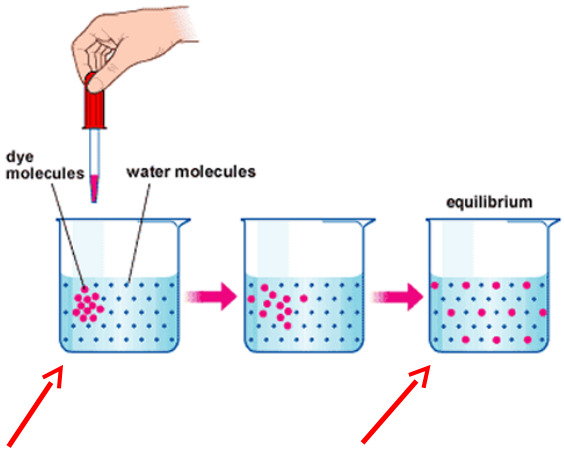


Take a balloon for example. We can describe its macrostate using a few parameters (volume, temperature, pressure). The microstate however is determined on the position, and velocity of every air molecule.

1.18 blub

Macrostates & Microstates

- The important quantity is *number of* **microstates** *compatible with a given* **macrostate**.
- E.g.: Diffusion of dye molecules:
  - **Macroscopic description:** Less spread out, more spread out.
  - **Microscopic description:** Position and velocity of every dye molecule.
  - As the blob of dye molecules spreads out, the number of distinct **micro**scopic states that *look the same* **macro**scopically, which we call W, increases very (**exponentially**) rapidly.



Few **micro**scopic states look like this **macro**scopically

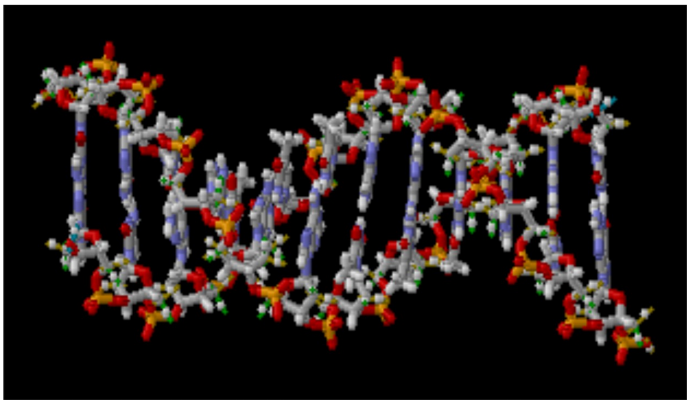
Many **micro**scopic states look like this **macro**scopically

1.19 blub

Macrostates & Microstates

- **"Disorder"** is a vague word. **The precise meaning of entropy** is: $S = k \log W$.
- Entropy is a measure of **how many different ways a set of particles can be rearranged** (position and velocity), and **still look the same**.
- E.g.: DNA is a highly ordered arrangement of atoms. Almost any rearrangement will make the DNA look different. Small $W \Rightarrow$ low entropy.
- E.g.: A rock crystal is **less** ordered in the sense that it is a repeating pattern of a **smaller set** of ordered atoms, which are interchangeable. Larger $W \Rightarrow$ higher entropy.

Periodic to "aperiodic" crystals: lower order/ complexity to higher order/complexity, or higher entropy to lower entropy



1.20 blub

Macrostates & Microstates

$S = k \log W$ is a powerful **bridge** between the **macro** and **micro** worlds.

1.21 blub

Example of $S = k \log W$ in action

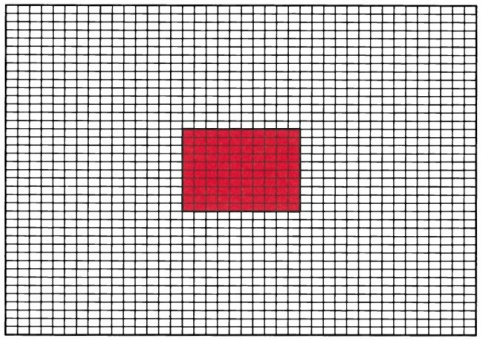
Consider a simple **model universe** (Atkins—*The Second Law*):

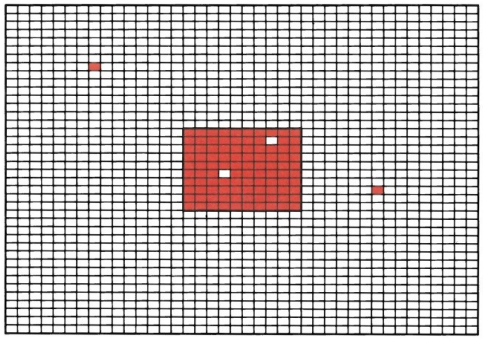
- Universe = 40 x 40 = 1600 atoms
- System = 10 x 10 = 100 atoms
- Environment = 1600 – 100 = 1500 atoms

- Atoms have either **one** unit of energy (red) or **no** energy (white)
- Universe starts with:
  - ✓ 100 units of energy in the system (all of its atoms “ON”)
  - ✓ No energy in the environment (all of its atoms “OFF”)

- Thermal motion of “ON” atoms jiggle neighboring atoms, transferring their energy: energy *naturally* disperses/diffuses

- But energy is **conserved**: **total** number of “ON” atoms = 100





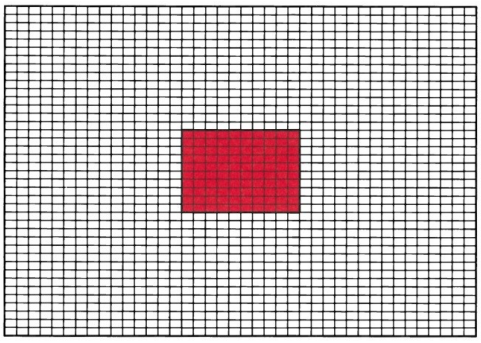
1.22 blub

Example of $S = k \log W$ in action

Example of in action

Initial entropy:

- There is only **one** way all the energy can be in the system, and none in the environment. Thus: $W = 1 = 10^0$
- Thus: $S = \log W = \log 10^0 = 0$. This is the state of lowest possible entropy of the universe
- Minimum entropy = minimum disorder = maximum order
- From here on, the universe inexorably ratchets itself towards higher and higher entropy, as it sinks further and further into disorder and chaos...



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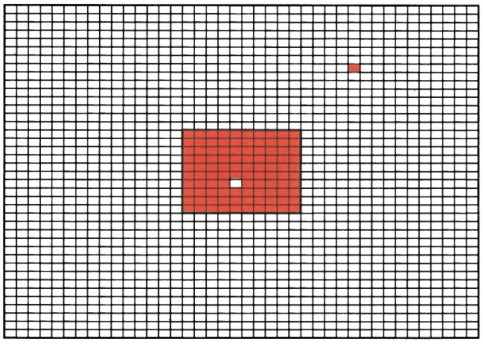
1.23 blub

Example of $S = k \log W$ in action

Example of in action



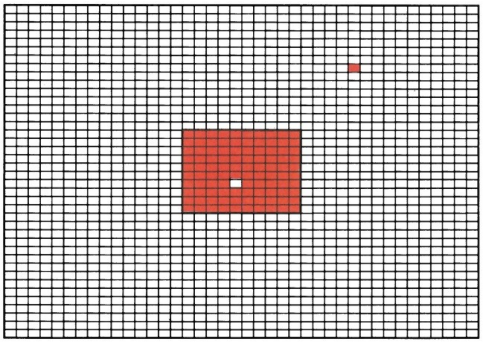
One unit of energy diffuses from the system into the environment:

- **Temperature** is a measure of the **average** thermal energy per atom. Thus:
  - ✓ The temperature of the **system decreases**, and that of the **environment increases**, like the cooling cup of coffee warming the air in the room
  - ✓ The universe has taken the first step towards **thermodynamic equilibrium:** system and environment at the **same temperature**
- Each different possible location of the single “ON” atom is a different **microstate** of the environment, but all of these microstates correspond to the **same macrostate** of the environment (same **average** thermal energy, or **temperature**). Similarly for the location of the single “OFF” atom in the system

1.24 blub

Example of $S = k \log W$ in action

One unit of energy diffuses from the system into the environment:

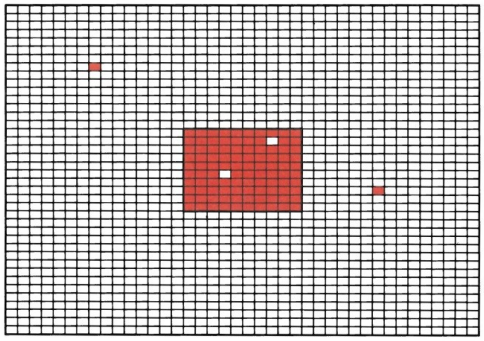


- The number of different ways **one "ON"** can be distributed in the **environment** (environment microstates) is 1500
- The number of different ways "0N's ON" (or **one OFF**) can be distributed in the **system** (system microstates) is 100
- The number of different ways **both** can happen (the number of distinct universe **microstates** compatible with this universe **macrostate**) is $W = 1500 \times 100 = 150{,}000 = 10^{5.2}$
- Entropy of the universe **increases** from 0 to $\log 10^{5.2} = 5.2$
- The flow of energy from hot to cold (the "lawless" dispersion of energy) has increased the disorder of the universe

1.25 blub

Example of $S = k \log W$ in action

Example of in action



Two units of energy diffuse from the system into the environment:

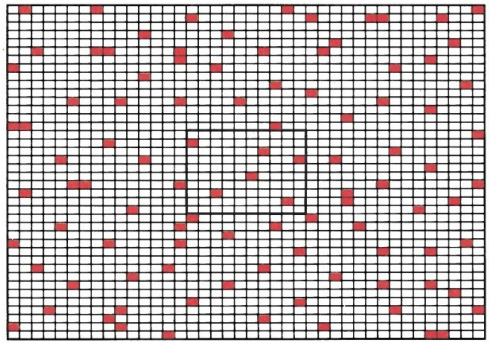
- The number of different ways **two "ONs"** can be distributed in the **environment** is $1500 \times 1499 \div 2 = 1{,}124{,}250$
- The number of different ways "2 ONs" (or **two OFFs**) can be distributed in the **system** is $100 \times 99 \div 2 = 4950$
- The number of different ways **both** can happen is $W = 1{,}124{,}250 \times 4950 = 5{,}565{,}037{,}500 = 10^{9.7}$
- Entropy of the universe **increases** from to
- Entropy of the universe **increases** from 5.2 to $\log 10^{9.7} = 9.7$
- The flow of energy from hot to cold (the "lawless" dispersion of energy) continues to increase the disorder of the universe
- The flow of energy from hot to cold (the "lawless" dispersion of energy) continues to increase the disorder of the universe

1.26 blub

Example of $S = k \log W$ in action

Example of in action

- This **"lawless"** diffusion of energy continues until **thermal equilibrium** is reached, i.e., the system and environment reach the **same temperature** (same **average** thermal energy per atom)



- E.g., the cup of coffee has cooled, and the room air has warmed up, such that they are now at the **same temperature**

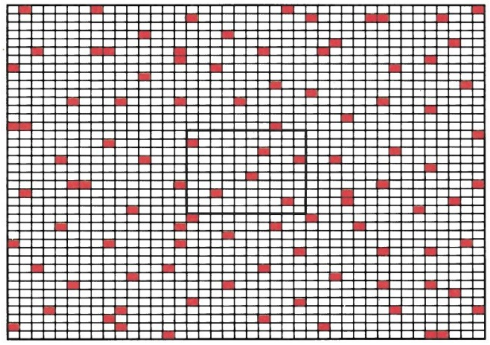
- In this example, **thermal equilibrium** corresponds to 6 or 7 "ONs" in the system, and 93 or 94 "ONs" in the environment, i.e., the **average** number of "ONs" is the **same** in both regions

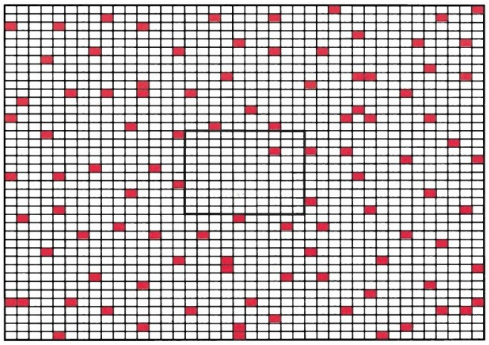
There is a point at which the temperature of the system is the same as its environment. At this point equilibrium has been reached. No more diffusion then.

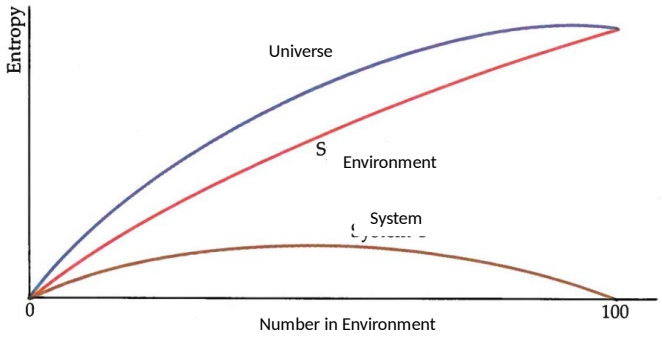
1.27 blub

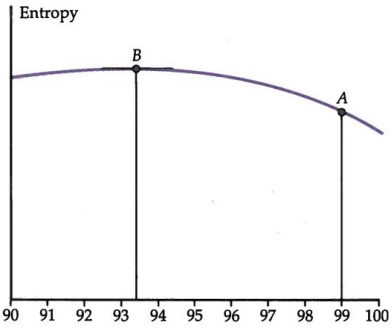
Example of $S = k \log W$ in action

- **Thermal equilibrium** is also the point of **maximum entropy**
- If **more** energy diffuses into the environment (more than 93 or 94), it leaves **fewer** "ONs" in the system. This has two effects:
  - ✓ While it **increases** the entropy of the environment, it **decreases** the entropy of the system **more** (because there are now so few "ONs" in the system), such that the **total** entropy (entropy of the universe) actually **decreases**





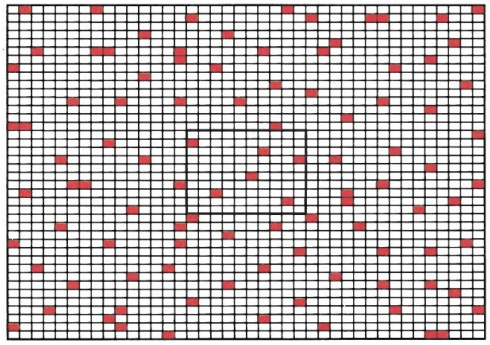


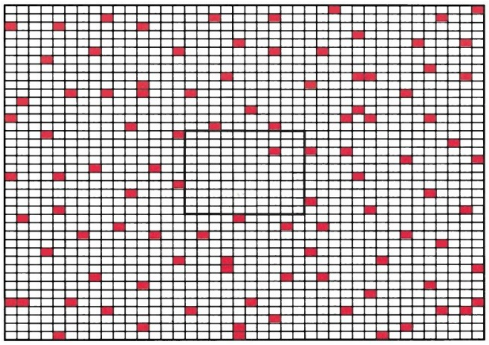


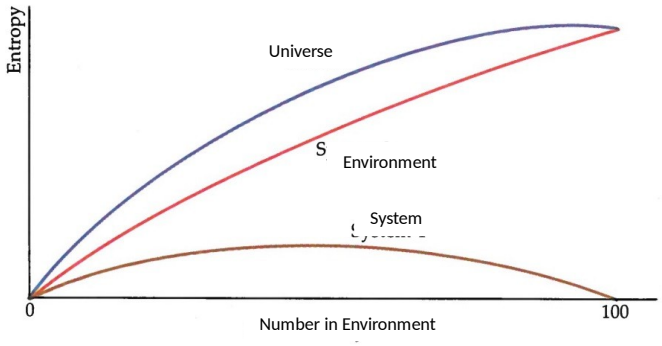
1.28 blub

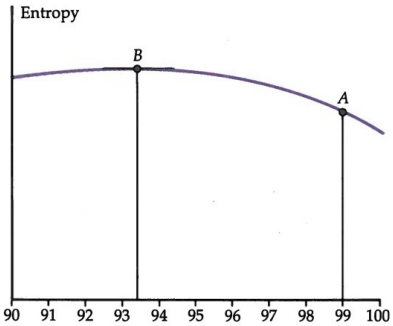
Example of $S = k \log W$ in action

- **Thermal equilibrium** is also the point of **maximum entropy**
- If **more** energy diffuses into the environment (more than 93 or 94), it leaves **fewer** "ONs" in the system. This has two effects:
  - ✓ The system gets **colder** than the environment, and so thermal energy would naturally flow **back** into the system, **restoring** thermal equilibrium and maximum entropy





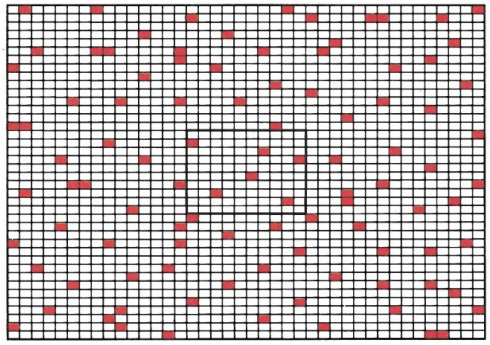


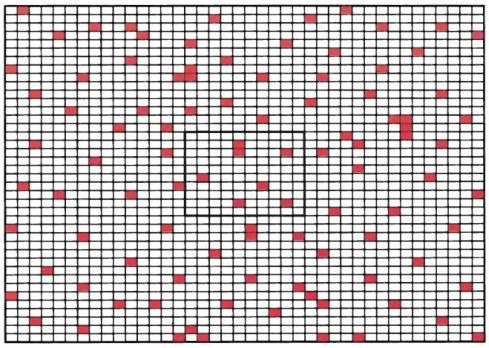


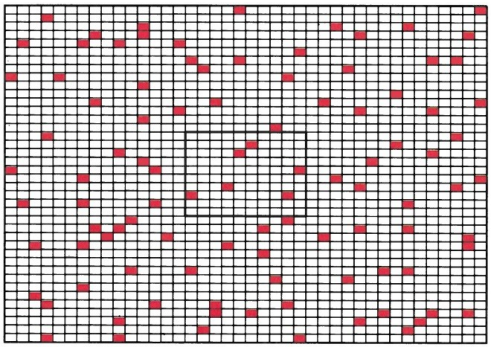
1.29 blub

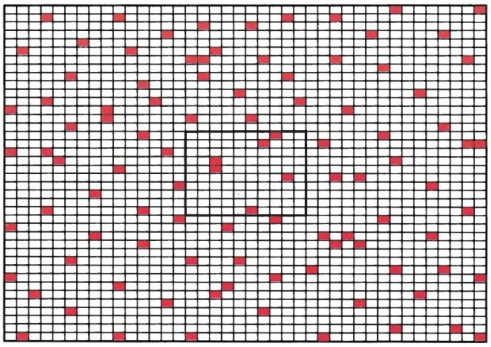
Example of $S = k \log W$ in action

- Two additional points:
  - ✓ This is a **dynamic** equilibrium. Thermal energy **continues** to flow randomly between the system and the environment, and between atoms within the system and atoms within the environment, but there no **net** flow. The **average** energy per atom in the universe remains constant





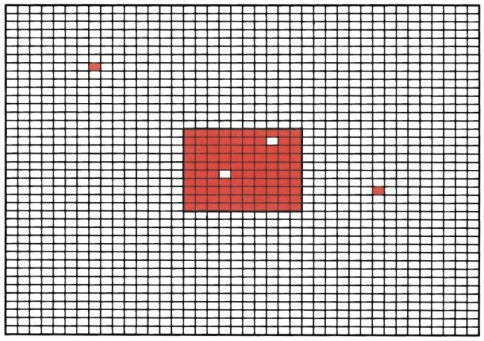


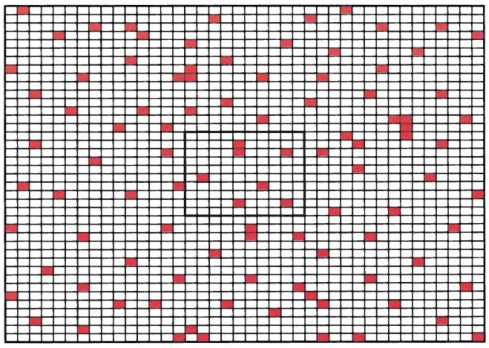


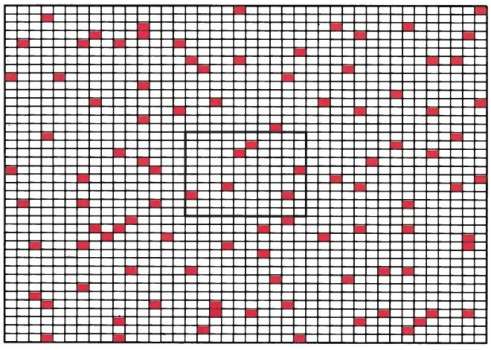
1.30 blub

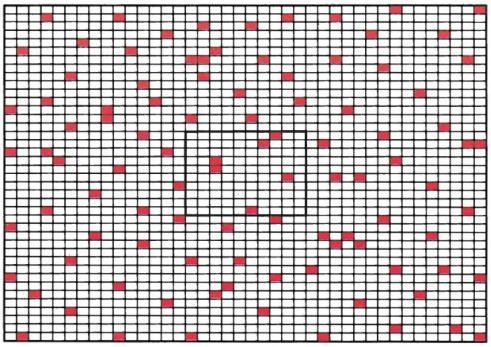
Example of $S = k \log W$ in action

- Two additional points:
  - ✓ There are **stupendously** more microstates in the **thermal equilibrium** (**maximum entropy**) macrostate, compared to any other non-equilibrium macrostate. There's no reason the universe can't return to a non-equilibrium macrostate, it's just **stupendously unlikely**. The process is effectively **irreversible**—the universe gets "locked out of the past"







