3 October 2019

EXOPLANETS, HABITABILITY, MONOMERS & POLYMERS

Homework 4 on WeBWorK due Monday, 10/21 (after Fall Break)

Volcanic lightning on Sakurajima (Martin Rietze), a naturally-occurring Miller-Urey experiment

Exoplanets, Habitability, Monomers, & Polymers

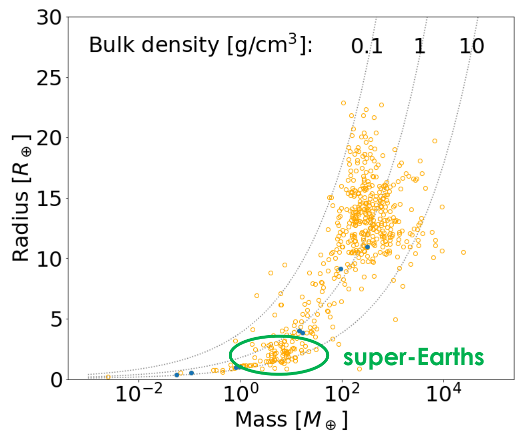
- Exoplanet properties
- Fraction of stars with planets: the Drake equation's f_p
- Evolution of orbits within planetary systems
- Tidal heating, tidal locking, and temperature of tidally-locked planets
- Liquid water and the Habitable Zone
- Earthlike planets and the Drake equation's n_e
- Habitability of tidally-heated moons
- Prebiotic molecules: delivered from the protoplanetary nebula or formed from the basics on infant planets?
- Origin of long, organic polymers, the predecessors of biomolecules that encode information

The engines of exoplanet discovery: measuring exoplanet masses and sizes

Note that if an exoplanet has RV and transit observations, then we know its mass (not just $M \sin i$) and its radius.

And therefore we also know its bulk density: mass divided by volume.

Its bulk density can be used to tell rocky planets like Earth from gas-giant planets like Jupiter and Saturn.



Based on Fig. 11 of Fortney & Nettelmann (2010)

Observing transits with *Kepler* and *TESS*

The common way to proceed is to seek both RV and transits.

First do transits, which is what *Kepler*/K2, and *TESS* are designed to do.

Kepler is succeeded in its transit work by the NASA Transiting Exoplanet Survey Satellite (TESS), which launched in April 2018. At the end of its 2-year mission, it will have imaged 85% of the sky (400x that observed by Kepler), and is expected to find more than 20,000 exoplanets.

TESS (MIT/GSFC/NASA)

Today's exoplanets

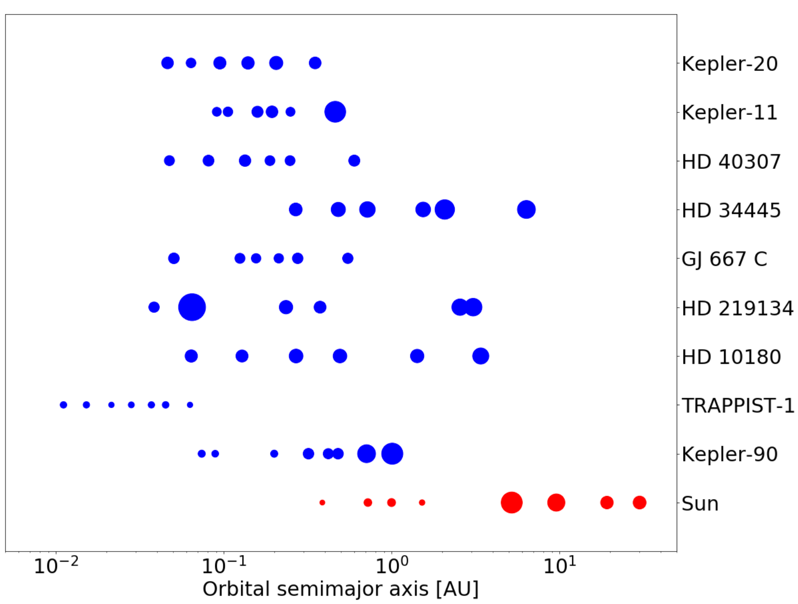
Today, there are 4112 objects listed as exoplanets.

These planets live in 3059 planetary systems: there are 669 multiple-planet RV or RV+T systems so far.

- 447 have two; 142 have three, 56 have four, 17 have five, 7 have six, 1 has seven, and 1 has eight. Seen so far, that is.
- With eight confirmed planets, the most populous system so far is Kepler-90.

Smallest planets found around normal stars.

- Kepler-37 b: $M = 2.78M_\oplus$, $R = 0.32R_\oplus$ (smallest radius)
- Kepler-1520 b: $M = 0.0200M_\oplus$, $R = 0.832R_\oplus$ (smallest mass)



Typical multi-planet systems

Today's exoplanets – multi-star systems

34 planets have been found in multiple-star systems, starting with Kepler-16AB in 2011.