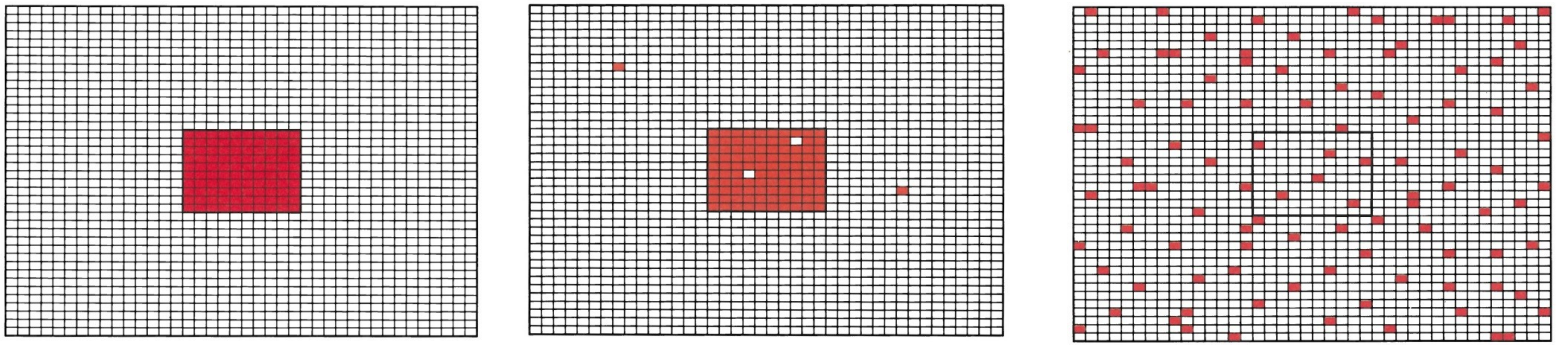


1.31 blub

Summary

"Energy tends to disperse" ⇒ "Entropy tends to increase"

What *drives* the dispersal is **random/purposeless** thermal motion

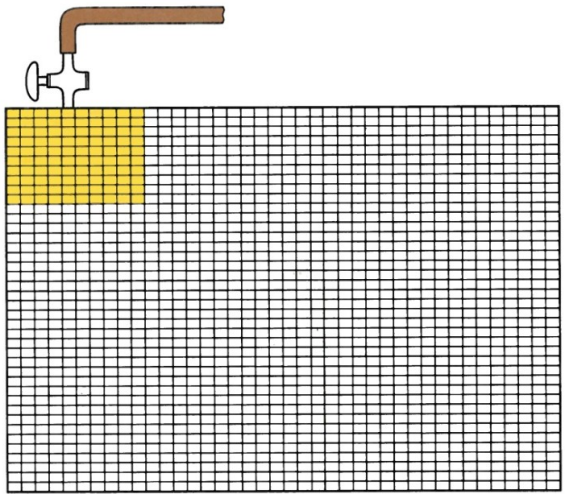


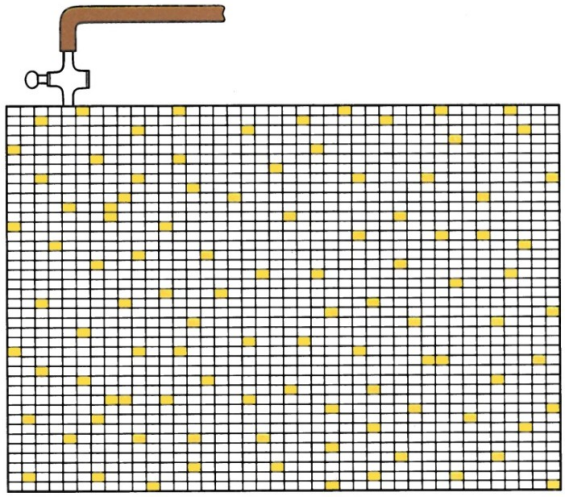
1.32 blub

Other ways entropy can increase...

When **particles** disperse, entropy also increases.

(There are **stupendously** more ways for particles to uniformly fill a volume, than to occupy one corner: $S = k \log W$ applies here too!)



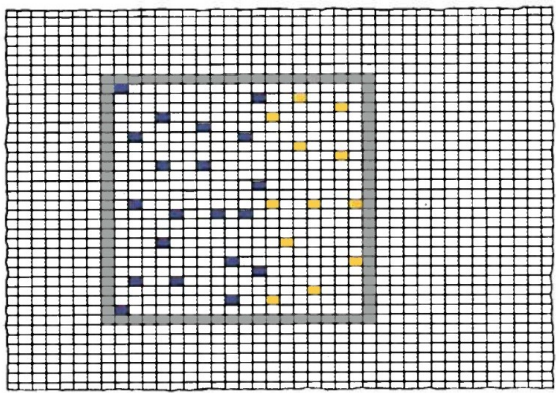


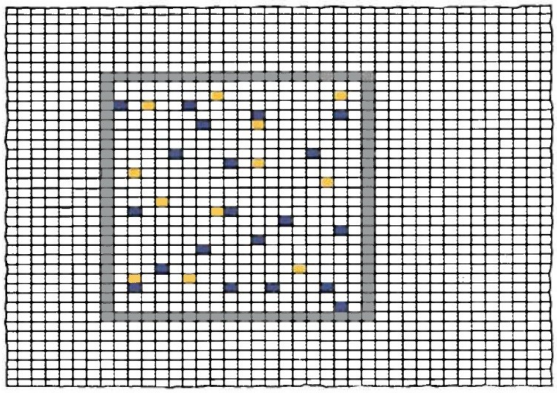
1.33 blub

Other ways entropy can increase...

When particles of **different type mix**, **entropy** also increases.

(There are **stupendously** more ways for particles of different type to be mixed, than remain separated: $S = k_{\ } \log W$ applies here too!)





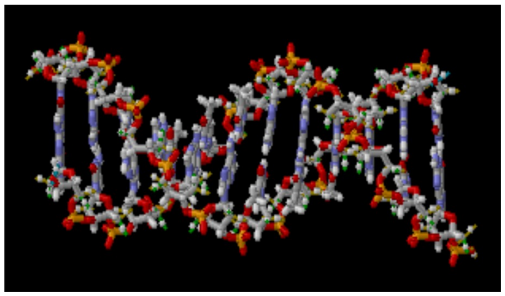
1.34 blub

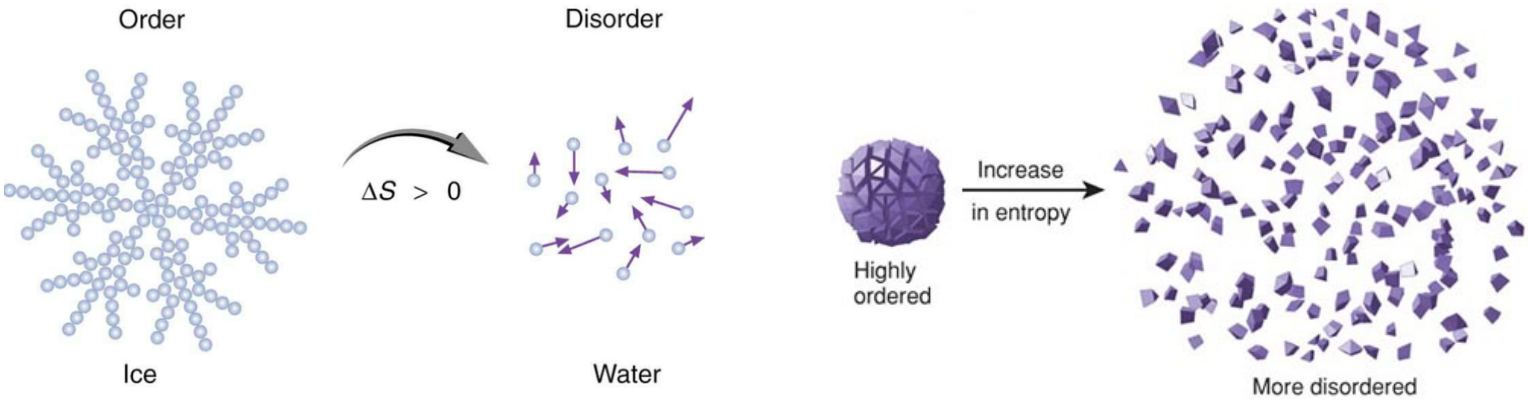
Other ways entropy can increase...

When **structural order** decreases, entropy also increases.

Conversely, when **structural order** *increases*, entropy *decreases*.

(There are **stupendously** more ways for particles to be structurally disordered than ordered: $S = k \log W$ applies here too!)





1.35 blub

Summary

- Boltzmann's formula [] $S = k \log W$ quantifies disorder in all of its forms. The **universality** of this connection between the **macroscopic** and **microscopic** worlds is why this formula is so important and far-reaching.
- The second law of thermodynamics [] $\Delta S \geq 0$ is **also universal**, at least in the "law of large numbers" sense. It determines the **direction of spontaneous change** for **all processes** in nature: ***all*** change is driven by the purposeless/lawless spreading of energy and particles.

1.36 blub

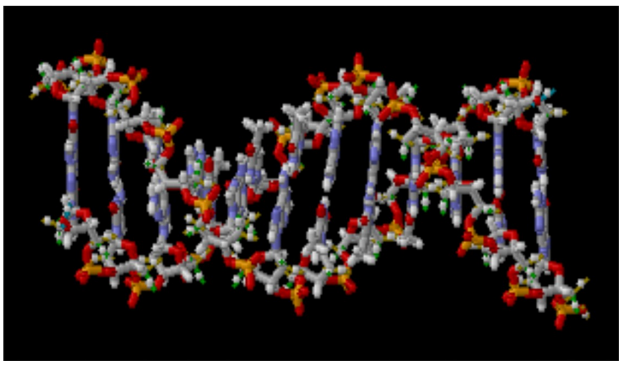
Summary

So what?

1.37 blub

Life and the Second Law

- Living organisms exhibit a very high degree of **order** or **complexity**, relative to the surrounding matter.
- How do they **maintain** this order against the tendency towards universal decay into disorder? *Doesn't life violate the Second Law*?
- What about **evolution** (to organisms of ever higher order or complexity)? Surely *it* violates the Second Law!?
- **No:** The universal ratcheting towards disorder is only **on balance**. Entropy can **decrease** in one location, as long as it **increases more** somewhere else, such that the **total** entropy increases (or stays the same).



1.38 blub

Life and the Second Law

Let’s look at a simple example of entropy decreasing *locally*, but increasing globally.

Theres an argument that life violates the second law of thermal dynamics because entropy goes down in cells. This is actually fine, there is nothing that says entropy can never go down, just that its net is increasing. Similar arguments are made for evolution which is dumb.

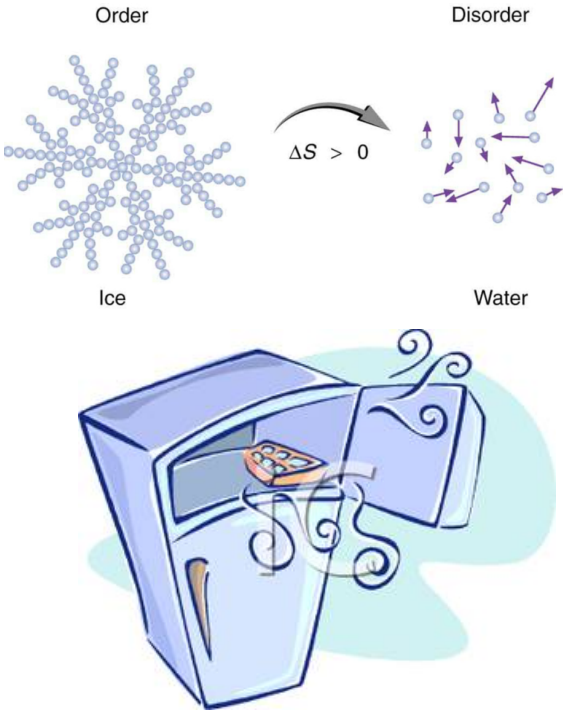
Yeah, at this point I totally stopped paying attention. He just sorta continued rambling on about how entropy works. You got this future lara, I believe in you.

Shame on you past Lara, you fucked up. But not as badly as Steven when he typed that.

1.39 blub

Life and the Second Law

- A **freezer** can convert water (at 0°C) to ice (at 0°C).
- Ice is a **more ordered** structure than water, so changing water to ice **reduces the entropy of the H_2O**.
- The water-to-ice transition **releases** energy ("latent heat") because H_2O bonds in ice are more stable (**stronger/lower energy**) than H_2O bonds in water.
- The freezer **removes** this energy and **dumps** it into the environment (outside air). The resulting entropy **increase** (energy spreading) ***exceeds*** the water-to-ice entropy decrease ⇒ ***net* entropy increase**.
- A freezer **does not** violate the Second Law.



1.40 blub

Life and the Second Law

Let’s look at a simple example of entropy decreasing *locally*, but increasing globally.

1.41 blub

Life and the Second Law

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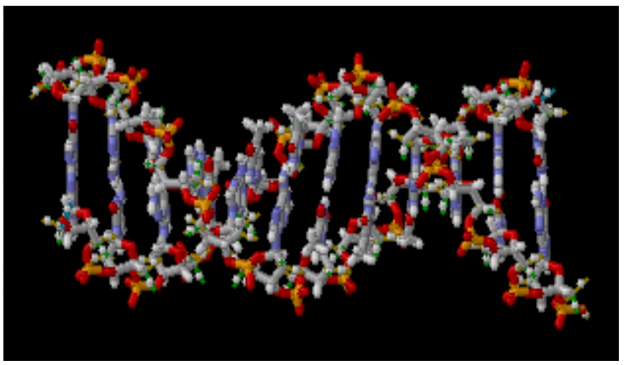

1.42 blub

Summary

So what?

1.43 blub

Summary

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- The second law of thermodynamics [] $\Delta S \geq 0$ is **also universal**, at least in the "law of large numbers" sense. It determines the **direction of spontaneous change** for **all processes** in nature: ***all*** change is driven by the purposeless/lawless spreading of energy and particles.

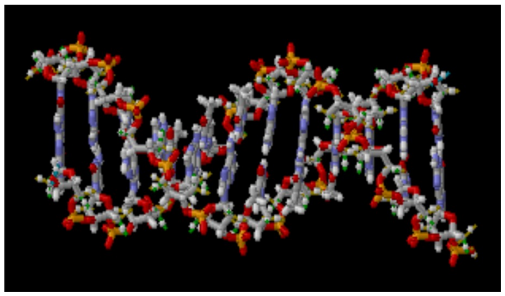
1.44 blub

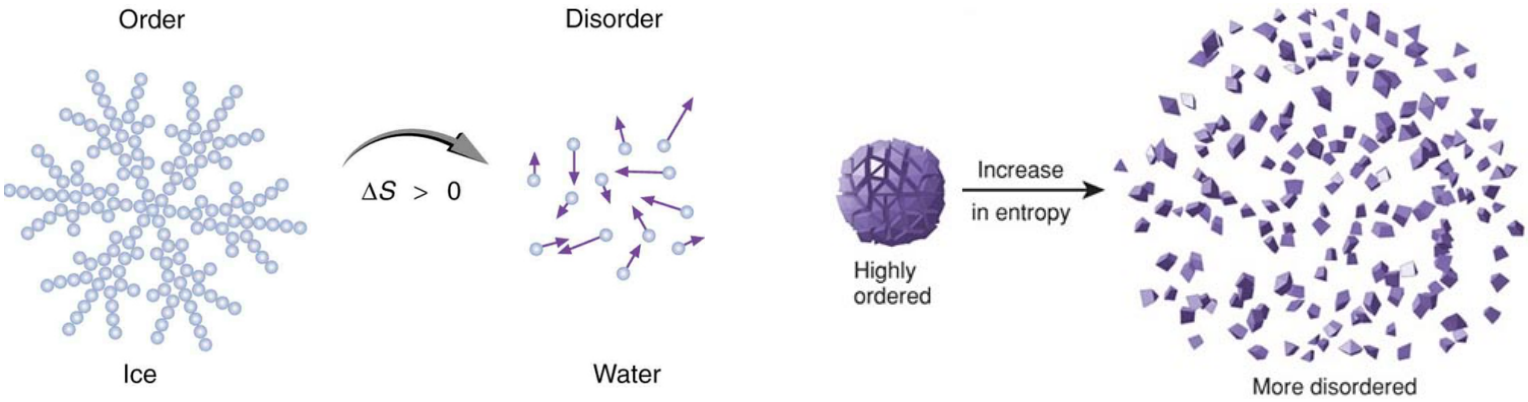
Other ways entropy can increase...

When **structural order** decreases, entropy also increases.

Conversely, when **structural order** *increases*, entropy *decreases*.

(There are **stupendously** more ways for particles to be structurally disordered than ordered: $S = k \log W$ applies here too!)





1.45 blub

Other ways entropy can increase...

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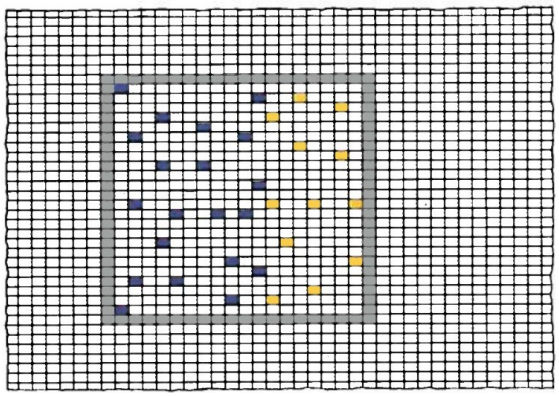
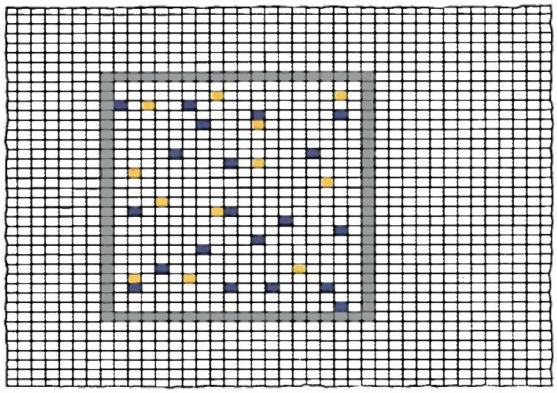
(There are **stupendously** more ways for particles of different type to be mixed, than remain separated: $S = k_{\cdot} \log W$ applies here too!)





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Other ways entropy can increase...

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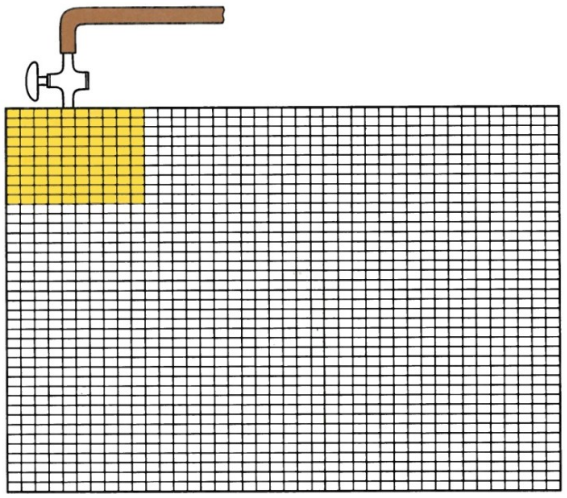

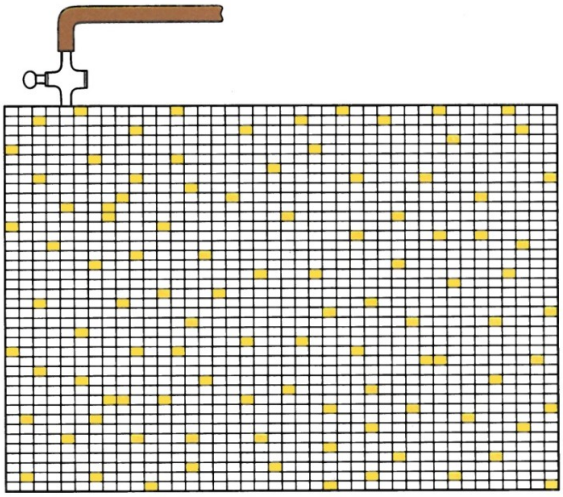

1.47 blub

Summary

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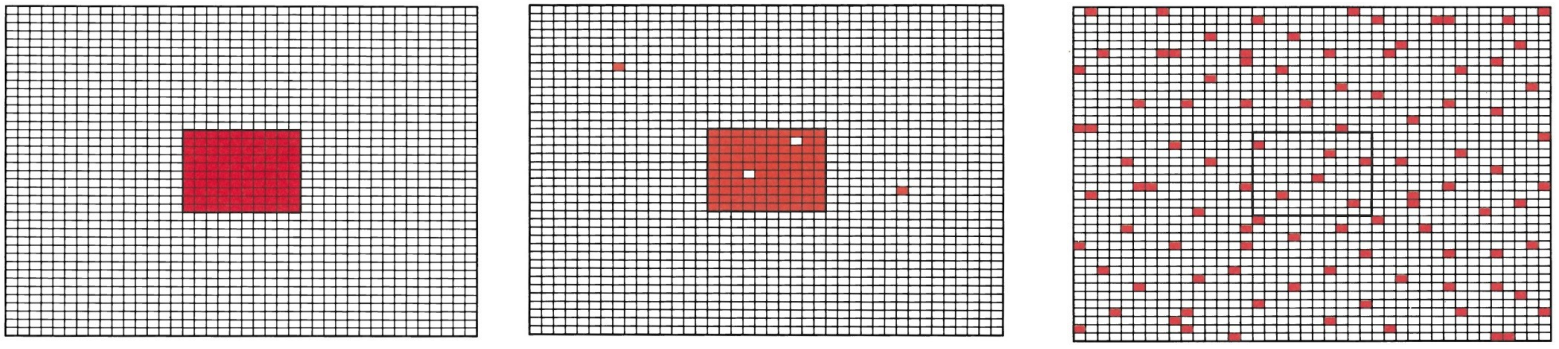
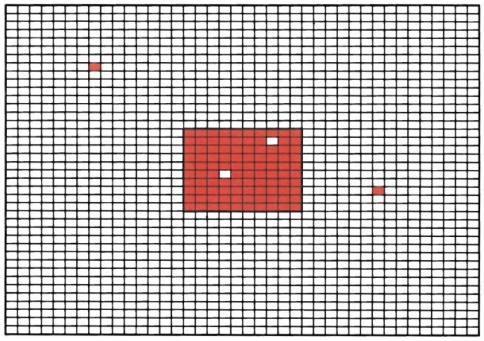
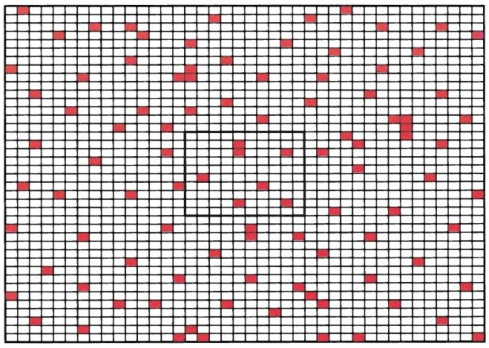


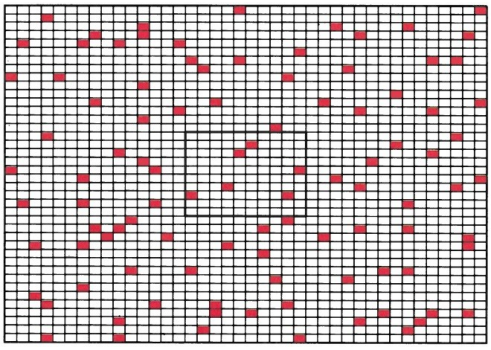
1.48 blub

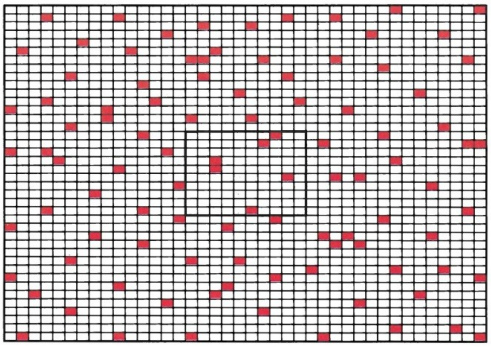
Example of $S = k \log W$ in action

- Two additional points:
  - ✓ There are **stupendously** more microstates in the **thermal equilibrium** (**maximum entropy**) macrostate, compared to any other non-equilibrium macrostate. There's no reason the universe can't return to a non-equilibrium macrostate, it's just **stupendously unlikely**. The process is effectively **irreversible**—the universe gets "locked out of the past"







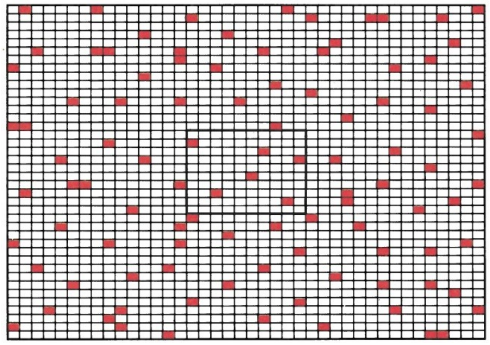


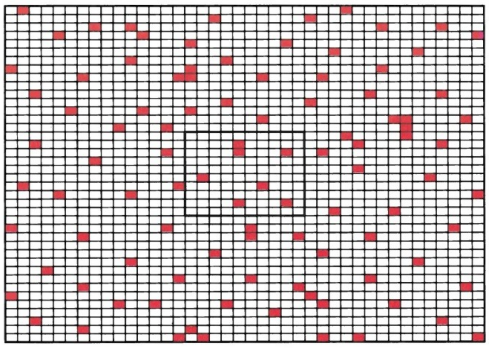
1.49 blub

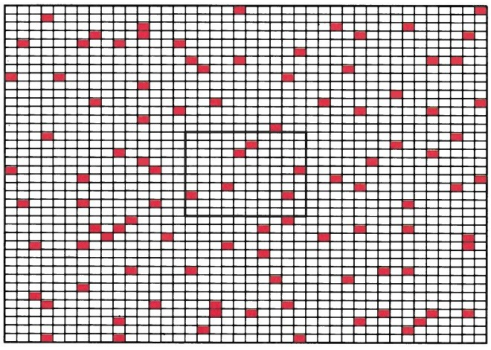
Example of $S = k \log W$ in action

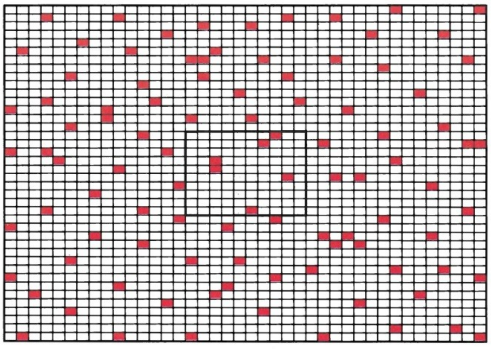
Example of in action

- Two additional points:
  - ✓ This is a **dynamic** equilibrium. Thermal energy **continues** to flow randomly between the system and the environment, and between atoms within the system and atoms within the environment, but there no **net** flow. The **average** energy per atom in the universe remains constant





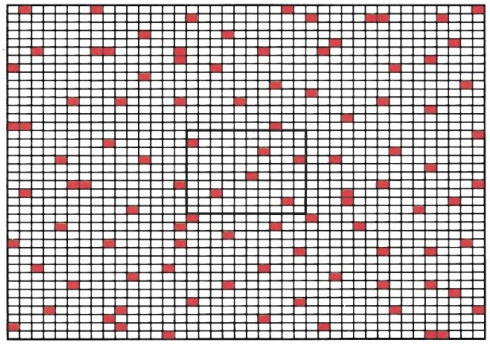


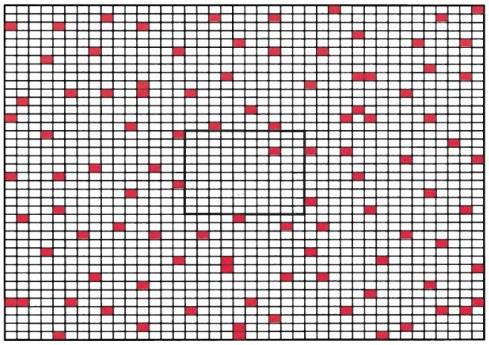


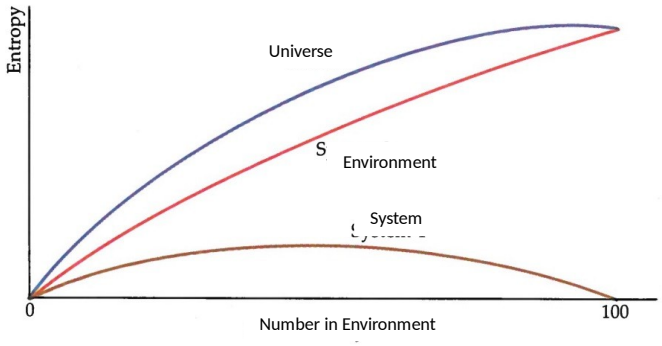
1.50 blub

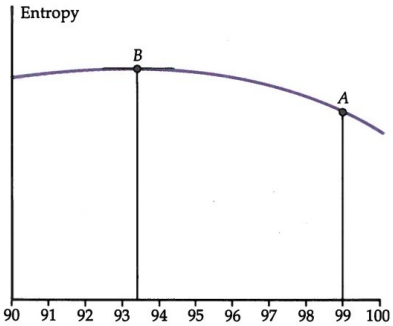
Example of $S = k \log W$ in action

- **Thermal equilibrium** is also the point of **maximum entropy**
- If **more** energy diffuses into the environment (more than 93 or 94), it leaves **fewer** "ONs" in the system. This has two effects:
  - ✓ The system gets **colder** than the environment, and so thermal energy would naturally flow **back** into the system, **restoring** thermal equilibrium and maximum entropy









1.51 blub

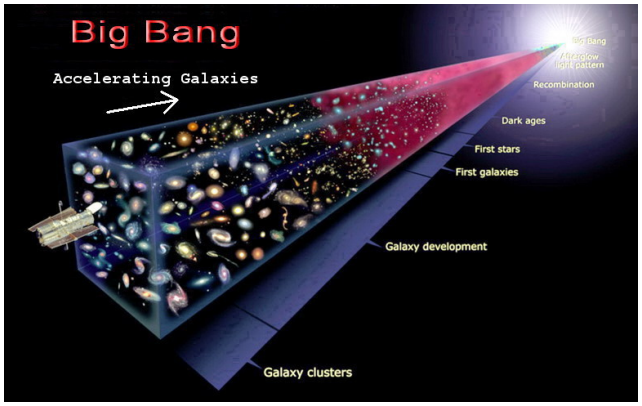
Natural order from disorder?

Can nature **spontaneously** create order/complexity?

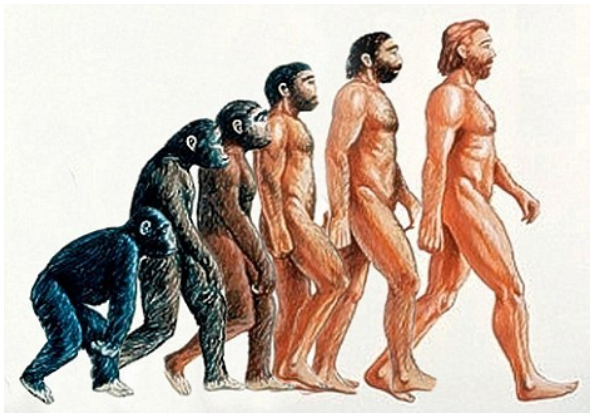
1.52 blub

Natural order from disorder?

Obviously, **YES**. **<u>The entire history of the universe if FILLED with precisely this process</u>.**



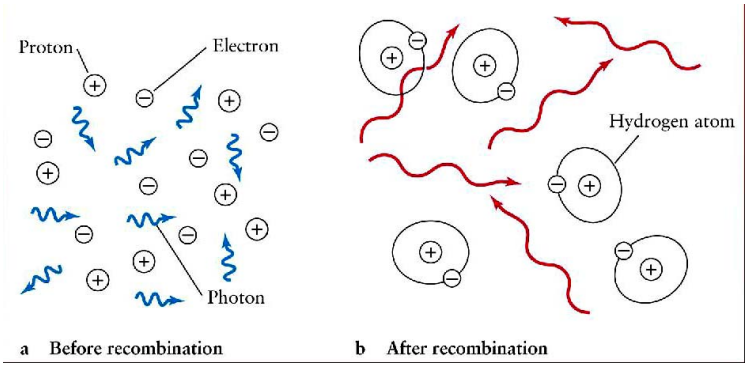
?



1.53 blub

Cooling

- Let's start by thinking about **cooling**:
  - ✓ The universe began in a hot dense state (Big Bang) with (almost) no structure. Ever since then it has been **expanding** and **cooling**, causing various structures to "**condense out**".
  - ✓ E.g., at one time, all of space was filled basically with hot protons, neutrons, electrons, and photons (particles of light). As these gasses **cooled**, the electrons combined with the protons, resulting in **neutral hydrogen atoms condensing out**
  - ✓ Because the electrons and protons were now together as hydrogen atoms (fewer possible arrangements), this condensation represented a **decrease in entropy/increase in order**. However, the *energy* released in this process, carried away and *spread out* as photons, represented **at least as great an *increase* in**



1.54 blub

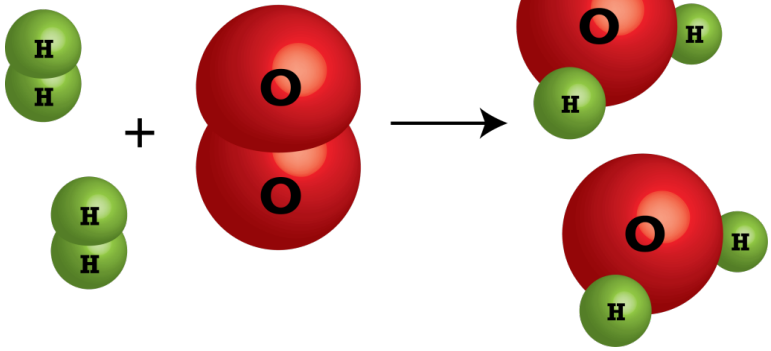
Cooling

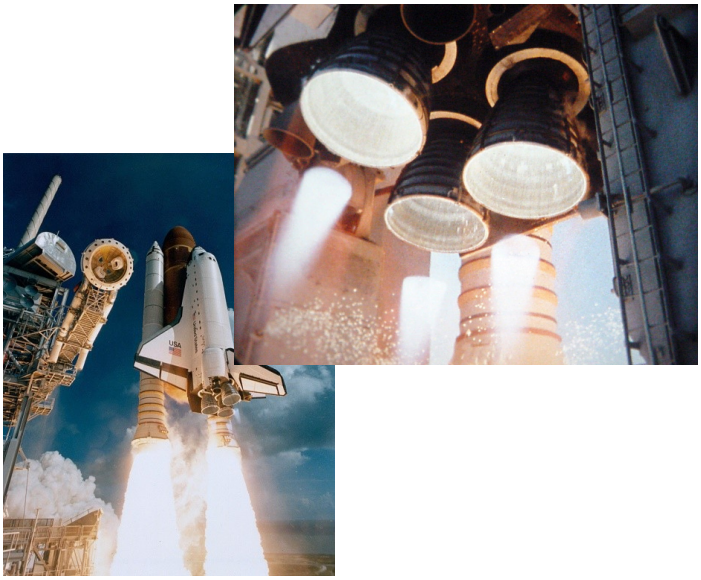
- The same thing happens when water molecules **condense into snowflakes**:
  - ✓ Ice is a **more ordered** structure than water vapor (less ways for the H_2O molecules to be spread out, analogous to the [electron + proton ⎵ hydrogen] condensation), so the condensation of water molecules into snowflakes **reduces their entropy**.
  - ✓ But as discussed before, when water freezes, **energy is released** (analogous to the energy released as a photon when a hydrogen atom forms).
  - ✓ This energy warms the surrounding, cooler air molecules, which then take it away (like the dispersing photons). This **dispersal of thermal energy** represents a greater entropy increase than the water-to-ice entropy decrease ⎵ **net entropy increase**.
  - ✓ Aside: The 6- (or 3- or 12-) sided symmetry is a result of the underlying symmetry of the water molecule (quantum…)

1.55 blub

Cooling

- Chemical reactions are the same: they are just a **type of cooling** (dispersal of energy).
- Example of **exothermic reaction**: the burning of hydrogen and oxygen gas:





1.56 blub

Cooling

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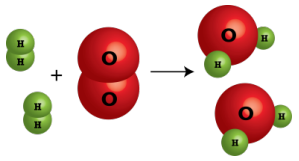


  - ✓ $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + (E \text{ (energy released)})$
  - ✓ Number of gas particles (per reaction) has **decreased** from 3 to 2. Fewer gas particles ⇒ fewer ways of arranging them ⇒ **decrease in entropy** (more order, like water-to-ice)
  - ✓ The electric field energy released (when the bonds change) goes into thermal energy (random KE) of the water molecules, then environment. This **increase in entropy**, by $\Delta S = E/T$, is **greater than the above decrease** (*many* ways of dispersing this energy)
  - ✓ This reaction is like water-to-ice cooling, except that the energy released is initially dispersed amongst the reaction products themselves (and then the environment)
  - ✓ Aside: Like many chemical reactions, an *activation energy* ("spark") is required...

1.57 blub

Cooling

- Key points:

  - ✓ Chemical reactions happen **not** because the energy in the bonds decreases. (E.g., in **endothermic** reactions, energy must be *supplied*, and the energy in bonds **increases**.) Energy is always **conserved**, so reactions don't occur because of a "lowering of energy".

  - ✓ Chemical reactions are driven by the **dispersal of energy**, i.e., a reduction in the **quality** of the energy, **not the quantity**. More generally, the driving force of *any* natural process in the universe is the random, purposeless dispersal of energy—analogous to "cooling".

  - ✓ There are many chemical (and physical*) reactions in which more structured (lower-entropy) products emerge **spontaneously** from less structured (higher-entropy) reactants, provided a compensating disorder is created in the surrounding environment.

*E.g., Carnot cycle: reactant = hot source; product = ordered KE of piston; compensating disorder created in cold sink

1.58 blub

Cooling

- So, assuming that life is just (complex) chemical reactions:

  - ✓ Could nature ***spontaneously* create**, as products of chemical "cooling", the complex structures (machinery) of life, from less structured reactants?

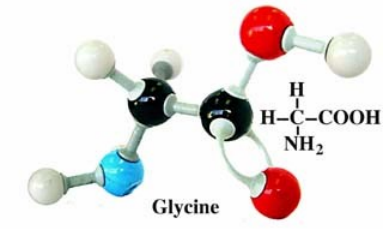
  - ✓ Would the very same "cooling" **animate** these machines?

  - ✓ Is **human consciousness** just a (marvelous) form of "cooling" —just another way in which the universe cools as it expands?

1.59 blub

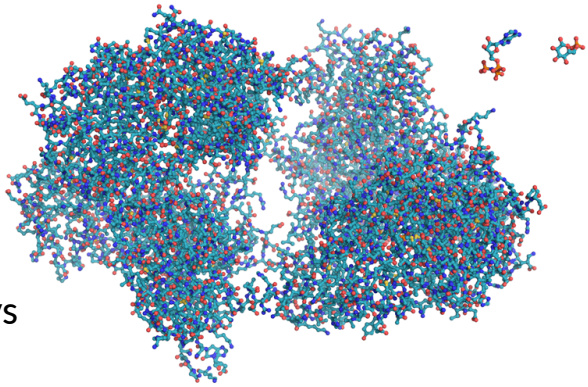
Proteins

- Recall: **amino acids** are the building blocks of life. The human body uses 20 of them to construct **proteins**, the bulk of living stuff. The simplest amino acid is glycine.



- The **origin** of amino acids on the early Earth is not a big mystery. (Recall: Miller-Urey experiment, chemical reactions near deep-sea vents, material from space.)

- The bigger question is, how can amino acids **spontaneously** come together in the form of proteins? Two steps:
  - ✓ Amino acids link together in **long chains**
  - ✓ These chains **coil** and **fold/intertwine** in complex ways



typical protein

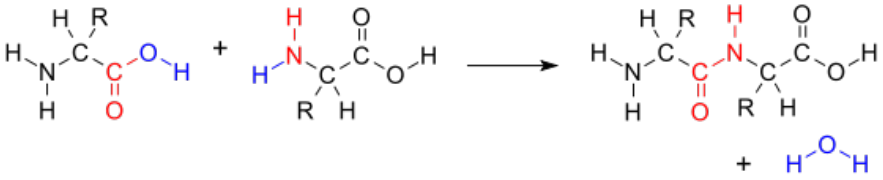
1.60 blub

Formation of Amino Acid Chains

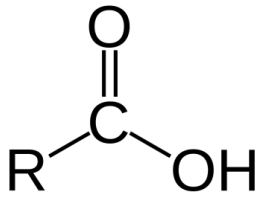
- Amino acids (e.g., glycine) have two key parts:
  - ✓ An NH_2 *amine* group
  - ✓ A COOH *carboxylic acid* group

N=blue, C=black, O=red, H=white

- Two amino acids join when the **amine group** in one approaches the **acid group** in the other, resulting in a **peptide bond** and the expulsion of a water molecule:



- This **consumes energy**, and is a big reason why we need to eat (more later…). But assuming we *have* a long chain of amino acids (a *peptide chain*), let's see how it **coils**.



carboxylic acid (note the OH)

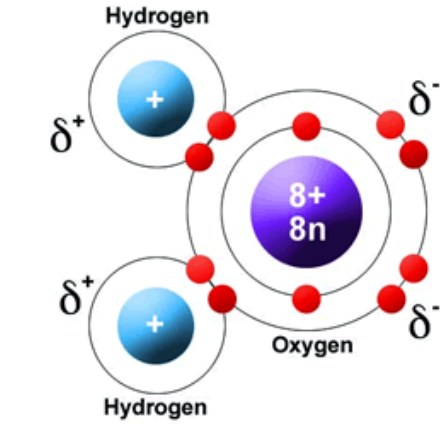
1.61 blub

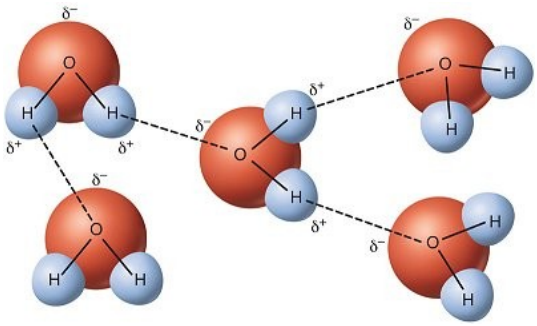
Coiling of an Amino Acid Chain into a Helix

- The water molecule, H_2O, is a **polar molecule**: Each H shares its electron with the O, making the protruding Hs **positive**. Also, the O has four more unshared electrons, opposite the Hs, making the side of the O opposite the Hs **negative**.