These planets orbit the center of mass of the pair of stars at a distance much greater than the separation of the stars. They are called Tatooines, after the planet on which Luke Skywalker grew up in *Star Wars*.

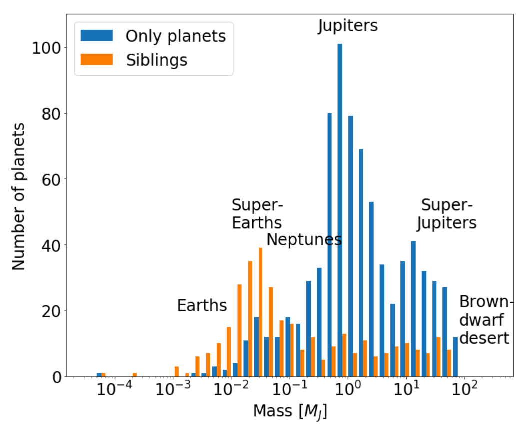
NASA's new travel-agency sideline features trips to exotic destinations.

Exoplanet masses

Numbers of Jupiters and Super-Jupiters in < few AU orbits are accurately represented, as is the **brown-dwarf desert**: the absence of "planets" with $m > 30M_J$.

The gap around $0.1M_J$ is also real (Mayor et al. 2012).

The smaller population of Neptunes and Earths, though, is a bias: planets this small are still much more difficult to detect than Jupiters.



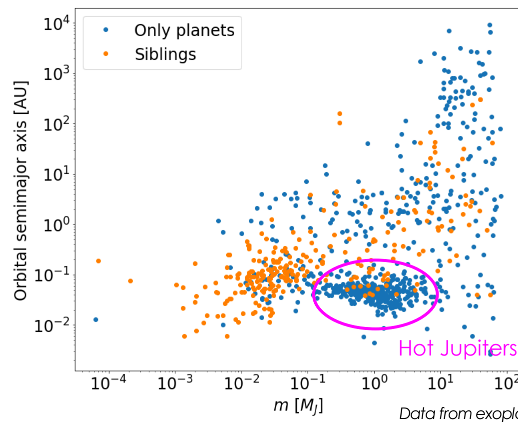
Data from exoplanet.au

Exoplanet orbit sizes

There is a sharp peak in the distribution of orbit radii for Jupiter-like masses around 0.06 AU.

These are the **hot Jupiters**. They do not comprise a large fraction of planets, but they are the easiest to detect.

There was not enough material in their locations in their protoplanetary disks for such massive planets to have formed where they are seen; they must have **migrated** from elsewhere in the disk.



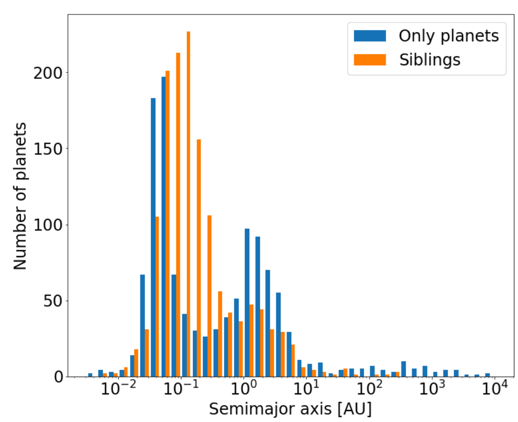
Data from exoplanet.au

Exoplanet orbit sizes

Orbit sizes are dominated by two peaks just past 0.1 AU and 1 AU.

The decline at 6 AU is, again, a bias against long-orbital periods: we have not watched such planets move far through their orbits.

It is widely suggested that the 1 AU rise reflects an onset of increased planet formation efficiency, as the snow line is usually around there.

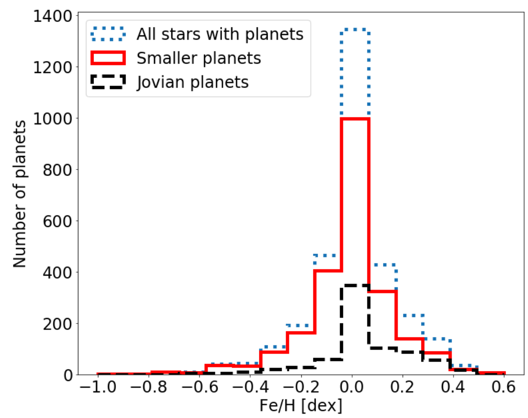


Data from exoplanet.au. Includes many planets not appearing in the previous graphs, for which Kepler has measured orbit sizes but for which there are not yet RV observations.

Composition of exo-solar systems

We are only starting to be able to measure planet composition, but we can measure heavy element abundances in their host stars, and the result is interesting:

- Jupiter-size exoplanets have a tendency to occur around stars richer in heavy elements than usual.
- There is less of a tendency for Neptunes and super-Earths to be associated with heavy-element-enriched stars.