- In **liquid water**, the positive Hs of one molecule attract the negative Os in neighboring molecules. This **hydrogen bond** is stronger than van der Waals interaction, and weaker than covalent or ionic bonds, and is responsible for various "magical" properties of water that make it integral to life.

- It's also responsible for the **coiling** of amino acid chains into the very important **alpha helix**. The H attached to the N of one peptide bond **hydrogen-bonds** with the O attached to the C of a neighboring peptide bond. This bond is strong enough to hold the helical structure in place.





1.62 blub

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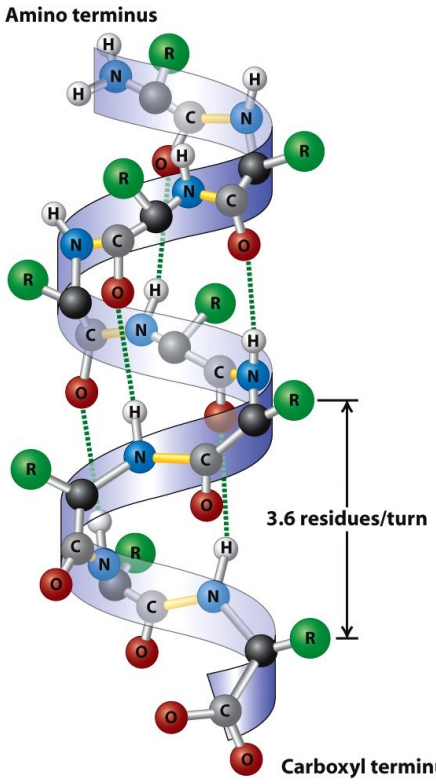
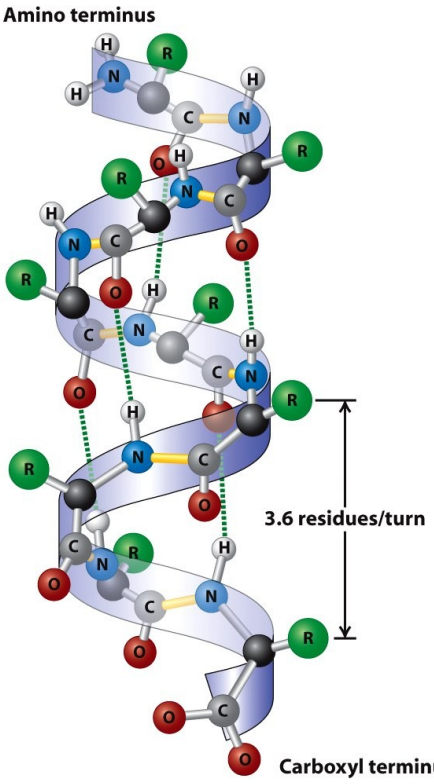


1.63 blub

Coiling of an Amino Acid Chain into a Helix

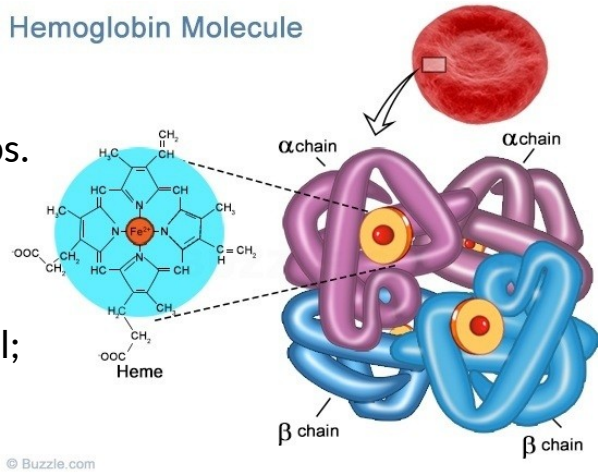
- The rigid alpha helix is a **more ordered** form of the amino acid chain, than just a random, floppy, linear chain. **How can this order arise spontaneously (via the Second Law)?**
- The O—H hydrogen bonds are sufficiently strong that, when they form, enough (electrostatic field) energy disperses into the environment (as thermal energy) that the resulting **increase in disorder** exceeds the increase in order of the alpha helix. The **universe** as a whole is **more disordered**!
- Moreover, the **formation** of the helix is **irreversible**: once the energy has dispersed, there's not enough concentrated energy around to break the bonds. (When you cook an egg, you're unzipping the helix.) This form of **local order** has "**condensed out**" of the universe's inexorable ratcheting towards **greater overall disorder**! $\Delta S > 0$.



1.64 blub

Folding and Intertwining of Helices

- **Hemoglobin molecules** (making up 96% of the non-water in red blood cells) carry **oxygen** to all the cells in your body.



- Each molecule is made of two alpha and two beta helices, bent and twisted in such a way as to hold four **heme** groups. Each heme group has one **iron atom** that oxygen binds to. (Blood is red because iron oxide is rust. So eat your iron!)

- The bending and twisting of the helices is not random at all; it is very precise. Each red blood cell contains zillions of **identical** hemoglobin molecules. Hemoglobin is a **highly ordered** structure. Can such order emerge **spontaneously**?

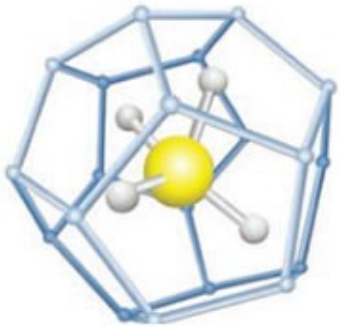
- **Yes**, in part for the same reason oil and water don't mix...

1.65 blub

Folding and Intertwining of Helices

- Why doesn't oil **disperse** in water, like a drop of ink? Surely this would **increase the entropy** of the universe, and so be spontaneous? Why does it do the **opposite**: clump together after we try to mix it?

- Hydrocarbons (like oil) are made of only C & H atoms, and are **hydrophobic**: when a hydrocarbon molecule is put in water, the surrounding (polar) water molecules interact with its H atoms and form a **highly structured** cage around it. (E.g., methane = CH_4.)



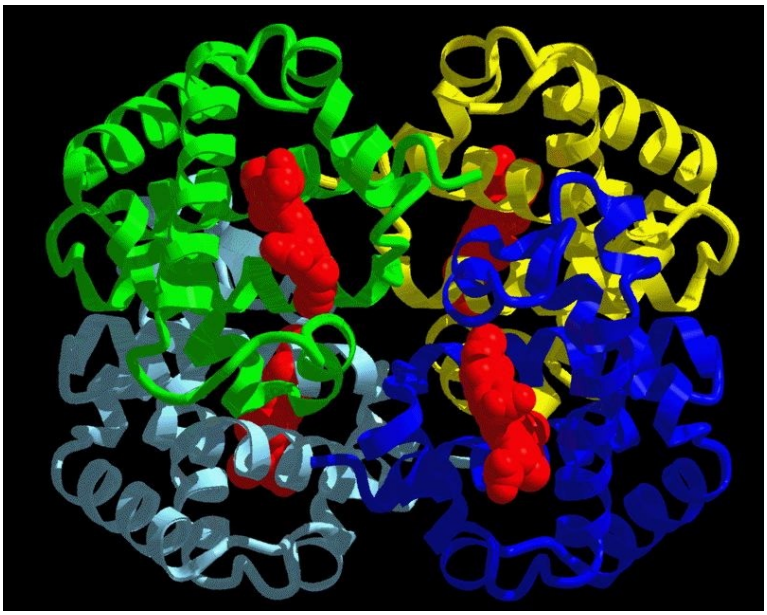
- The resulting **increase in order** would outweigh the **decrease in order** caused by the spreading out of the oil molecules (and their energy). Oil molecules clump together to show as few of the themselves to the water as possible: hydrophobic = water-hating.

- What does this have to do with folding & intertwining of helices?

1.66 blub

Folding and Intertwining of Helices

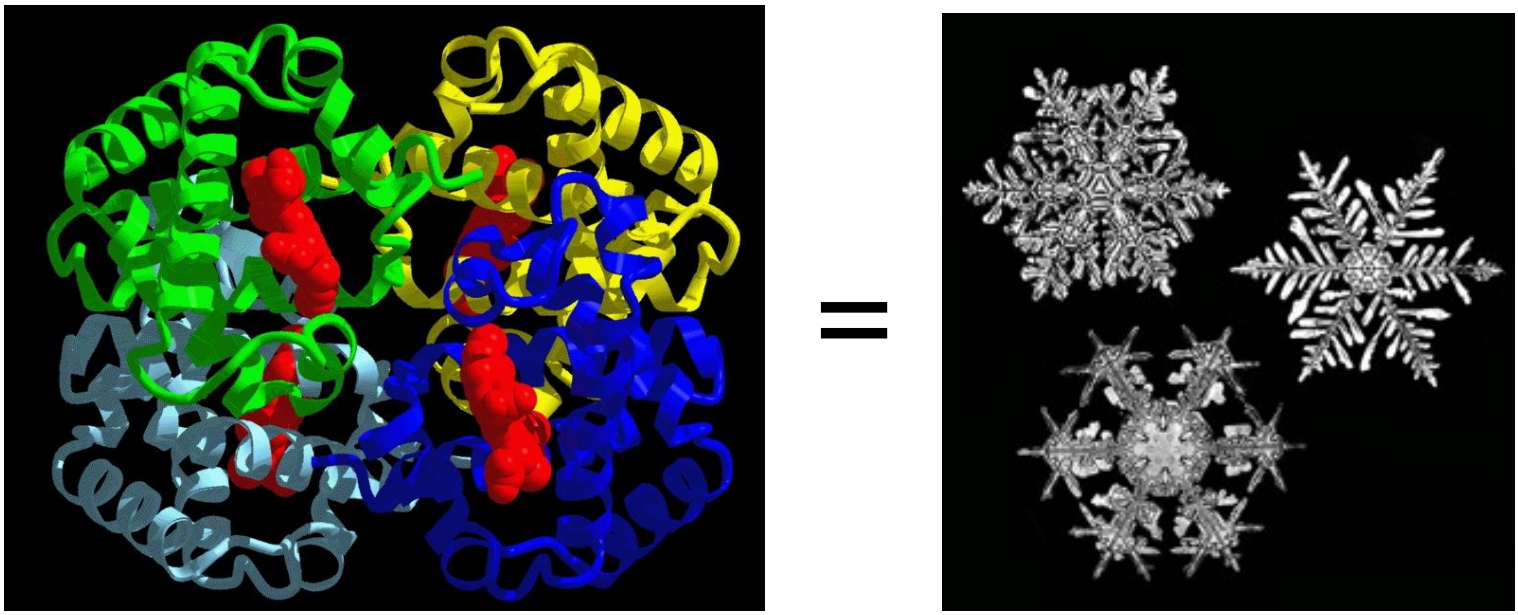
- Many of the amino acids in the helices have **hydrocarbon parts**, and so **behave like oil** (hydrophobic).
- Water molecules would form **intricate cages** around any hydrocarbon parts sticking out into the surrounding water, **increasing the order** in the universe.
- The helices fold in ways that tend to **minimize** exposure of hydrocarbon parts to the water, and thus **minimize order** (**maximize disorder**).
- The same effect probably plays a role also in the four helices **intertwining** in hemoglobin.



The formation of this complex structure **increases the disorder** of the universe

1.67 blub

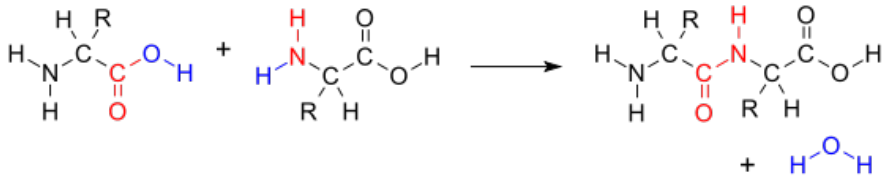
Folding and Intertwining of Helices



1.68 blub

Formation of Amino Acid Chains

- But how are amino acid chains formed **in the first place**?
- Recall that forming the peptide bonds between the amino acids in a chain **consumes energy**.



- So the short answer is obvious:
  We eat food that provides this energy.
- But the long answer is more interesting…

1.69 blub

Formation of Amino Acid Chains

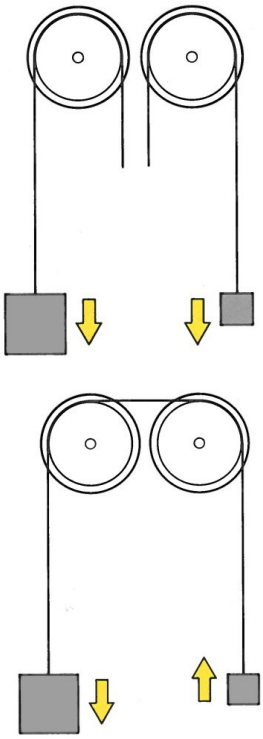
- The ordered chain has more structure (**lower entropy**) than the scattered amino acids it was made from. Thus, there must be a **compensating disorder** created elsewhere. **How?**
- We eat, in part for the energy, but more importantly: we take in **high quality** (low entropy) energy, and allow it to **decay** to **low quality** (high entropy) energy, which we expel as body heat and excrement. This **spontaneous order-to-disorder** process *drives* **non-spontaneous disorder-to-order** processes in our bodies, sustaining our relatively low entropy bodies against decay, and thus staving off death.
- This **low entropy energy** ultimately comes from the **Sun**, or more ultimately, from the **Big Bang** itself. Life is **intimately connected** with the very ***dynamics of the universe itself***. Life is **not** an ***isolated*** phenomenon. "Biosphere"= Universe!



1.70 blub

Coupling Spontaneous to Non-Spontaneous Processes

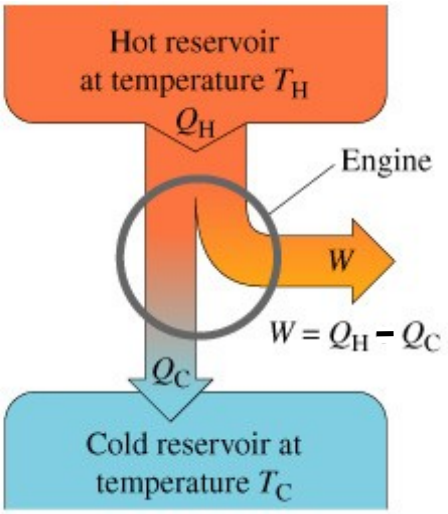
- "This **spontaneous order-to-disorder** process *drives* **non-spontaneous disorder-to-order** processes in our bodies." **HOW??**
- Analogy:
  - ✓ **Top Picture:** Both masses will **spontaneously** fall.
  - ✓ **Bottom Picture:** When **coupled together**, the heavier mass will raise the lighter. A **stronger** spontaneous reaction can ***drive*** a weaker spontaneous reaction in the **reverse (non-spontaneous or unnatural) direction**.
- Questions:
  - ✓ How do we assess the **"driving power"** of a reaction?
  - ✓ What are the "gears and wheels" that **couple** life's chemical reactions?



1.71 blub

Driving Power of a Reaction

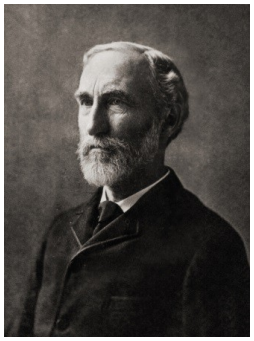
- Recall:
  - ✓ In a heat engine, the **spontaneous** flow of thermal energy from hot to cold is **harnessed** to do useful work, W, which can be used to **create structure and order**. "Order from disorder".
  - ✓ But not all of Q_H is converted into useful work, W. A minimum of "waste heat", Q_C (energy), must be dumped into the environment (increasing its entropy) to ensure **entropy increases** overall in the universe.
  - ✓ The amount of energy that is **free to do work** (create structure and order) is called the ***free energy***. For a heat engine, the free energy **available goes down** as it does work: $\Delta W = -W$. What about in the case of chemistry?



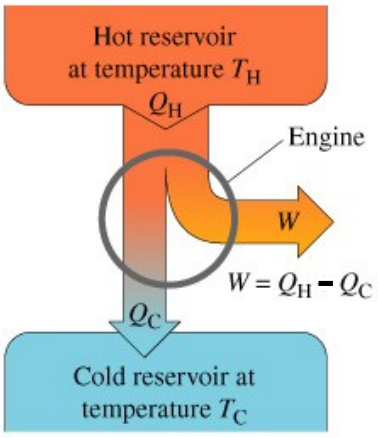
1.72 blub

Driving Power of a Reaction

- Josiah Gibbs (1839–1903), in Boltzmann's generation, was the first person to apply thermodynamics to chemistry, and hence make thermodynamics more readily applicable to life.



- E.g., we can think of an exothermic chemical reaction as a heat source with total energy U at temperature T_H. When the system liberates energy Q_H, its energy goes down, $\Delta U = -Q_H$, and its entropy is reduced: $\Delta S = -Q_H/T_H$.



- In order for this to happen spontaneously, a minimum of "waste heat" Q_C (usable energy) must be dumped into the environment (at temp T_C), increasing its entropy by (at least) the same amount. Like the heat engine, $\Delta S_{env} = Q_C/T_C$. The free energy of the system goes down as it does work: $\Delta F = -W = -Q_H + Q_C = \Delta U - T\Delta S$.

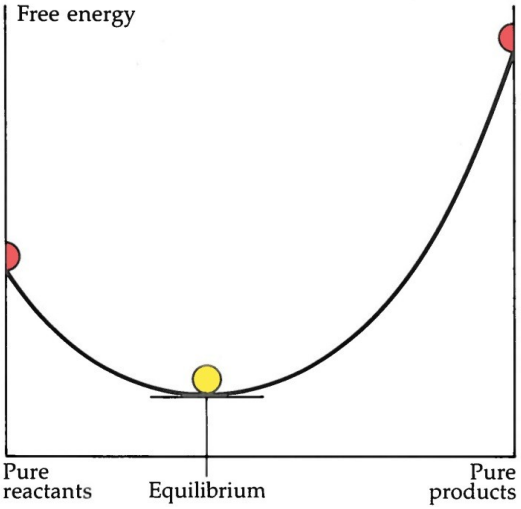
1.73 blub

Driving Power of a Reaction

- **All** chemical reactions **spontaneously** move towards **lower free energy**:

$$\Delta F = \Delta U - T\Delta S < 0$$

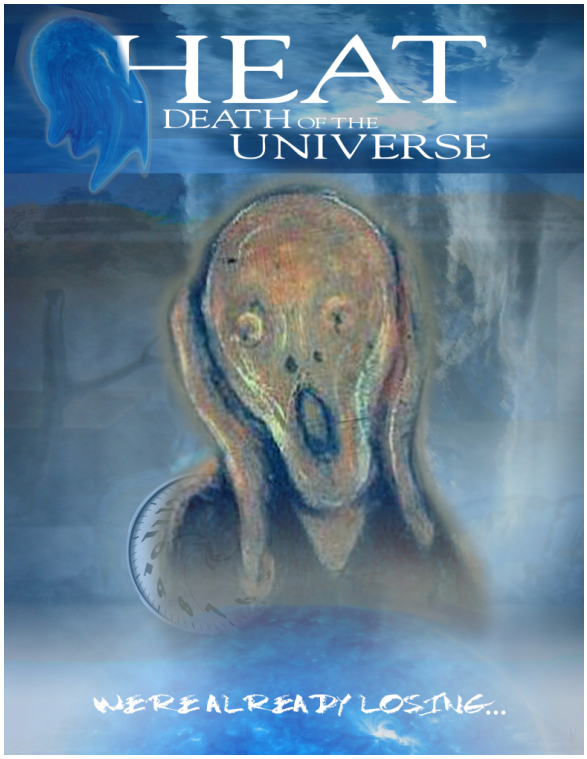
- This is the "**driving power**" of the reaction: the greater the "fall" in free energy, the more **useable energy** ("work") is liberated to **create structure and order** elsewhere.
- This applies to **all natural processes** in the universe:
  - ✓ Systems do **not** spontaneously move to **lower energy** (e.g., when you heat a gas).
  - ✓ Systems spontaneously move to **lower *free energy***. This drives **all** process, including **animating life**.
  - ✓ Systems fall **down** in free energy, as the universe falls **up** in total entropy.



1.74 blub

The End of Free Energy

As the total entropy of the universe steadily ratchets up, we are not running out of energy (energy is **conserved—*eternal***). We are running out of ***free*** energy. ***Useful*** energy. Energy that can be used to **create structure and order**, and **animate life**.