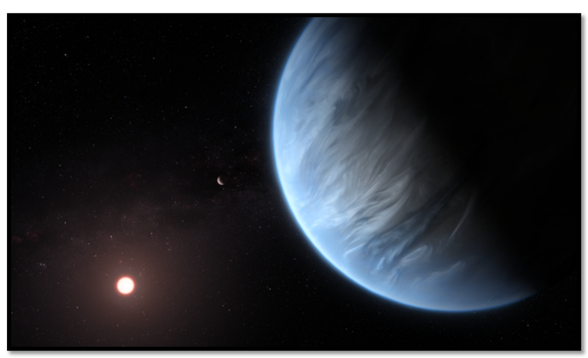
Iron-abundance census (based on Fig. 16 in [Mayor et al. 2012](#))

Composition of exoplanet atmospheres

The light from a star as it passes through an exoplanet's atmosphere allows us to measure different elements and molecules present in the exoplanet's atmosphere.

Recently, water (H_2O) molecules have been identified in the atmosphere of K2-18b, an exoplanet about twice the size of Earth, nine times as massive, and has a 33-day year.

- It is in the habitable zone of its star!



Artist's impression of K2-18b orbiting its red dwarf star (ESA/Hubble, M. Kornmesser)

Back to the Drake Equation: f_p

Essentially 100% of stars are born with enough material around them to make multiple planets of all sorts.

We have made surveys of nearby stars for planets that are unbiased over certain ranges of masses and orbital periods.

The resulting score (Mayor et al. 2012) for stars with mass $0.6 - 1.5M_\odot$

- About 0.9% host a hot Jupiter
- 14% ±2% host a gas-giant planet with $P < 10$ years
- 75% ±2% host a planet of any currently-detectable mass with $P < 10$ years

And we are not even good at detecting Earthlike planets, so it seems clear that **f_p is very close to 1**.

Planets move around each other

After planets form, they begin (with the gravitational forces they exert) to perturb the orbits and rotation of smaller Solar System bodies and each other. This results in

- Orbital **migration**: the large-scale changing of planetary orbits
- Capture into, or ejection from, **resonant orbits**
- Systematic **ejection** of small planetesimals, sometimes *en masse*
- **Tidal locking**: the slowing of rotation of a body due to tidal forces by another orbiting body

These effects influence the habitability of given planets and the existence of habitable planets in a planetary system.

Planets are constantly under the influence of the gravity of each other as well as that of the central star.

Gravitational influence on orbits

These effects are largest when they are closest together in their orbits because the gravitational force is steeply dependent upon distance.

You can think of each body suffering an impulsive "tug"– technical term **perturbation** – at closest approach.

If the closest approach happens in the same place in each orbit – a situation in which the orbits are called **resonant** – the perturbations can build up over time to large differences instead of averaging out.

If the orbital periods of two bodies have a ratio very close to the ratio of integers (whole numbers), they are resonant.

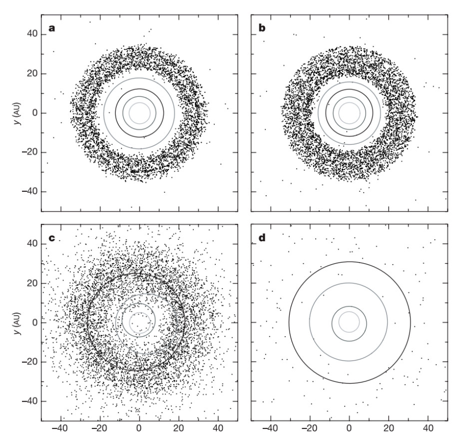
Planets, especially giant ones, can force each other to drastically change orbits.

Orbital readjustments

This can have huge effects on smaller bodies. If a giant planet migrates by a substantial amount, small bodies in between are subject to ejection or consumption.

Example: the early history of our Solar System according to the Nice Model

Main events: perturbation of Jupiter and Saturn by each other migrate these planets outward, eventually resonantly perturbing Neptune and Uranus, swapping their orbits and ejecting 99% of the smaller bodies.



Rotation-rate changes and tidal locking

Though planets (or moons) are many diameters away from their stars (or planets), their diameters are not negligible.

- As a planet and star orbit each other, they tug on each other's near side significantly harder than the far side.
- This results in the left and right sides getting pulled closer together.
- These force differences are known as **tides**.
- When two bodies pass each other, they stretch and compress in response to tidal forces, and relax back to their previous shapes after the perturbation is over.