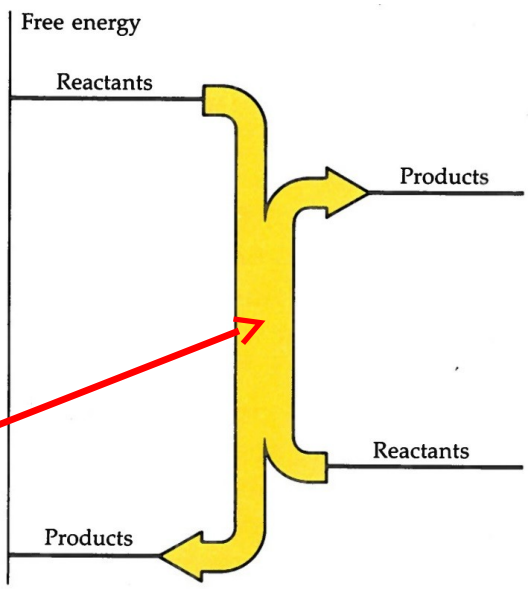
1.75 blub

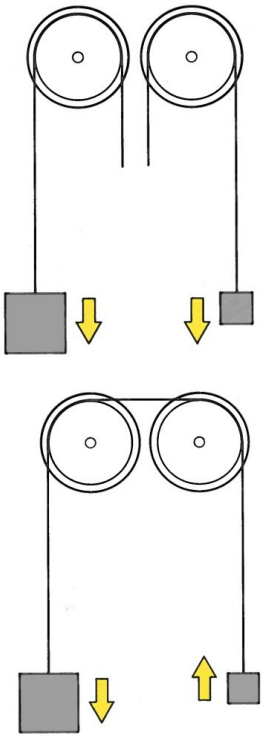
Coupling Reactions

- **How does this inexorable slide into disorder <u>animate life</u>?**

When **coupled** together, a reaction that **falls further** in free energy (a more vigorous slide into disorder) can ***drive*** one that **falls less** in free energy (less vigorous slide into disorder) in the **reverse direction**.

Life's **"gears and wheels"**





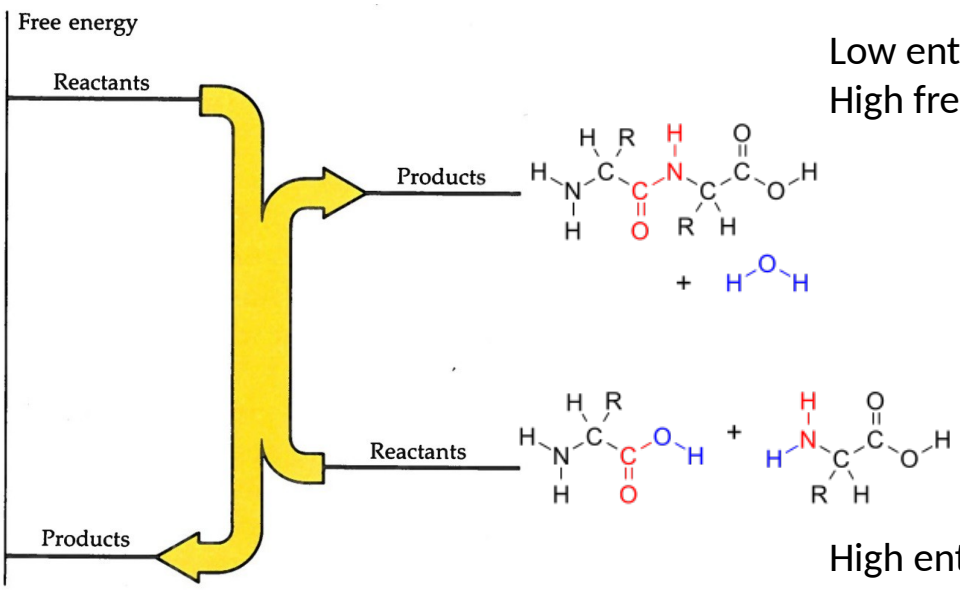
1.76 blub

Example: Bioenergetics Coupled to Biosynthesis

Bioenergetics (LEFT: degradation of food) coupled to Biosynthesis (RIGHT: linking amino acids)

Low entropy
High free energy

High entropy
Low free energy



Low entropy
High free energy

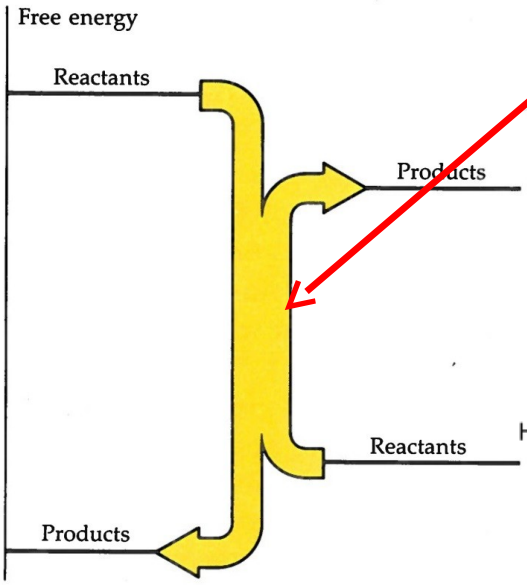
High entropy
Low free energy

1.77 blub

The Gears of Biosynthesis

Let's first look at some of the "gears" of Biosynthesis (RIGHT)

Low entropy
High free energy



Low entropy
High free energy

High entropy
Low free energy

High entropy
Low free energy

1.78 blub

The Gears of Biosynthesis

It's complicated...

https://www.youtube.com/watch?v=gG7uCskUOrA

1.79 blub

The Gears of Biosynthesis

It's complicated…

https://www.youtube.com/watch?v=WFCvkkDSfIU

1.80 blub

The Gears of Biosynthesis

It's complicated...

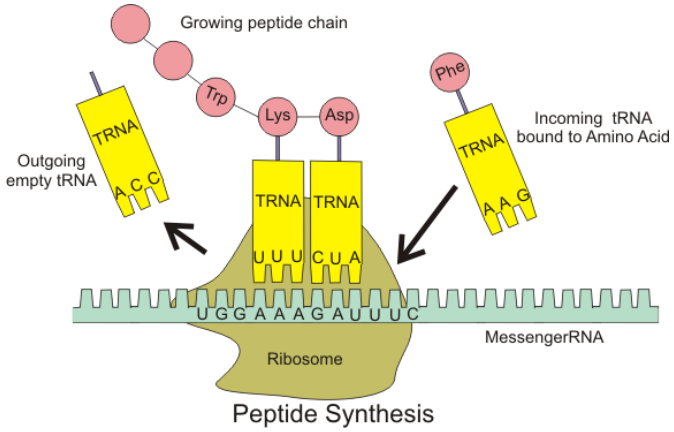
Other similar animations, emphasizing different aspects:

https://www.youtube.com/watch?v=D3fOXt4MrOM
https://www.youtube.com/watch?v=lpb5s2F1pyM
https://www.youtube.com/watch?v=28mgfg8nRT4
https://www.youtube.com/watch?v=JX2MdZX6Bys
https://www.youtube.com/watch?v=B_zD3NxSsD8

1.81 blub

The Gears of Biosynthesis

The “gears” of biosynthesis are **highly complex, microscopic machines**!



How could they *possibly* arise spontaneously?

We’ll return to this question later…

First we’ll look at some “gears” (microscopic machines) of bioenergetics

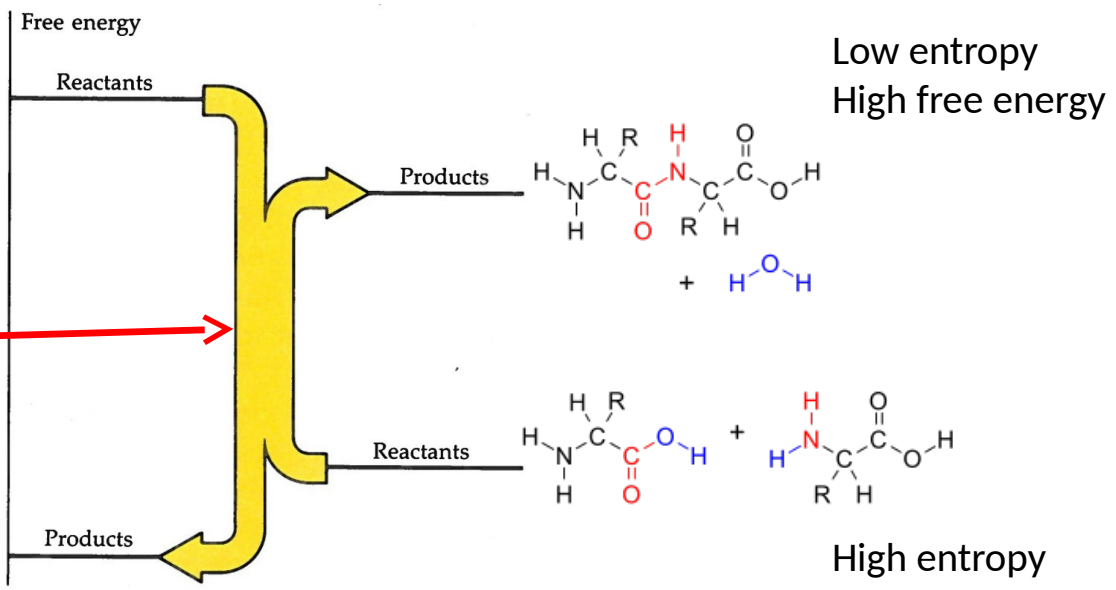
1.82 blub

The Gears of Bioenergetics

Let's now look at some of the "gears" of Bioenergetics (LEFT)

Low entropy
High free energy

High entropy
Low free energy



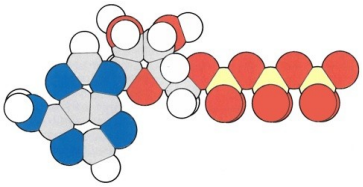
Low entropy
High free energy

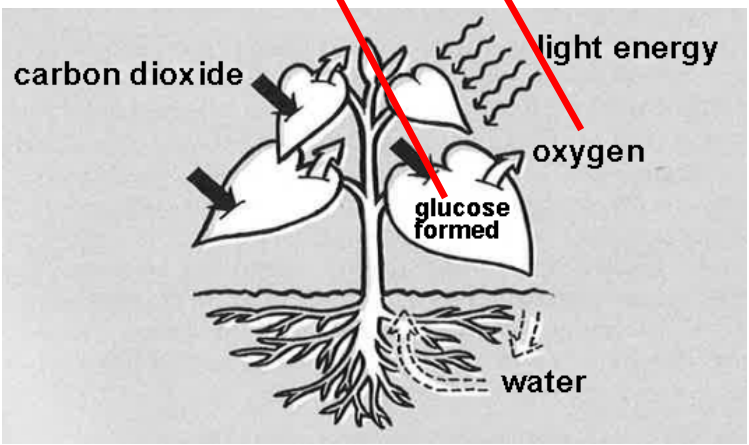
High entropy
Low free energy

1.83 blub

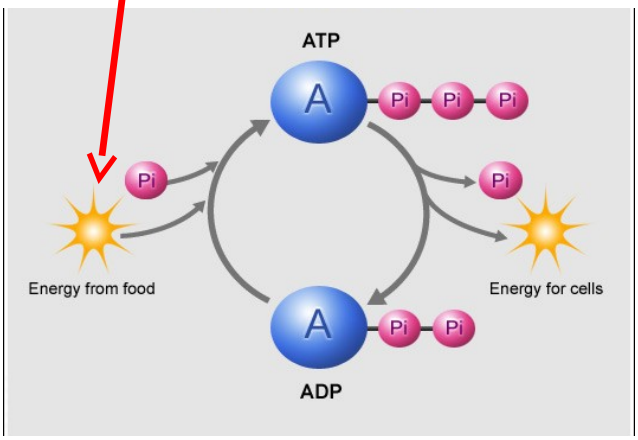
The Gears of Bioenergetics

glucose + oxygen ⇌ carbon dioxide + water + energy





photosynthesis (more later...)



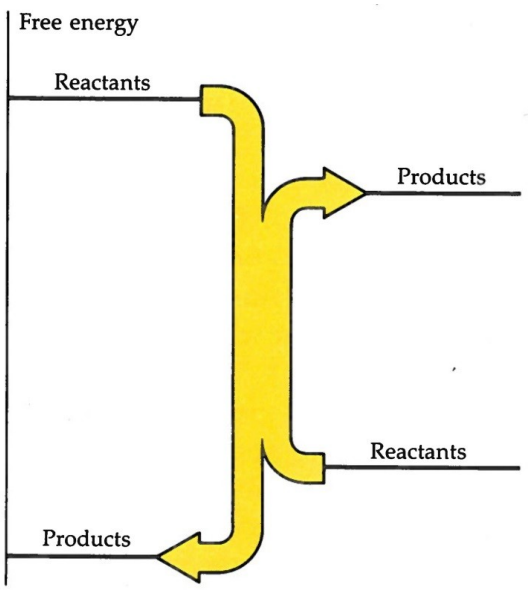
adenosine diphosphate ⇌ triphosphate (PO_4)

Light energy is highly ordered, when plants process it they make glucose which is less ordered. We burn that chemical energy and turn it into kinetic/thermal energy which is highly unordered. We have this molecule adp which has only two phosphate groups, meaning its in its low energy state. We use energy to attach another phosphate making it atp, the high energy state. This is used all over the fucking place in our body.

1.84 blub

The Gears of Bioenergetics

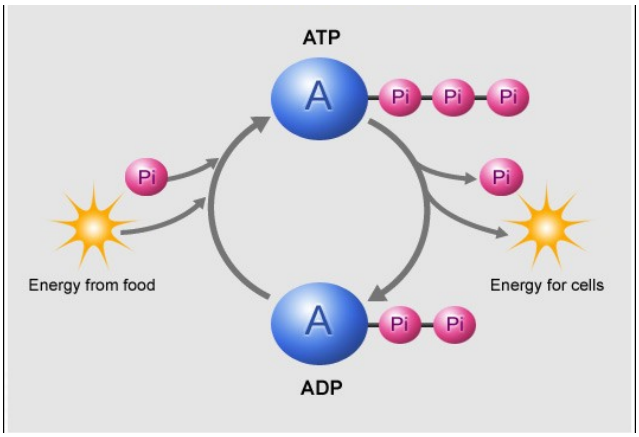
glucose
+ oxygen



ATP

ADP

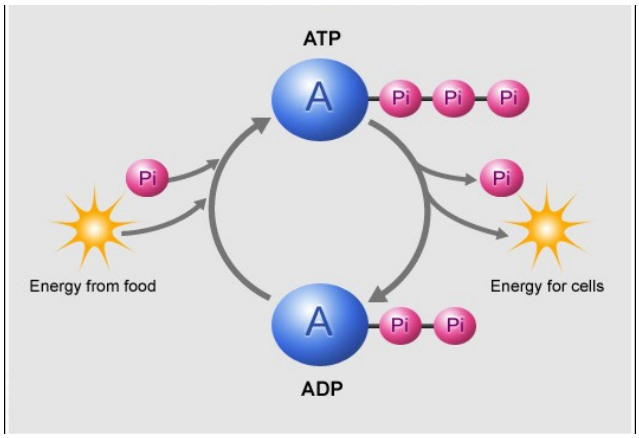
carbon dioxide
+ water

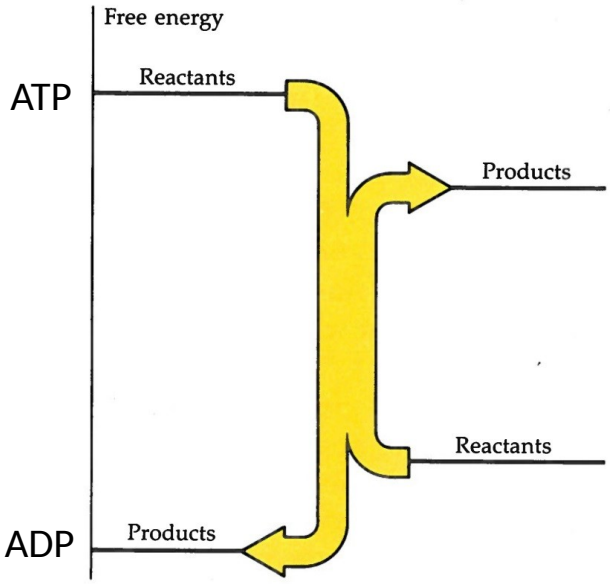


This is a **spontaneous** process that
increases the entropy of the universe

1.85 blub

The Gears of Bioenergetics





amino acid **chain**

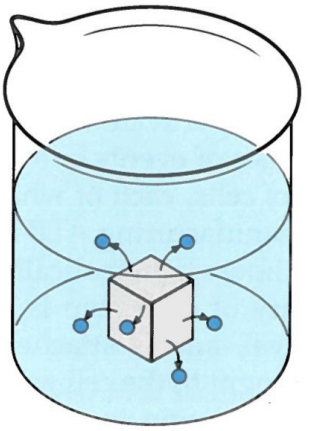
scattered amino acids

This is a **spontaneous** process that **increases the entropy** of the universe

1.86 blub

The Gears of Bioenergetics

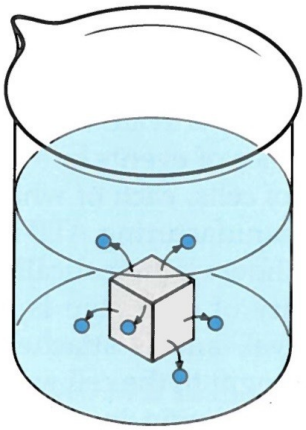
- ADP & ATP are the **life blood** of **bioenergetics**
- The energetic "charging" of ADP to ATP is done by an **electrochemical battery**
- **Example** of electrochemical battery:
  - ✓ Drop a cube of **iron** (Fe) into a **copper** (Cu) sulfate solution
  - ✓ The **Cu^{2+} ions** in the water have a **strong affinity** for electrons
  - ✓ When they touch the cube, the **Fe atoms** give up 2 electrons to the **Cu^{2+} ions**. The Fe atoms become **Fe^{2+} ions** in solution, & the Cu^{2+} ions become neutral **Cu atoms** that deposit on the cube
  - ✓ **Net result:** the **copper precipitates** and the **iron dissolves**

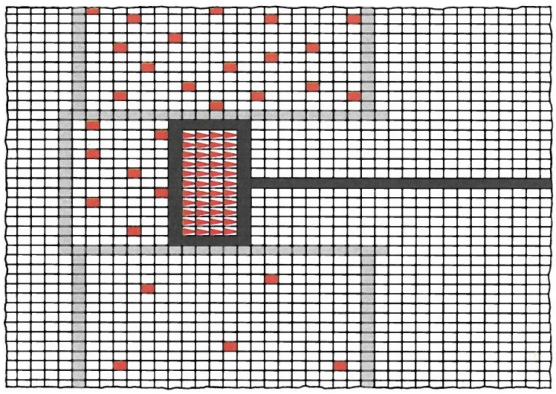


1.87 blub

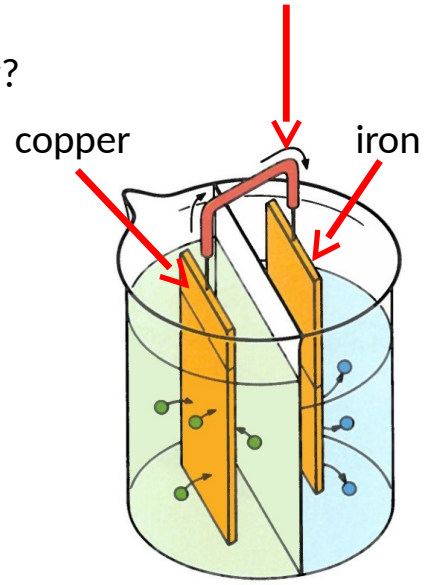
The Gears of Bioenergetics

- **Key Idea:**
  - ✓ As it stands, the ***spontaneous flow*** of electrons from the **Fe atoms** to the **Cu^{2+} ions** is in **random** directions.
  - ✓ What if we force the electrons to flow in **one direction only**? (Exactly like we extracted **ordered KE** in the heat engine!)





Electric current (opposite electron flow) can be used to do **work**!



ignoring "salt bridge"...

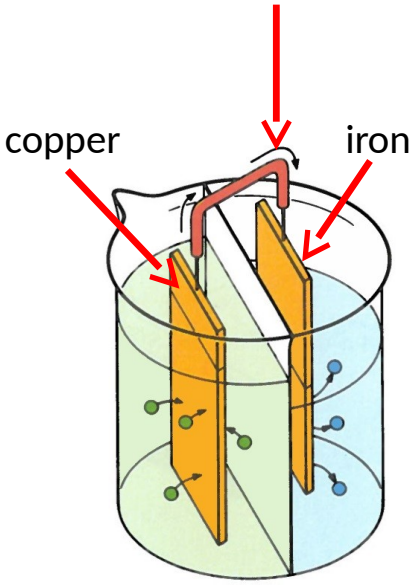
By providing the elections with a very specific path to go through (the copper wire). This is how we make a battery. Like the piston this is a one way valve.

1.88 blub

The Gears of Bioenergetics

- **Aside:**
  - ✓ Where does the energy released by such a copper-iron battery actually come from?
  - ✓ The nuclear furnaces in long-dead stars, which created the elements heavier than hydrogen, up to iron.
  - ✓ Fission reactors today use uranium, which is created when stars explode as supernovae.
  - ✓ Fusion reactors being developed today will use hydrogen, which was created by the Big Bang itself. **It is the most ancient (and abundant) of all fossil fuels**.

Electric current (opposite electron flow) can be used to do **work**!



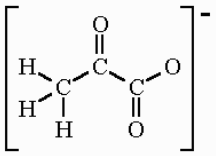
ignoring "salt bridge"...