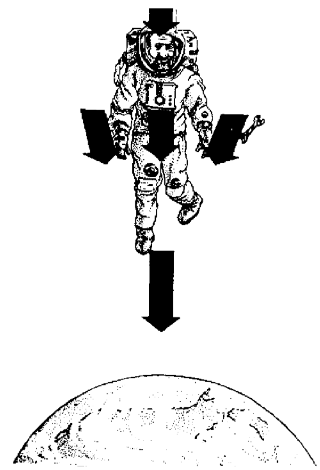
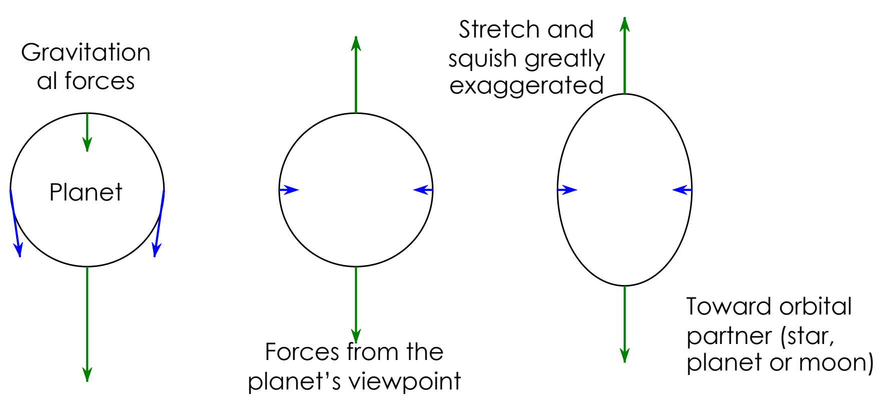


Figure from Thorne, Black Holes and Time Warps

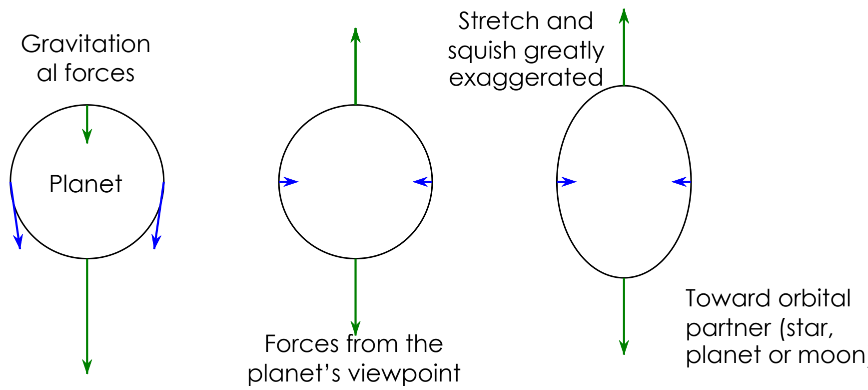
Tidal forces and tidal stretching

The force of gravity decreases with distance, and a spherical mass exerts the force as if all of its mass lies at its center.



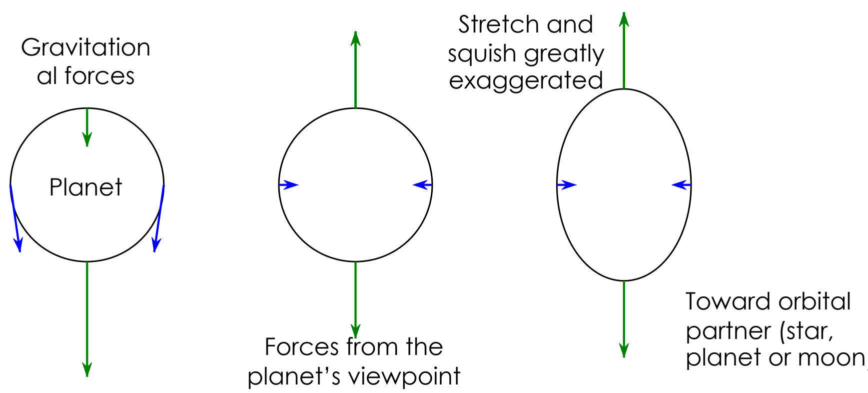
Tidal forces and tidal stretching

The planet is **stretched in the direction toward the other body, as the near side gets tugged harder than the far side**.



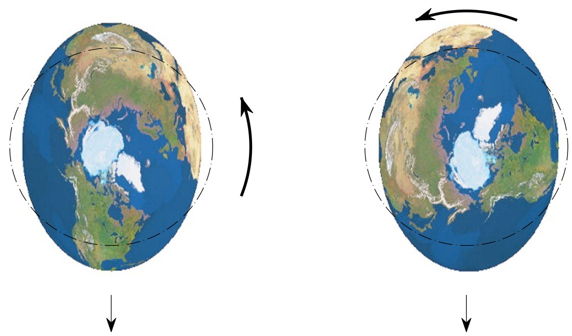
Tidal forces and tidal stretching

And is **squished in the perpendicular direction by the convergence of the forces at the other body's center**.



Tidal forces and tidal stretching

The **stretch and squish stay fixed in the direction toward the other body**, so if the planet rotates faster than it revolves, every point on the surface will be pushed up multiple times a day from the stretch, and down multiple times a day from the squish.



Stretch and squish greatly exaggerated

Tidal locking

It takes work to stretch/compress the planet, and not all the energy springs back when the forces decrease.

- Friction and viscosity within the planet dissipate some of the energy as heat, which is then radiated away (via blackbody radiation).

Because the tidal heating depends upon the state of rotation of the body as well as its orbit, radiation of the tidal heat drains the rotational and orbital energy.

The planet (or moon) rotates more slowly and **drifts to a larger orbital distance**.

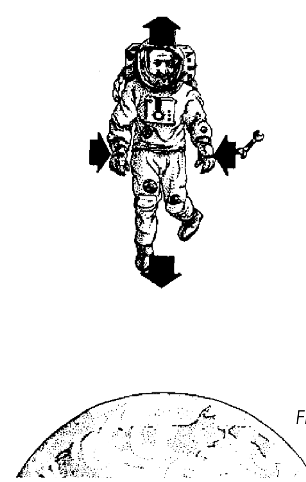


Figure from Thorne, Black Holes and Time Warps

Tidal locking

Eventually (in 1-100 Myr), this results in a special relation (such as equality) between the orbital and rotation period, corresponding to the minimum of tidal heating. This is called **tidal locking**.

Tidal locking happens in both star-planet and planet-moon systems.

- The Moon is tidally locked: it rotates once per revolution.
- Pluto and its largest moon Charon are mutually tidally locked: each rotates once every 6.4-day revolution.
- All the large moons of Jupiter and Saturn are tidally locked.
- **Planets in orbits very close to their stars will tend to be tidally locked.** (Mercury, for example.)
- This changes their heating situations.

Temperatures for fast and slow rotators

Implications for the temperature of a revolving body that is mainly heated by starlight:

- If a body rotates faster than it can cool off, its surface will have a fairly uniform temperature, given by the formula for dust grains. This is the case for the Earth and Mars, for example.
- If not, it will have hot and cold sides.
  - If it is tidally locked in circular orbit around its star, it will have **permanently** hot and cold sides.

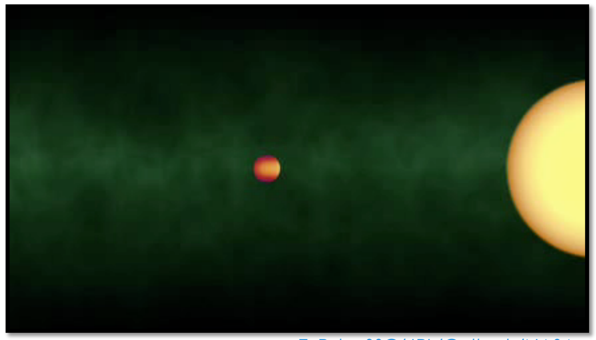
Temperature of slow rotators

For a slow rotator, the maximum temperature, which is generally reached at the substellar ("noon") point, is

$$T = \left(\frac{(1-A)L}{4\pi\sigma r^2}\right)^{\frac{1}{4}} = 394\ \mathrm{K} \times \left(\frac{(1-A)L[L_\odot]}{(r[\mathrm{AU}])^2}\right)^{\frac{1}{4}}$$

You need to understand how to use this formula.

Fortunately, it is the same as the last one, just with 394 K replacing 279 K.



T. Pyle, SSC/JPL/Caltech/NASA

The habitable zone

Since the interstellar medium already provides infant solar systems with the basic, and some processed, ingredients for life, the next basic requirement for habitability is for the ingredients to have the correct temperature.

What is the correct temperature? Clues from Earth:

- Simple organisms are not killed by prolonged exposure to temperatures *slightly* below the freezing point of water, or *slightly* above the boiling point. (These beasts are called **extremophiles**.)
- Complex organisms are most abundantly found in habitats between freezing and boiling.

Earth suggests that **liquid water** promotes habitability by organic chemical/water based life.

Is this geocentrism, to presume that life requires water?

Does life require water?

As we will discuss, **chemistry in liquids is by far the fastest way for life to evolve**.

Usually, this means having a solvent: a liquid for other molecules to dissolve in, that can facilitate their reactions.

Water is by far the most abundant solvent molecule in protoplanetary disks, and it is a great solvent chemically.

The temperature range within which water is liquid overlaps that of many other solvent candidates like methanol and ammonia.

While it is possible that life requires water, we do need to be wary of this Earth-centric bias.

Habitability

The most common definition of habitability in a planetary system is that water exists permanently in liquid form on a suitable planet.

- That is, $T = 273 - 373$ K under normal pressure conditions on Earth, and this range is often used.
- The water need not be exposed on the surface; if it is, the planet better have an atmosphere.

Such planets are found this far from their stars:

$$r[AU] = \left(\frac{T_0}{T}\right)^2 \sqrt{(1 - A)L[L_\odot]}$$

Where $T_0 = 279$ K for fast rotators and 394 K for slow ones, and T runs from 273 to 373 K if the planets are just "large dust grains."

Question

By this token, the habitable zone for Earthlike planets ($A = 0.37$) in the Solar System lies between 0.44 and 0.82 AU from the Sun. Which planets lie in the Solar System's habitable zone?

(Feel free to use the internet to look up distances!)

The greenhouse effect

Planets are not large dust grains: they have atmospheres.