1.89 blub

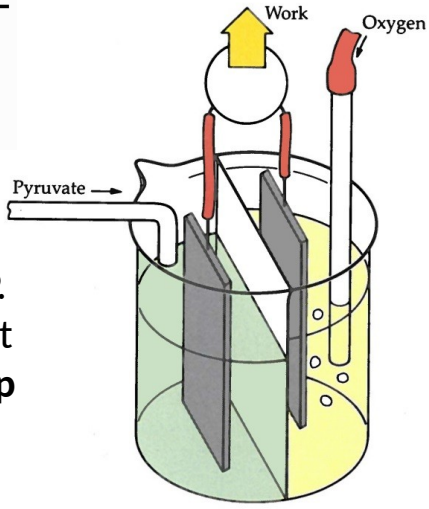
The Gears of Bioenergetics

- **Nature has evolved a similar battery, in which glucose & oxygen are "burned" to charge ADP to ATP:**

  - ✓ Like Cu^{2+} ions, **oxygen** has a **strong affinity** for electrons; it likes to become O^{2-}
  - ✓ Glucose gets "snipped" into two **pyruvate** ions: (which can easily give up their extra electron) …and two **protons** (H^+ ions) are produced



  - ✓ The **spontaneous flow** of electrons from pyruvate to oxygen (the "burning of sugar") does the work to charge ADP to ATP. The ATP have higher order (**lower entropy**) than the ADP, but with everything else, the **net** entropy of the universe **goes up**
  - ✓ The pyruvate falls apart into carbon dioxide (we exhale), and each O^{2-} picks up two **protons** to become water…

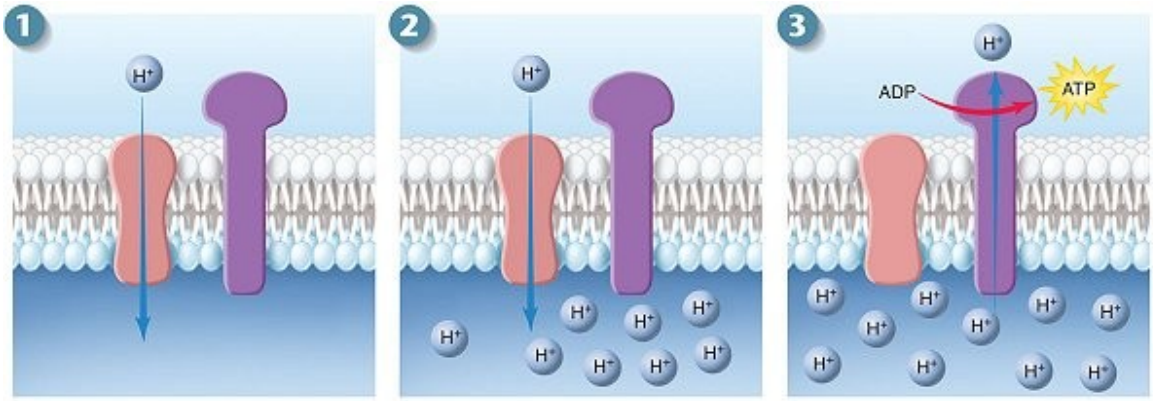


ignoring "salt bridge"…

1.90 blub

The Proton Gradient

- The **spontaneous flow** of electrons **does not *directly*** charge the ADP to ATP. *Instead*:
  1. It drives a **proton pump** that forces protons across a membrane
  2. This creates a **proton gradient** that stores potential energy across the membrane (in an **electric field**).
  3. This **store of energy** can be tapped by allowing protons to flow back across the membrane through an protein called **ATP synthase**. The **electric field accelerates the protons**, and this extra **kinetic energy** is used to charge ADP to ATP.

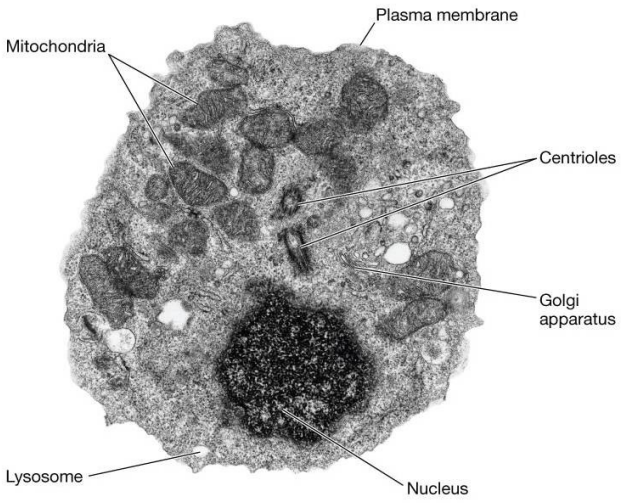


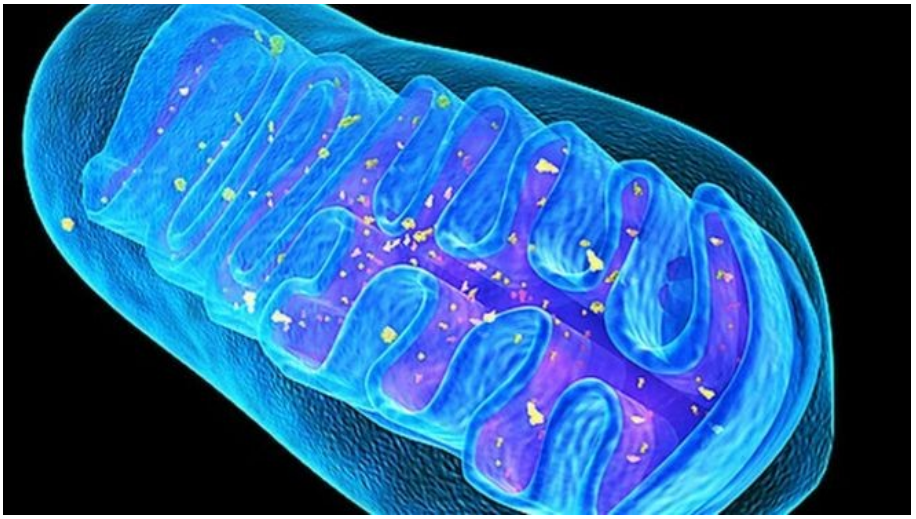
The election flow does directly charge the conversion to atp. Instead it drives a protein pump. The elections pump out proteins from the cell. There is a valve called atp synthase. It opens to allow adp into it and when a proton is pushed out the adp converts into atp.

1.91 blub

The Proton Gradient

- All of this takes place in **mitochondria** inside cells:





1.92 blub

The Proton Gradient

- All of this takes place in **mitochondria** inside cells:

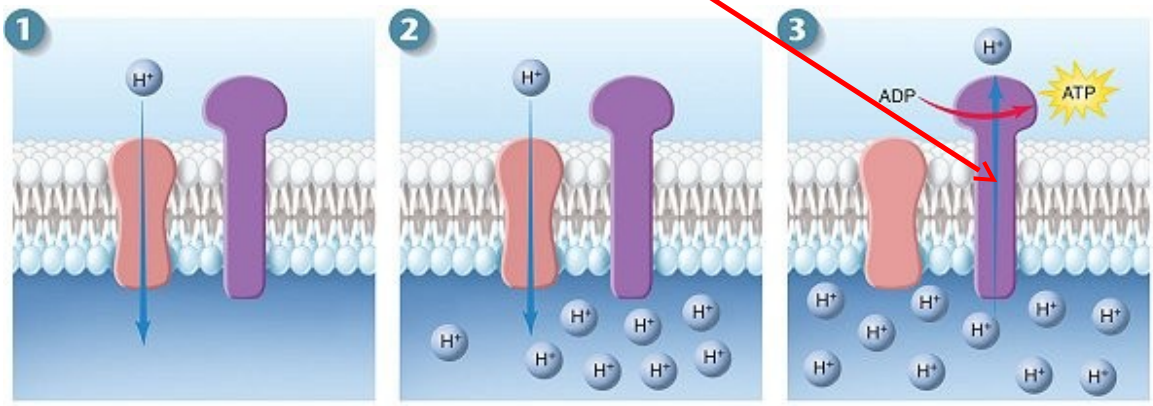
https://www.youtube.com/watch?v=nD9fyuisMkg

The conversion of adp to atp acually happens due to the mitochondria. Its hella complicated. Watch the video.

1.93 blub

The Proton Gradient

- Let's look at how **ATP synthase** actually **works**...



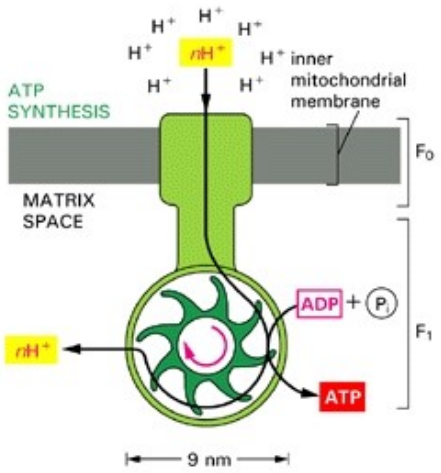
1.94 blub

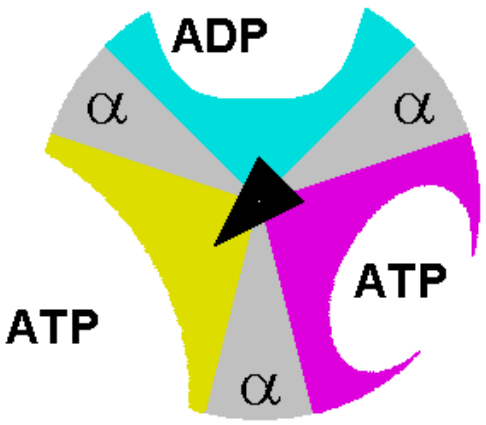
The Proton Gradient

The **proton gradient** creates an **electric field** that **accelerates** the protons let back across the membrane.

These accelerated protons push on a **rotary mechanical motor**, which converts ADP to ATP (it's a **physical machine**, not what one usually thinks of as "chemistry"!)

About 3 protons need to pass through to charge one ATP (100 charges per second).



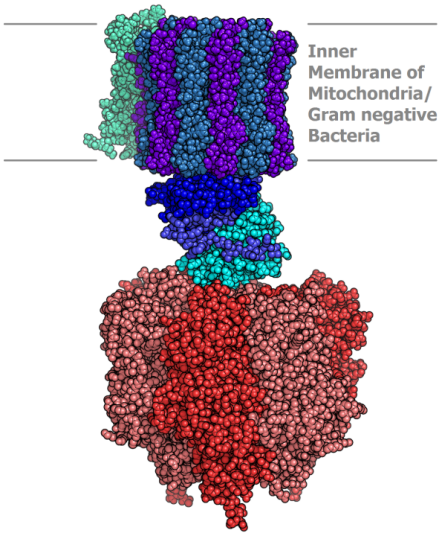


The proton pump moved a bunch of ions on one side of the cell membrane. They want to come back in but the cell wall stops them. The valve opens when the cell needs energy to allow some protons back in. The protons rush in and turn a wheel (an actual wheel). The wheel has some adp on it and it slams it into a phosphate group clicking them together. You can even run the motor in reverse. Its boss.

1.95 blub

The Proton Gradient

- The ATP synthase **machine**:



https://www.youtube.com/watch?v=XI8m6o0gXDY

1.96 blub

The Proton Gradient

intelligent design?

1.97 blub

The Proton Gradient

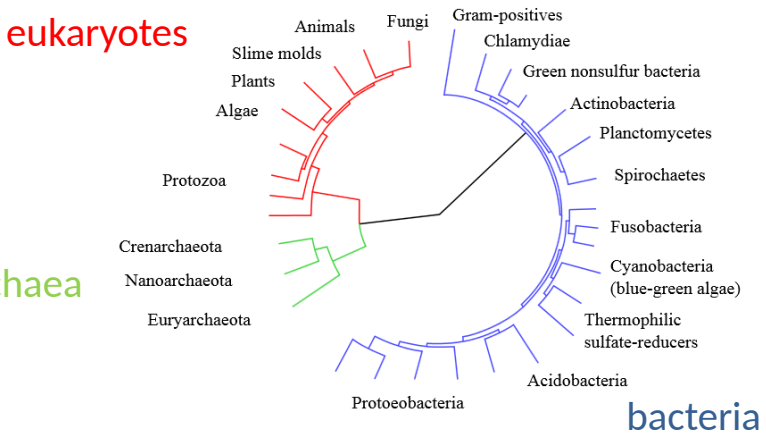
proton gradient...so what?

1.98 blub

The Proton Gradient

- Today, ***all*** energy that living organisms use ultimately comes from **generating and tapping a proton** (or other ion) **gradient**.
- It is the **universal "battery" that powers all life on Earth**, as universal as the genetic code itself. Thus, it is an important clue to the **origin of life**.

- For example, the **ATP synthase** (the machine that **taps** energy from the gradient) is as **universal** as the **ribosome** (the protein synthesis machine), and it displays the same deep "phylogenetic" split between archaea and bacteria ⇒ **it was present in the last universal common ancestor (LUCA)**, and must have "evolved" prior to this. (How? More later…)



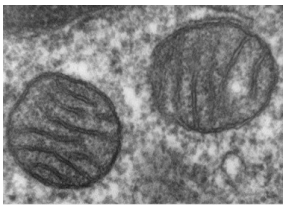
The universal battery that powers all life is this action of creating a proton gradient and using it with atp sythase. Because all life uses this its clear that its a clue to the origin of all life.

1.99 blub

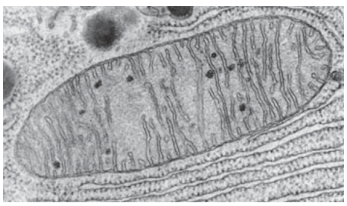
The Proton Gradient

- In eukaryotes (like us), this proton gradient “battery” is inside **mitochondria.** The mitochondria across all eukaryotes have the **same general structure** (see pictures)
- These bacteria-sized organelles may have originally been **aerobic bacteria** that **invaded and colonized** early eukaryotic cells (they have an independent bacteria-like genome!)

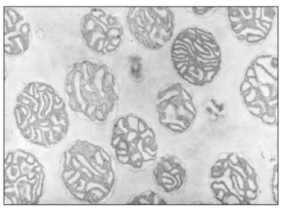
examples of eukaryotes



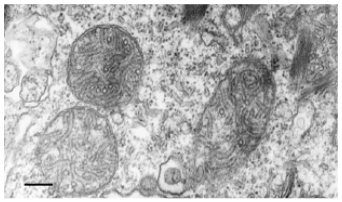
mammalian lung



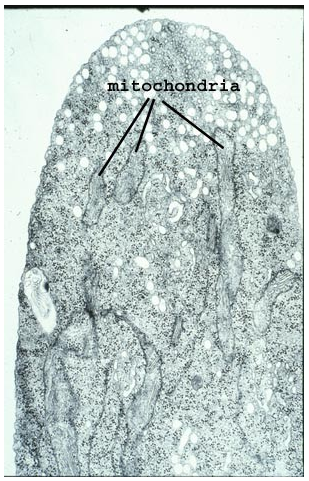
bat pancreas



mung bean



paramecium



fungus

1.100 blub

The Proton Gradient

- Okay, so ion gradients are the universal battery of life. But this raises a **severe evolutionary chicken-and-egg problem:**
  - ✓ **Proteins** are used to generate and tap ion gradients (e.g., the ATP synthase is used to tap the proton gradient and convert ADP to ATP)
  - ✓ But **energy** is needed to build proteins (like ATP synthase) in the first place (protein synthesis consumes 75% of a cell's ATP budget)

Proteins are required to generate energy, but energy is needed to build those proteins. *So where did the energy come from that built the first proteins?*

- This has long been a **deep mystery**, but recently progress has been made: ***Naturally occurring*** proton gradients at **deep-sea hydrothermal vents** have been shown to **spontaneously synthesize amino acids** (building blocks of proteins) and **nucleotides** (building blocks of RNA & DNA), and may have been the **initial spark of life**. We are one step closer to understanding how it ***might*** have been possible for ***rocks to "come to life"*** !

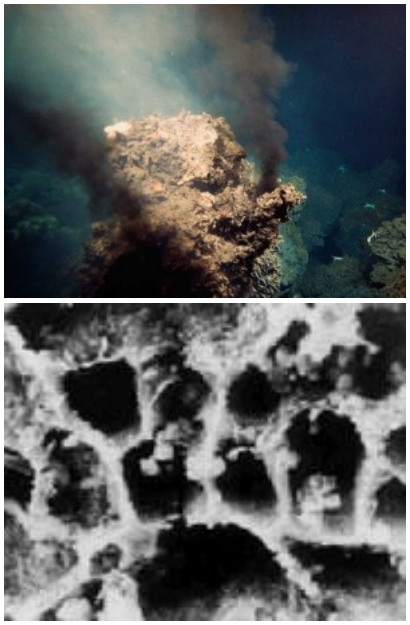
We need proteins to create a proton gradient but the way we build proteins uses energy that we get from atp which requires a protein gradient. So where did the original energy come from to create the first proteins, the spark of life so to speak.

Fairly recently we realized that if you look at hydrothermal vents you can find naturally occurring proton gradients. These can just randomly synthesize things. The theory is that the rocks around the vents "came to life".

1.101 blub

The Proton Gradient

- See: The Origin of Membrane Bioenergetics (Lane & Martin 2012). Also: Nature News. Martin: “There are lots of theories [of the origin of life] but ours is the first to **start with the cell**.” (Most scientists assume that **self-replicating molecules** or proteins came first.)
- Rocks of deep-sea thermal vents contain labyrinths of tiny thin-walled pores, which could have acted as ‘**proto-cells**’, the first life-forms:
  - ✓ **(CO_2- and H^+-rich) acidic** ocean water on the outside and **(H_2- and OH^--rich) alkaline** vent water on the inside, separated by a thin mineral (iron sulfide, FeS) wall, sets up a natural proton gradient *of magnitude & orientation used by modern cells*;
  - ✓ Powered by the proton gradient, the FeS wall can **catalyse** conversion of **CO_2** and **H_2** into organic carbon-containing molecules, and **concentrate** them inside, enabling them eventually to generate **genes, proteins and a proto-membrane**.



Iron sulphide (FeS) honeycomb: “a fertile environment.”

There are two groups for theories of life. One is self replication first (RNA world). The other is metabolism first (deep sea hydrothermal vents).

1.102 blub

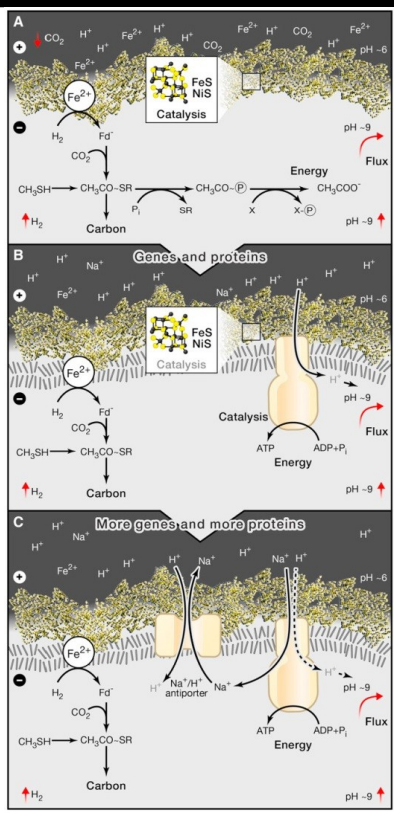
The Proton Gradient

Some details are shown in diagrams A and B:

A. In the presence of the proton gradient, FeS catalyses $CO_2 + H_2 \rightleftharpoons$ Carbon + Energy (CH_3COO^- - glucose). **Note:** Modern microbes near vents, that similarly live off CO_2 and H_2, use enzymes (protein catalysts) **also** based on FeS and Fe(Ni)S (a hint this may be right...)

B. The carbon, plus this relatively **low entropy** energy inside the proto-cell, allows the formation of **complex** organic carbon structures like amino acids, RNA bases, sugars, lipids, and possibly (?) even **ATP synthase** (a very efficient coupling to the proton gradient). [Note that the H^+ (acid) passing through the ATP synthase is neutralized by continuous supply of OH^- (base) in the vent water.]

The proto-cell evolves towards **ever more efficient** coupling to the proton gradient, since this increases the rate at which energy is dissipated (and the universe moves to a state of **higher entropy**).



1.103 blub

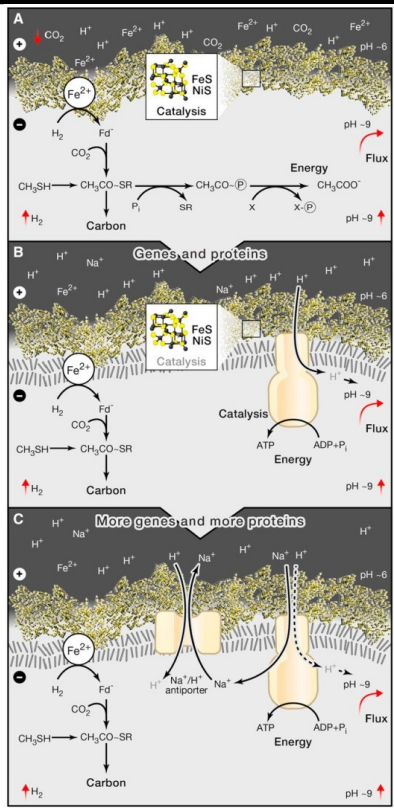
The Proton Gradient

Such proto-cells could **tap** the naturally occurring proton gradient, but how could they evolve to **generate** their own gradient, and become **free-living** cells, floating around in the ocean?

Three things would be needed:

- ✓ A completely sealed **organic cell wall** (to replace the FeS rock wall)
- ✓ A **proton pump** (to pump out the protons that enter through the ATP synthase, which are no longer neutralized by vent water OH^-)
- ✓ An **energy source** to drive the pump

Idea: The FeS wall was **leaky** to H^+, reducing efficiency. Lipids (fats) may have naturally formed an organic cell wall (more later…), which would help reduce the leakiness, and would **improve efficiency**.