Recall that the reasoning above gives only $T = 294$ K for the Earth. This is the temperature of the cloud tops; it is (definitely) warmer down below. Why?

Because the atmosphere is transparent at shorter wavelengths (visible, ultraviolet,…) at which stars emit much of their light.

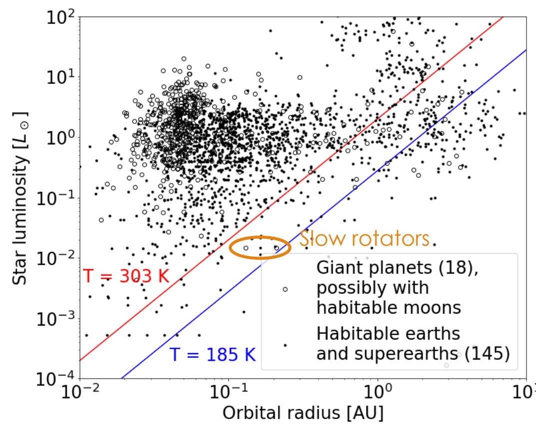
- This light directly heats the planet's surface.
- The extra energy cannot escape quickly. It is trapped: the surface radiates at the same infrared wavelengths at which the atmosphere is opaque.
- Therefore, the surface is warmer than the cloud tops.

This is called the **greenhouse effect**. We will go into more detail about it at the end of the semester.

The habitable zone (w/ greenhouse)

A simple estimate of the magnitude of the greenhouse effect, popularized by the *Kepler* team, is to use $A = 0.3$ and to take the temperature bounds to be **$T =$ 185 K and 303 K**, which in typical atmosphere models would correspond to surface temperatures of 273 K and 373 K.

- By this token, at least 145 of our current known Earth-sized planets (less than twice the size of Earth) lie in the habitable zone.
- There are some giant planets which also exist in the habitable zone. Any moons with atmospheres around these giant planets would be habitable.



Data: [exoplanet.eu]

The Drake equation: n_e

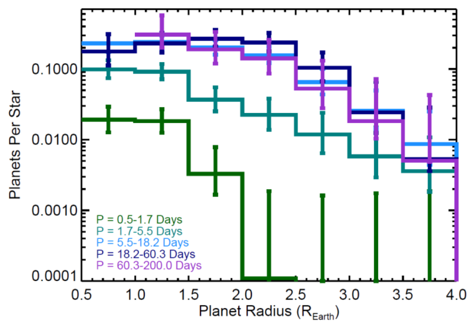
This is what the NASA *Kepler* mission was designed to measure, and it has succeeded.

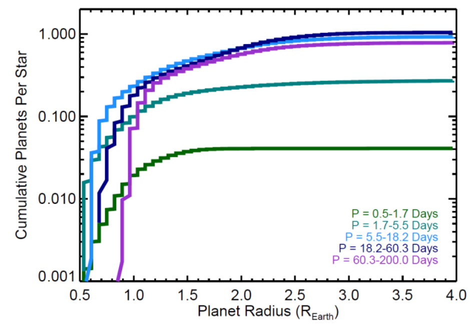
Originally, the n_e factor was supposed to count Earth-like planets, meaning habitable ones. Now, with such unexpected things as super-Earths, abundant tidally-locked planets, and the trickiness of the greenhouse effect, there is more context required around the numbers.

- Around Sun-like stars, there appear to be more planets of radius $2 - 2.8R_\oplus$ – super-Earth size – than planets larger or smaller (Silburt et al. 2015).
- Earths and super-Earths are more abundant around low-mass, cool stars ("M") than around Sun-like stars (G-K):
  - G-K: 46% ±3% of stars have E or SE (Silburt et al. 2015)
  - M: 56% ±6% of stars have E, 46% ±7% have SE (Dressing & Charbonneau 2015)
- Within the habitable zone as modeled by Kopparapu et al. (2013), the fraction of stars possessing planets is
  - G-K stars: 6% Earths, 17% SE (Silbert et al. 2015)
  - M stars: 16% E, 12% SE (Dressing & Charbonneau 2015)

The Drake equation: n_e

Splitting the difference in percents and ignoring the difference in E/SE, we will adopt $\boxed{n_e = 0.25}$ (25%)





Dressing & Charbonneau (2015)

Question

Ignoring habitable moons of giant planets, about how many stars would we have to visit to find one habitable planet (on average)?

Habitability outside the habitable zone

We chose starlight as the energy source above because it is generally provided at a steady rate for billions of years while other heat sources are not. All but one, anyway:

- Tidal heating of suitably-placed moons and planets can be significant sources of energy for as long as they rotate rapidly and/or do not have circular orbits.
- On the other hand, as the moon or planet radiates the energy away, the rotation slows and the orbit circularizes over time, reducing the tidal heating to zero. But on the other…
- …If something can force a suitably-placed planet or moon to rotate or follow an elliptical orbit permanently, the tidal heating would be permanent.
- And something can: perturbations of moons and planets on each other's orbit can result in orbits being locked into orbital resonance.
- Since there is an attractive impulse at closest approach, and since for resonant orbits this happens in the same spot in the orbit every time, these **resonantly-locked** orbits cannot be precisely circular.
- Thus, tidal heating can be permanent and substantial.