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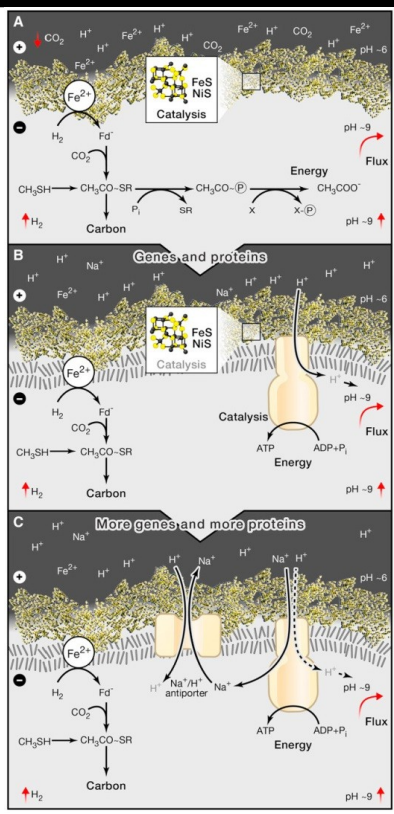
The Proton Gradient

Assuming the evolving organic cell wall **tightened up slowly**: was **first** impermeable to **large** ions like Na^+, then to **small** ions like H^+ (protons)…

C. …there would have been a long transition time during which a Na^+ gradient would have been **more efficient** than a H^+ gradient. This could explain **why** modern vent microbes have a very simple Na^+/H^+ "**antiporter**", which runs for **free**, converting **H^+ bioenergetics** to **Na^+ bioenergetics**. In such a transition-stage proto-cell, the natural proton gradient is still used (H^+ passing through the antiporter is still neutralized by the continuous supply of OH^- in the vent water).

This suggests a **plausible** path to an **organic cell wall** and a **Na^+ pump**. What **drives** it? Just switch from proton gradient to **energy from metabolizing CO_2 + H_2**. The newly "living" cell could then detach from the rock and become a free-living cell floating in the ocean.

Many details are **still mysterious**, but we are **one step closer**!



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Summary

Summary:

- We **may never be certain** how life on Earth began. The further back we push the question, the less direct evidence survives.
- Nevertheless, scientists are making **stunning progress** towards a variety of possible/plausible ways that life **may** have begun.
- But we still have a long way to go, which is good in the sense that **science thrives on mystery**, and **dies as knowledge becomes complete**.

Basically we are taking our models and making them more and more probable. It is unlikely that we will ever find definitive proof since almost everything around at the beginning of life have been subducted into the earths course.

Well thats the end of the slides on learn, but not his slides. WEEEEEE.

Thermodynamics is the study of a closed system near equilibrium, but life needs things to be out of wack to work

Dissipative structures were disovered by Progoine. When they are open they have energy flowing through them. This results in a steady state not equilibrium which is basically ordered energy. When you start with a low energy system and add heat to it we get convection cells, called Benard cells. These appear spontaneously. This decreases entropy because it brings order. These also carry energy through much more quickly. This could be considered analagous to a living system.

With this logic we can see that it is possible to have a system be continuously out of equilibrium, so long as we have energy going it we can maintain our weird state.

If you have tons of little things interacting with each other we can have self-organizing systems. This is basically order occuring spontaneously which is neat. An example of this is the formation of cell membranes.

We have expanded our understanding of the second law of thermaldynamics by understanding that withing microscopic system we can have a fluctuating entropy. This is the fluctuation theorem. In small fluctuations the probability of it being increasing is equivalent to it decreasing. In large fluctuations its more probable to be increasing.

$$\frac{P(+\Delta S)}{P(-\Delta S)} = e^{\Delta S} \tag{1}$$

We then expanded more and more on this by creating a generalized theorem and then getting that to apply it to life.

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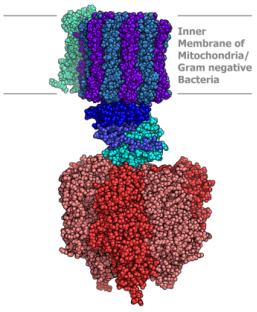
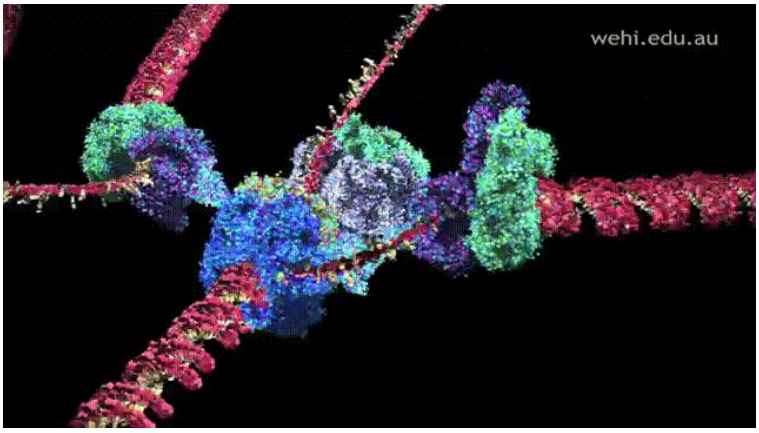
The Real Question

Problem: all of these scenarios rely on complex machines, e.g., ATP synthase, protein synthesis machinery, DNA replication machinery, etc.



So the **REAL QUESTION** is:

How might such complex machinery have arisen ***spontaneously***?



kinesin protein

1.107 blub

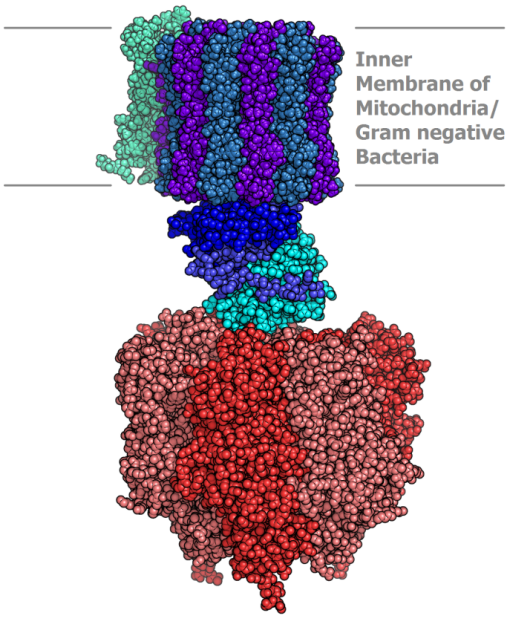
The Real Question

Recall:

- Physicists have discovered two fundamental laws of nature:
  - ✓ 1st Law: **Quantity** of energy is **constant**
  - ✓ 2nd Law: **Quality** of energy **continually decreases**

- We have shown that life is **consistent** with these basic thermodynamic laws.

- But can thermodynamics explain **why** life should arise in the first place? **How** its complex machinery evolved ***spontaneously?*** *This* is the sort of explanation of the origin of life scientists would like to have!



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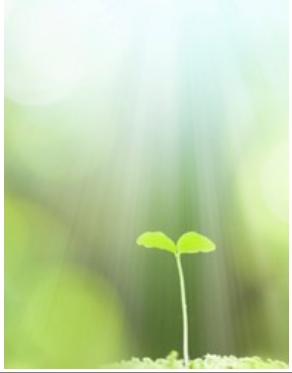
The Real Question

The problem is:

- Thermodynamics was originally the study of **closed systems** at or near **equilibrium**.
- But living organisms are:
  - ✓ **NOT closed systems:** They *exchange* matter and energy with their environment
  - ✓ **NOT in equilibrium:** They are continually *changing*, animated, not static
- Lane: “Cells require **dynamic <u>dis</u>equilibrium**—that is what being alive is all about.”



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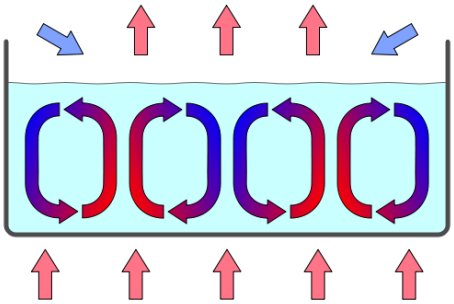
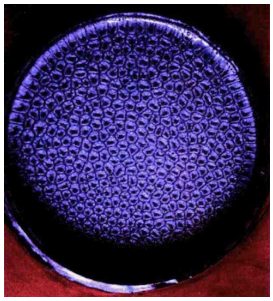
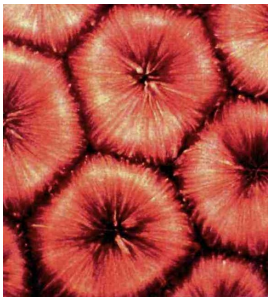
Dissipative Structures

- Late 1960s–early 1970s: **Ilya Prigogine** (1977 Nobel Prize) discovered **dissipative structures** in systems that are:
  - ✓ **Open**: they have energy (or matter) **flowing through them**
  - ✓ **Non-equilibrium**: *Steady* state, but *not static* (flow = motion)
- Example: **boiling water** (or other **convection cell** structures)







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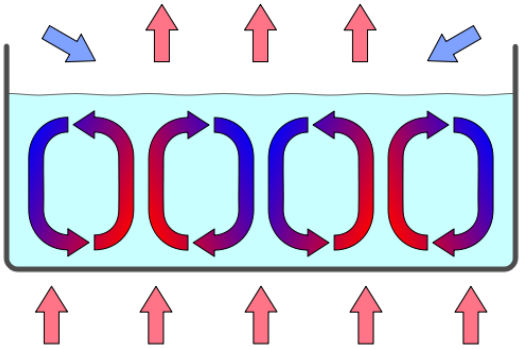
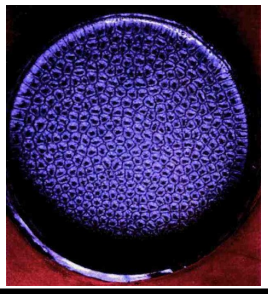
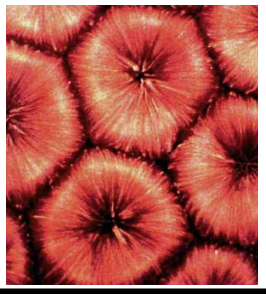
Dissipative Structures

- Energy **flows through** the system: $Q_{\text{in}} = Q_{\text{out}}$
- But: $T_{\text{in}} > T_{\text{out}}$ → **entropy increase** of the cold sink is greater than the **entropy decrease** of the hot source: entropy of universe is **increasing** (at certain **rate**)
- Energy is first carried by **conduction**. But above a critical ΔT, **convection** sets in (**non-equilibrium**): an ordered structure of *Bénard* cells **spontaneously** appears:
  - ✓ This ordered structure **increases** the energy flow & dissipation rate, **increasing entropy generation rate**
  - ✓ This allows the system (like life) to be in a **state of lower entropy**, i.e., more ordered form (cells)
  - ✓ Energy must continually **flow** and be **dissipated** (degraded); when it stops, the structure "dies"







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Dissipative Structures

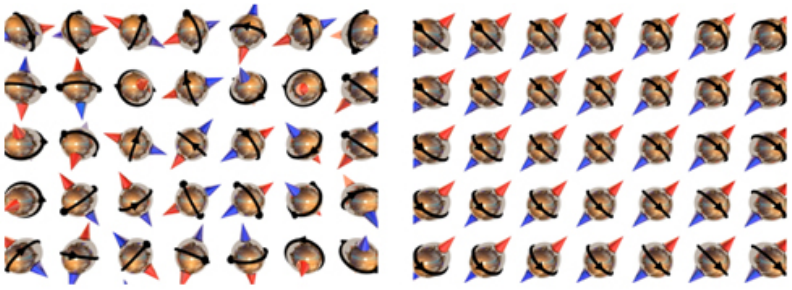
- This is *analogous* to a living organism:
  - ✓ An **open system with energy/matter flowing** through it (sunlight, food, etc.), operating **out of thermodynamic equilibrium**
  - ✓ E_{sun} (sunlight, food) (body) → E_{out} (heat, waste), but the **quality** of the energy is **degraded** → entropy of universe **increases** (at some **rate**)
  - ✓ This **external entropy production** is what allows the system to maintain a state of relatively **low internal entropy** (high order)
  - ✓ The system survives only while energy is being **dissipated** (dispersed, degraded). When it **stops**, the organism (ordered structure) **dies**.
- ∴ *analogous*, yes, but life is a **much richer** phenomenon. **But it's a start!**

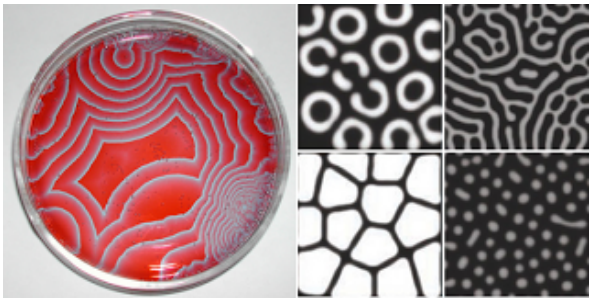
1.112 blub

Self-Organization

- **Dissipative structures** are related to **self-organizing** systems: order arises out of the local interactions between smaller component parts of an initially disordered system.

- **Many** examples of this general phenomenon:
  - Physics: Spontaneous magnetization
  - Chemistry: Oscillating & reaction-diffusion reactions
  - Biology: Birds flocking, fish schooling, etc.





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Self-Organization

- Biology: **Spontaneous protein folding**

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Self-Organization

- Biology: **Spontaneous formation of lipid bilayers**

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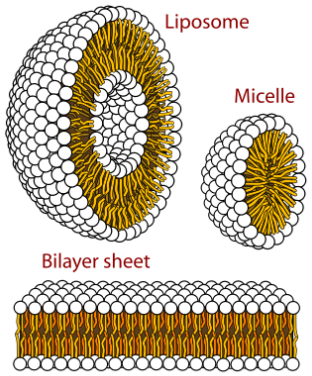
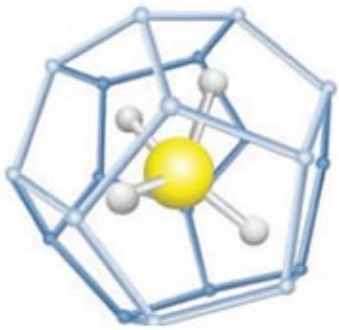
Self-Organization

- Biology: **Spontaneous formation of lipid bilayers**



  - ✓ The cell membranes of **almost all living organisms** are made of a lipid bilayer (including organelles inside the cell)
  - ✓ Recall: the **hydrophobic tails** point inward to avoid contact with the water. The resulting cell membrane is highly structured, but it is **less ordered** (**higher entropy**) than when the tails are in water, because that requires very low entropy water molecule "cages"
  - ✓ The self-assembly is **driven** by random thermal jostling by the environment, which allows the system to **explore nearby configurations**, finding ones that **maximize total entropy** (minimize total free energy), that get "locked in" when the available energy disperses into the environment

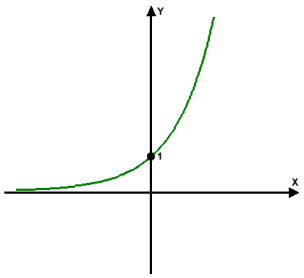


1.116 blub

Deeper Understanding of the Second Law

- 1994: Denis Evans & Debra Searles proved:
  - ✓ The Second Law ($\Delta S \geq 0$) is not strictly true. In microscopic systems, the entropy of an isolated system can fluctuate, sometimes increasing, but sometimes **decreasing**. This has been observed in experiments.
  - ✓ Roughly speaking, the **fluctuation theorem** states:

$$\frac{\text{Probability}(+\Delta S)}{\text{Probability}(-\Delta S)} = e^{\Delta s}$$

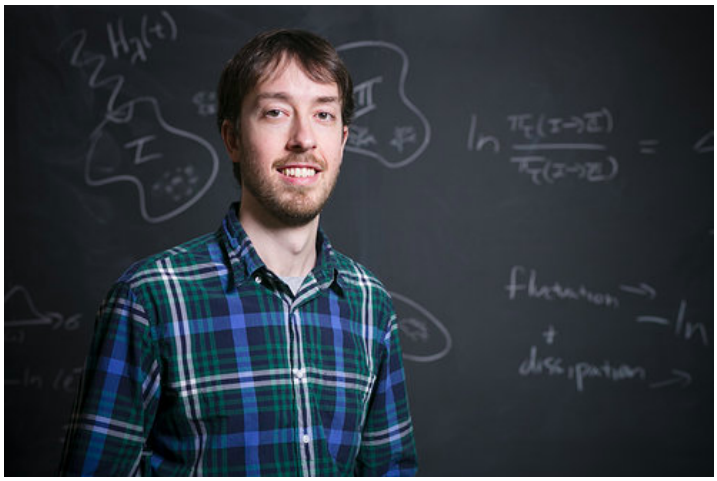


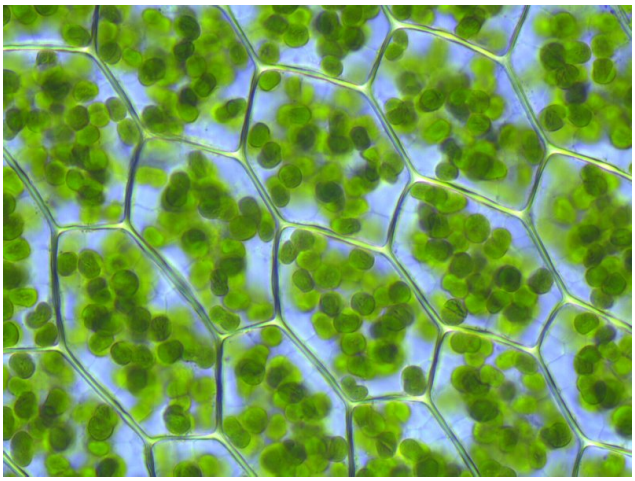
  - ✓ In words:
  - ✓ In words:
    - **Small** fluctuations are **equally likely** to be **positive** or **negative**
    - **Large** fluctuations are **almost always positive**
  - ✓ ...but **on average**, the Second Law **is** strictly true: .
  - ✓ ...but **on average**, the Second Law **is** strictly true: $\langle \Delta S \rangle \geq 0$.

1.117 blub

Deeper Understanding of the Second Law

- 1999: Gavin Crooks proved a **generalization** of the fluctuation theorem…
- 2013–2015: Jeremy England, a **biophysicist at MIT**, has applied the above to **living organisms** in "Statistical Physics of Self-Replication" and "Dissipative Adaptation in Driven Self-Assembly". See also: Quanta Magazine & Nature Physics & Talk & Radio





1.118 blub

Why is there life?

- In doing so, England **may** be close to answering the question "**Why is there life?**"

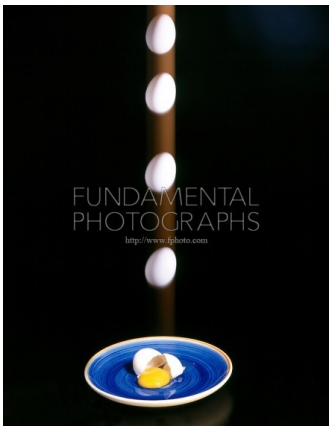
- **Important:** Some of this is still **speculative**, not fact; it is a good example of **science in action**:
  - ✓ There are **skeptics** (important in science!): "Jeremy's ideas are interesting and potentially promising, but at this point are extremely speculative, especially as applied to life phenomena"—Eugene Shakhnovich (chemistry professor at Harvard)
  - ✓ But there is also **great excitement**:
    - "[England has taken] a very brave and very important step…the 'big hope' is that he has identified the underlying physical principle driving the origin and evolution of life"—Alexander Grosberg (physics professor at NYU)
    - "As an organizing lens, I think he has a fabulous idea. Right or wrong, it's going to be very much worth the investigation [in her lab]"—Mara Prentiss (physics professor at Harvard)

1.119 blub

Why is there life?

- Basic Idea:

  - ✓ Like smashing an egg, cell replication (and other cell processes) are obviously **irreversible**. But **irreversibility** and **increase in entropy** are intimately connected, so thermodynamics ***should*** be able to tell us something about life.



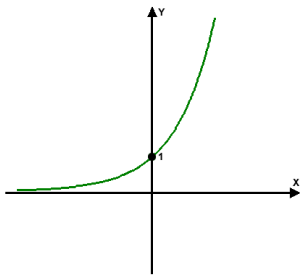
  - ✓ But living organisms are **far-from-equilibrium** systems interacting with their environment, and **strongly driven** by external sources of energy (e.g., plant blasted with sunlight). Before work like Crooks', and others, physicists didn't have the mathematical tools to understand such systems. **Now they do**.

1.120 blub

Why is there life?

- The Physics/Mathematics:

✓ Roughly speaking: England took Crooks' **microscopic** formula and figured out its consequences for **macroscopic** things, and discovered a **generalization** of the Second Law, that applies even for systems **driven far from equilibrium** by **energy flows**:



$$\frac{\text{Probability}(Forward)}{\text{Probability}(Reverse)} = \langle e^{\Delta S} \rangle$$

✓ It says: The **more irreversible** a spontaneous process is (e.g., cell division), the **more it increases the entropy** of the universe.

✓ Or: The **most probable** outcomes are the ones that, on the way to getting there, **increase the entropy of the universe the most**

1.121 blub

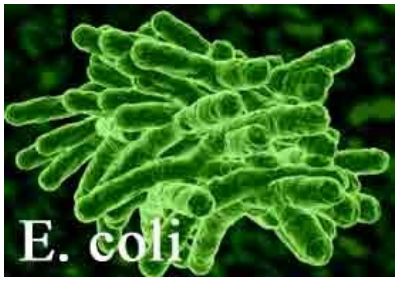
Why is there life?

- Analysing the new equation gives a key new insight:

  ✓ Other things being equal, the better a **driven** system can **absorb <u>and</u> dissipate** energy from that driving force (sunlight, food), the better it is able to do highly irreversible things like cell division.