Habitability on tidally-locked bodies

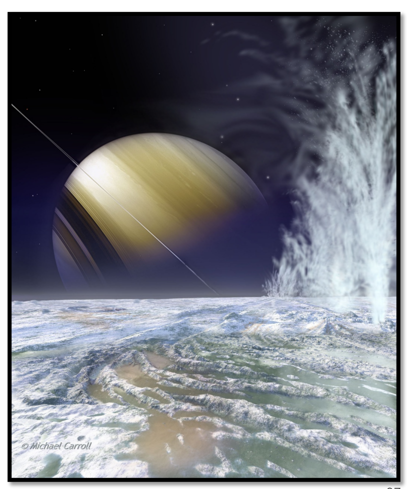
This is the case for the large moons of Jupiter and Saturn, particularly **Io, Europa, and Ganymede** (orbital periods in ratio 1:2:4).

- Permanent liquid water further away from the star than the habitable zone!

We will discuss this further when our talk turns to the search for life elsewhere within the Solar System.

Questions to ponder:

- In what important ways would life be different on such a habitable world outside the habitable zone?
- Do you think that microbial life could develop in such a place? Complex organisms?
- Do you think life could survive in such a place if implanted from elsewhere?



Michael Carroll (spacedinoart.com)

We are about to move on to topics in which we will include much more scientific speculation than we have so far. Which of the following statements is speculation? Select **all** that apply.

Question!

A. The Solar System is 4.567 billion years old.
B. The chemical composition of the universe evolved over the Universe's life.
C. About 16 new stars form in the Milky Way galaxy each year.
D. Practically every star has one or more planets.
E. One out of four Earth-like or super-Earth planets is habitable.
F. All of the above.
G. None of the above.

Which of the following statements is theoretical? Select **all** that apply.

Question

A. The Solar System is 4.567 billion years old.
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F. All of the above.
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Which of the following statements is experimental fact? Select **all** that apply.

Question

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F. All of the above.
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The origin of biology on habitable planets

A rocky planet survives migration and settles down in an orbit in which the temperature will stabilize in the liquid-water range. The temperature will stay there for billions of years, either because it is in the habitable zone, or because it is tidally heated in a resonant orbit.

The temperature will not equilibrate to that happy value for a long time, though, since the planet is born molten and will take millions of years to cool off to a solid, silicate-rock surface.

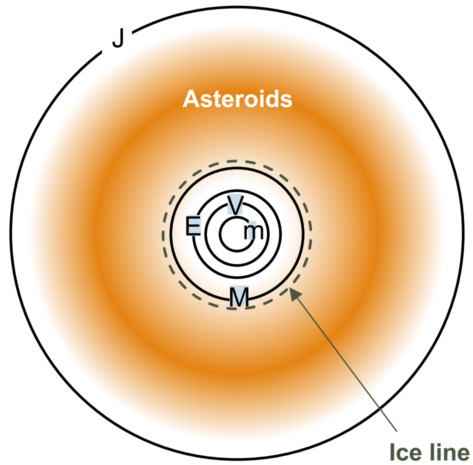
While the planet is molten, it retains very few of the **prebiotic** or **volatile** molecules that went into its creation, except for the heavier gases in the atmosphere (e.g. N_2, CO_2).

These molecules are extremely important for life, so it is a good thing that there are still smaller bodies around which had never completely melted and therefore still retain some volatiles.

The Solar System's smaller bodies

The best-known nearby collection of small bodies is the **Asteroid Belt** between the orbits of Mars and Jupiter.

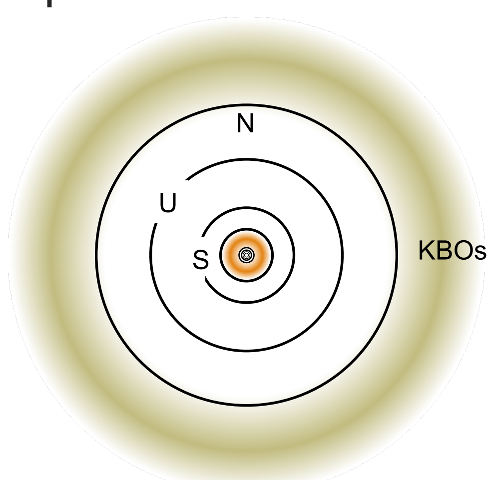
The total mass in the main belt is thought to be about 0.04% of Earth's mass. There are about 200,000 asteroids larger than 1 km in diameter. They typically lie about 0.07 AU (about 3.5 million miles) apart – not close together as is normally depicted in the movies.



Asteroids in the Kuiper Belt

Outside Neptune's orbit is the **Kuiper Belt**, best known as the source of short-period comets, and as the family to which Pluto belongs.