  ✓ England has applied the idea to predict the amount of dissipation that should occur during **self-replication of RNA molecules** and **E. coli bacteria**. England: "A great way of dissipating more is to make more copies of yourself."

  ✓ England: "Thus, the empirical, biological fact that reproductive fitness is intimately linked to efficient metabolism now has a clear and simple basis in physics."



Basically we are explaining why things that are based on thermaldynamics want to replicate. This ties physics to biology.

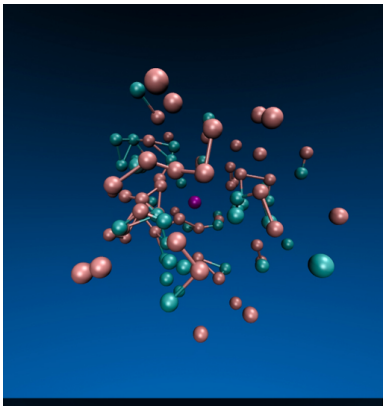
1.122 blub

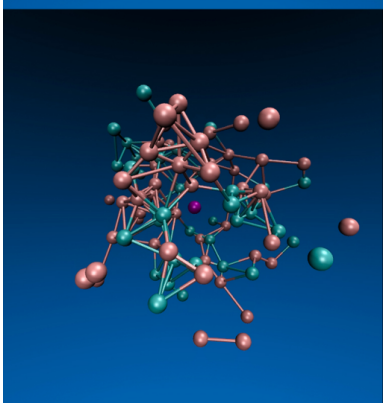
Why is there life?

- Speculation: "Dissipation-Driven Adaptation of Matter"

  ✓ A deeper analysis of the new equation **suggests** that "…clumps of atoms surrounded by a **bath** at some temperature, like the atmosphere or the ocean, should tend over time to **arrange themselves** to **resonate better** and better with the sources of mechanical, electromagnetic or chemical work in their environments [**driving forces**]."

  ✓ **Analogy:** the length of the ropes of a swing will **spontaneously** adjust themselves so the **natural frequency** of the swing matches the **driving frequency**, allowing the swing to absorb (and later dissipate) the most energy (!)





Clumps of atoms in a bath at some temperature (the water molecules are moving very fast with thermal energy). Any life molecule is being struck millions of times violently from every direction by water molecules. Overtime the atoms will rearrange themselves to ressonate better with the forces acting on them. AAAAAHHHHHHH CAPS LOCK NOOOOOOO

fuck you steven

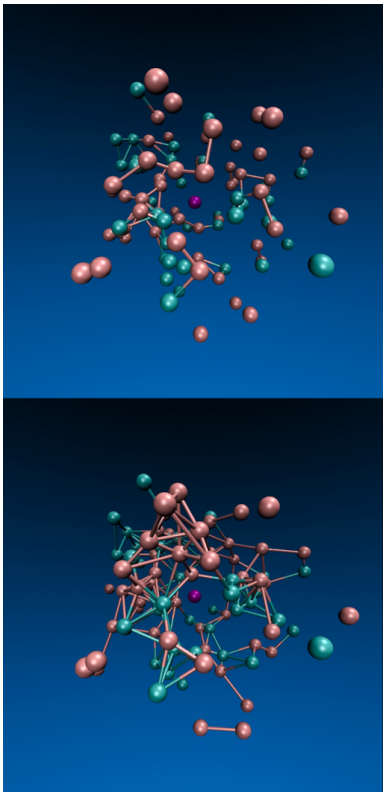
1.123 blub

Why is there life?

- Speculation: "Dissipation-Driven Adaptation of Matter"

  ✓ Why is this **plausible**?

1. Alone, thermal jostling of the atoms is not enough to change their configuration (atomic bonds are hard to change).
2. But a periodic driving force (like pushing a swing) can help the thermal jostling make configuration changes happen.
3. After a change, if the additional energy absorbed from the driving force is dissipated as heat into the environment, it is not available to help the system go back, like a ratchet. So **irreversibility is connected to dissipation (entropy increase)**.



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Why is there life?

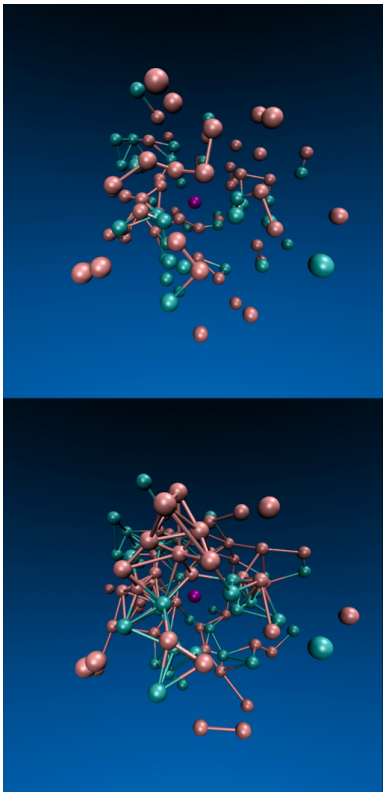
- Speculation: "Dissipation-Driven Adaptation of Matter"

  ✓ Why is this **plausible**?

4. While configuration changes are **mostly random**, the **most irreversible** (or **durable**) changes are those that happen when the system, at that moment, happens to be **better** at absorbing and dissipating energy from the driving force.

5. As time passes, these **less erasable** changes **accumulate**, like a ratchet, shifting the system preferentially in the direction of **better absorption and dissipation**.

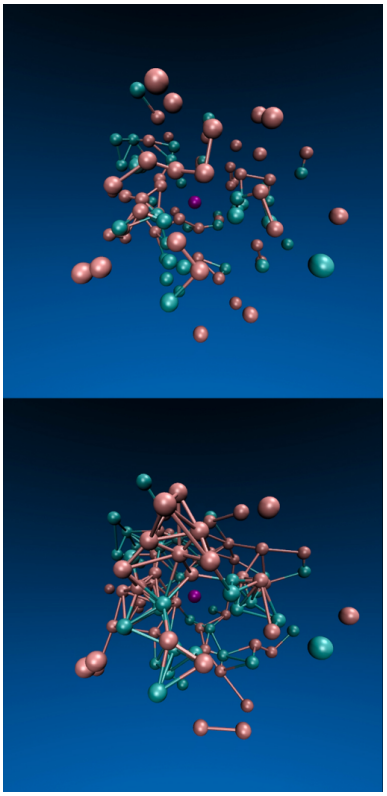
6. After a long time, it looks like the system has **self-organized** into a state that is **'well adapted' to its environment**.



1.125 blub

Why is there life?

- Speculation: "Dissipation-Driven Adaptation of Matter"
  - ✓ This idea is starting to be tested:
  - ○ England has run **computer simulations** of a **random clump** of toy atoms, driven at some frequency.
  - ○ Result: "…we do indeed see **emergent 'adaptive' resonance** of our system…", supporting the hypothesis that "…**organized, kinetically stable structures emerge** and persist because their formation is reliably accompanied by extra work absorption and dissipation".
  - ○ "There may be many examples of 'well-adapted' structures that did not have parents." (**Non-Darwinian adaptation**…)



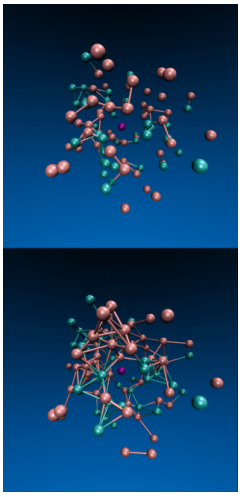
So you have these atoms in a bath being jostled, this jostling is not enough to break atomic bonds. When you get an external force (like the sun, or deep sea vents) the jostling becomes enough to make atomic changes. So we are making these atomic changes at moments when the atom is particularly susceptible to it. This makes the atom more able to obsorbe energy so they are less likely to fall apart. This results is entropy moving in one direction more and more.

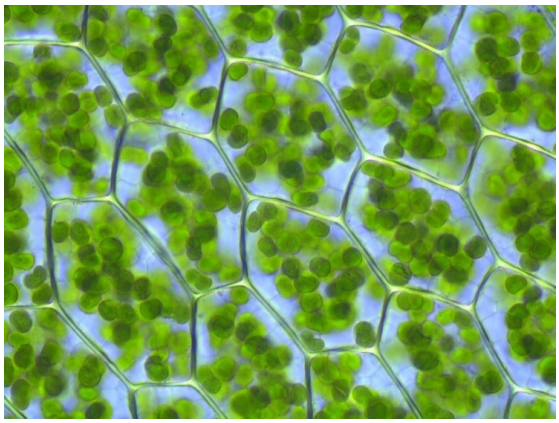
1.126 blub

Why is there life?

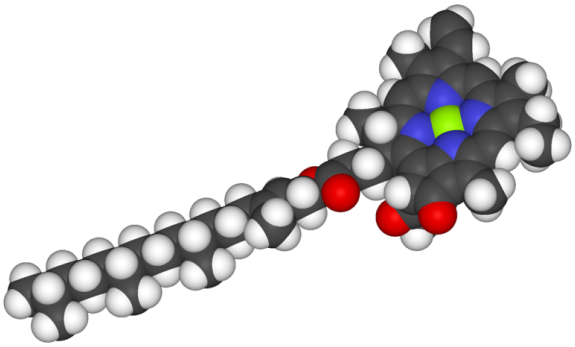
- Example: Plants/Photosynthesis

  ✓ England: **"You start with a random clump of atoms, and if you shine light on it for long enough, it should not be so surprising that you get a plant."**





Chloroplasts in plant cells



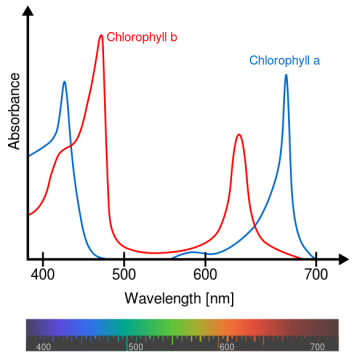
Chlorophyll molecule inside chloroplast

1.127 blub

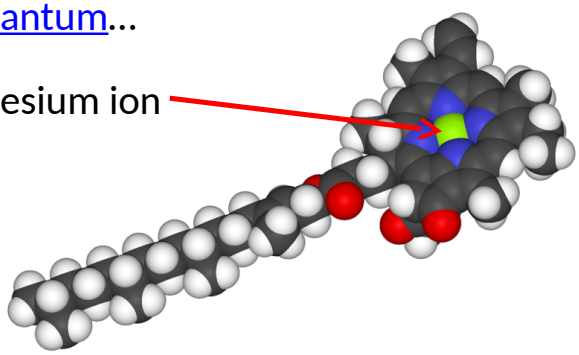
Why is there life?

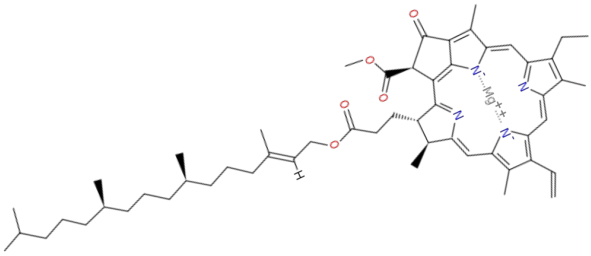
- Example: Plants/Photosynthesis

  ✓ The **chlorin ring** is a simple ring of molecules with Mg^{++} at the center, of exactly the right size and shape ("length of swing") to **resonate** with photons (electromagnetic waves from the Sun that "push the swing") of two different **frequencies** (colours): red and blue. These are **absorbed and dissipated** (but green photons are not, which is why leaves are green). Quantum...



Magnesium ion





1.128 blub

Why is there life?

- Example: Plants/Photosynthesis

  - ✓ Ultimately, the **energy absorbed** from the photons is used to **generate** a **proton gradient** across the **chloroplast membrane**; an **ATP synthase** is used to **tap** the gradient and "**charge**" ADP molecules to ATP, which then carry the energy to all the cells.

  - ✓ This energy is used to make sugar and oxygen (and power other cell functions):

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} \xrightarrow{\text{Light}} \underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2}$$

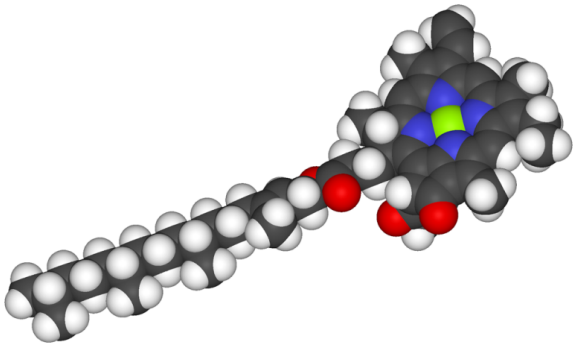
  - ✓ The rest is **dissipated in the environment** as waste heat. This is **crucial**: The resulting **increase** in entropy of the environment is precisely what allows the plant to build and maintain **low entropy structures** (like the chlorin ring).

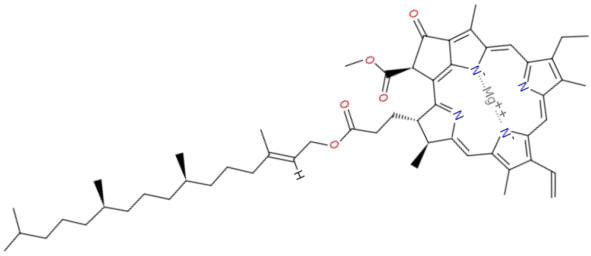
1.129 blub

Why is there life?

- Example: Plants/Photosynthesis

  ✓ Could the **chlorin ring** be an example of an **ordered structure** that **spontaneously evolved** by "dissipation-driven adaptation of matter" to allow photosynthetic organisms to harness (and dissipate) more energy from the Sun? (Speculation!!)





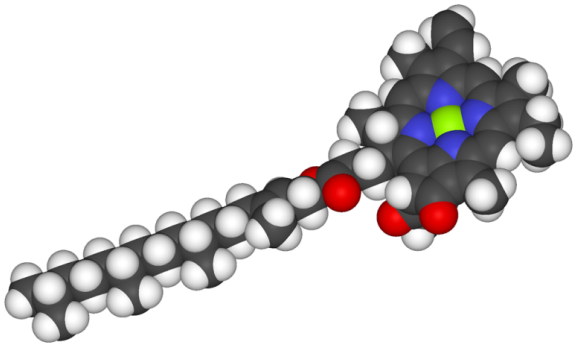
We think that if we shine light on water these structures could spontaneously occur to obsorb the light. An experiment was done with silver nano rods and showed that the rings would spontaneously form rings that can absorb sunlight.

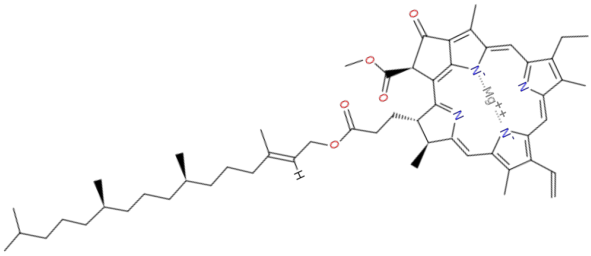
1.130 blub

Why is there life?

- Example: Plants/Photosynthesis

  - ✓ Recent experiments (Ito et al, 2013) have shown that, in the presence of light of a given frequency, silver nanorods will **spontaneously self-assemble** into a ring-like structure that **resonates at that frequency**, to best absorb (and dissipate) the energy in the light.



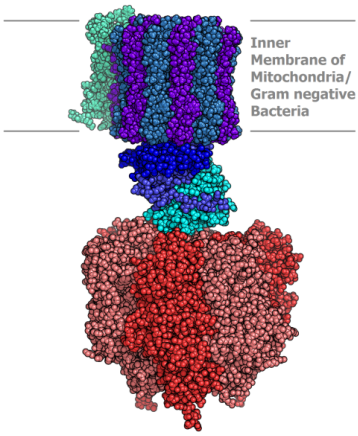


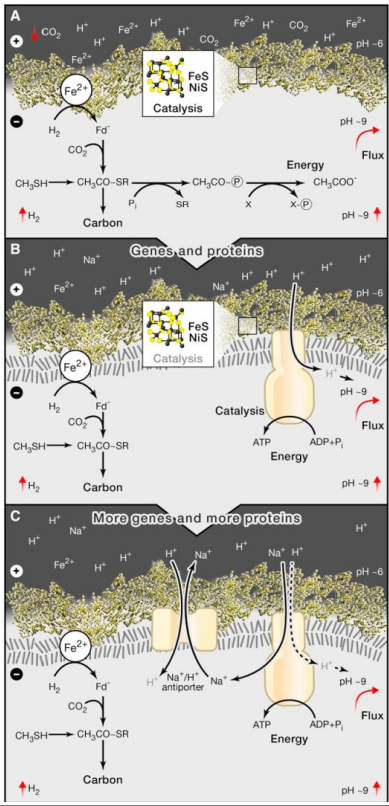
1.131 blub

Why is there life?

- Could the **ATP synthase** be another (more complex) example of an ordered structure that **spontaneously evolved** by "dissipation-driven adaptation of matter" to allow proto-cells to harness (and dissipate) more energy from the natural proton gradient near deep-sea hydrothermal vents? (Speculation!!)

- This could explain how the top picture evolved to the middle picture without replication of cells and Darwinian natural selection (Recall England: "**There may be many examples of 'well-adapted' structures that did not have parents**.")





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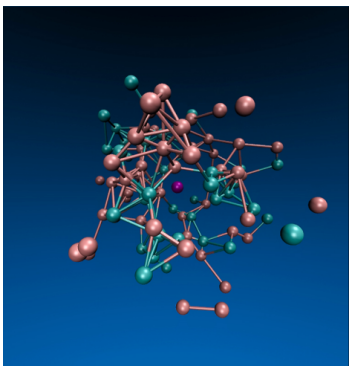
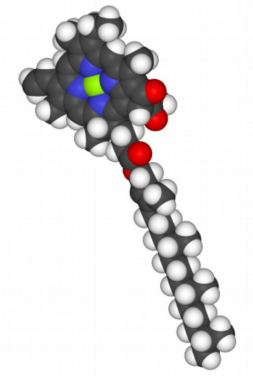
Why is there life?

- Application to Evolution & Origin of Life:



  - ✓ Darwinian evolution explains how life evolved **after it began**, but not **how it began**. If correct, "**dissipation-driven adaptation of matter**" might explain **both**. England: "from the perspective of the physics, you might call Darwinian evolution a special case of a more general phenomenon."
  - ✓ Key new idea is **adaptation without replication**: Dissipation-driven adaptation could have **spontaneously** evolved structures that got better and better at **eating energy** in the environment, e.g., the chlorin ring that eats sunlight.



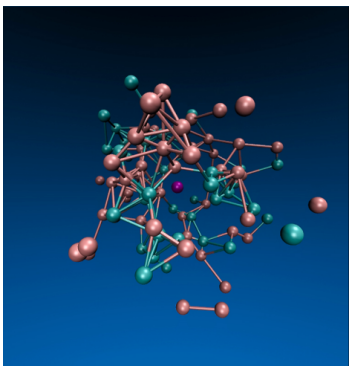
  - ✓ Such structures would then be available in the "pre-biotic soup" as building blocks for yet more complex structures, and eventually replicating life. It didn't have to happen "suddenly".

If we liken this to darwinian evolution its adaptation without replication. Here we just have shit randomly adapting to their environment.

1.133 blub

Why is there life?

- Application to Evolution & Origin of Life:
  - ✓ **Replication itself** may be understood under the **same** umbrella of dissipation-driven adaptation. Recall England: “A great way of dissipating more is to make more copies of yourself.”
  - ✓ England: “Under the right circumstances, which aren’t rare at all, matter **tends naturally** toward greater organization, complex structures and adaptive behavior, **making life a likely, even inevitable result of physics**.”
  - ✓ This is arguably plausible, but still highly speculative. It’s exciting, though, because it **might** explain, for very general reasons tied to the basic physics of the universe, **why** there is life!



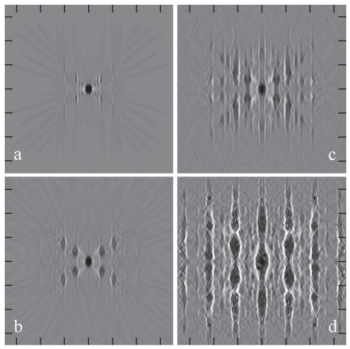
Replication is a great method of dissipation. We can also conclude that life emerging randomly is not only possible but highly probable.

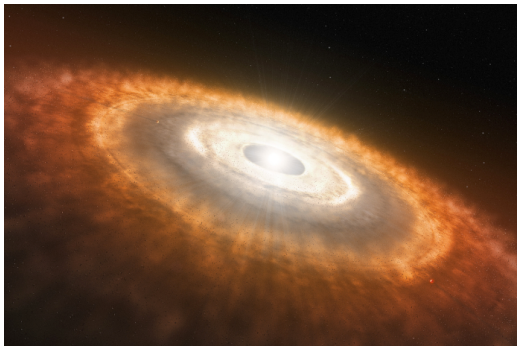
1.134 blub

Why is there life?

- Applications Beyond Life:

✓ Dissipation-driven adaptation of matter may underlie **many physical phenomena**, ranging from snowflakes and sand dunes, to self-replicating vortices in the protoplanetary disk.





✓ **The point is:** The transition from non-living matter to living matter may not be such a big leap.

Vortices in a shear flow **spontaneously replicate** by absorbing energy from the surrounding fluid. This has applications to “dead zones” in protoplanetary disks, and may play a role in star and planet formation.

Votices just use free energy. They just straight increase entropy in the universe. They also replicate, those fuckers, increasing the growth of entropy.