Kuiper-belt objects (**KBOs**) are small and cold, and therefore faint; it will take another 10-20 years to complete their census. But there used to be many more.



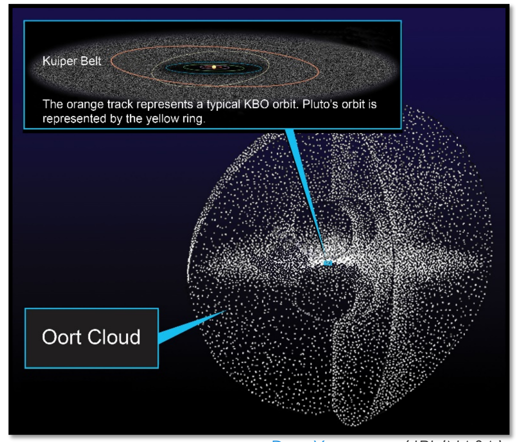
The Oort Cloud

Even further out, at about 10,000 AU, we find the **Oort Cloud**, best known as the reservoir of long-period comets.

- There is only one non-cometary candidate known to be an Oort Cloud object – Sedna.

When Uranus and Neptune switched orbits due to perturbations by Jupiter and Saturn around 600-800 Myr after the Sun formed, something like 99% of the small bodies of the Solar System were violently displaced.

- Many were ejected and formed the Oort Cloud.
- Many others were driven into the inner Solar System, where the episode known as the Late Heavy Bombardment is evident in the cratering records of the Moon, Mars, and Mercury.



Don Yeomans *(JPL/NASA)*

Sweeping up the small bodies

Like all the planets, Earth constantly sweeps up smaller bodies. The rate is always much larger than the rate at which Earth loses mass (hydrogen, helium, satellites,…)

The accumulation rate seems to vary quite a bit: 10^7–10^9 kg per year.

Much of the mass is in rather large bodies, most of which come from the asteroid belt. Since these are relatively infrequent, they are responsible for this variation.

There is substantial mass, though, in the small bodies and interplanetary dust particles (**IDPs**), nearly all of which come from comets (comet tails, specifically).

All of these bodies come from beyond the snow line (1.5–1.9 AU).

About 4 Gyr ago, the rate was about 1000 times the present rate.

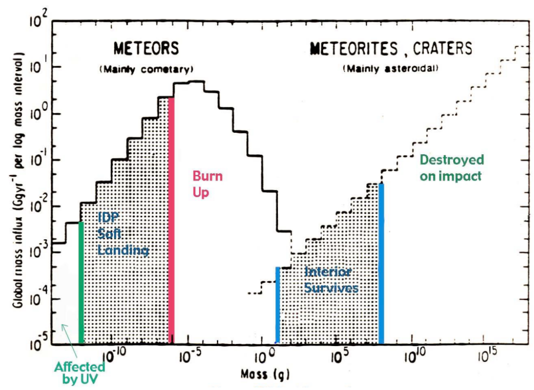
Sweeping up the small bodies

These small bodies have been decorating the surface of the Earth with ices and organics.

Much of it burns up, which of course does not necessarily destroy small molecules like water.

90% of Earth's oceans were probably delivered by asteroids, the rest by comets.

However, not all of them burn up: IDPs make a soft landing with their molecules intact, and moderate-size meteorites land with their interiors intact. Molecules that have been preserved since the object's beginning are then released.



Anders (1989)

Sweeping up the small bodies

Of particular interest are hydrocarbon molecules, since Earth's surface is so poor in carbon.

IDPs are rich in organic molecules (10% by mass). They account for most of the 3.2×10^5 kg per year of carbon the Earth currently sweeps up (Chyba & Sagan 1992).

But large parcels arrive as well, like the Murchison meteorite (1969, Australia), which contained a treasure trove of biomolecules (table from Machalek 2007).

Prebiotic molecule	Concentration by mass
Water	12%
Amino acids	17-60 ppm
Ordinary hydrocarbons	> 35 ppm
Aromatic hydrocarbons (PAHs)	3319 ppm
Fullerenes	> 100 ppm
Organic acids	> 315 ppm
Purines and Pyrimidines	1.3 ppm
Alcohols	11 ppm
Sulphonic acids	68 ppm
Phosphonic acids	2 ppm

Of the five most abundant classes of molecules present in the Murchison meteorite, how many are found in the interstellar medium?

Question

A. Only water
B. Water, PAHs, and fullerenes
C. Water, organic acids, and alcohols
D. All but amino acids
E. All five

Is delivery necessary? Formation of prebiotic molecules *in situ*

It was long assumed that any prebiotic molecule would need to be formed *in situ* (in place, so on Earth) from simpler, inorganic molecules.

In the 1920s and 1930s, Oparin (USSR) and Haldane (UK) proposed that the early Earth would have had no prebiotic molecules and that a **reducing** atmosphere similar to the giant planets would give rise to them.

- Reducing = components of gas easily give up electrons. Examples include hydrogen, ammonia, methane.
- Opposite of **oxidizing**.

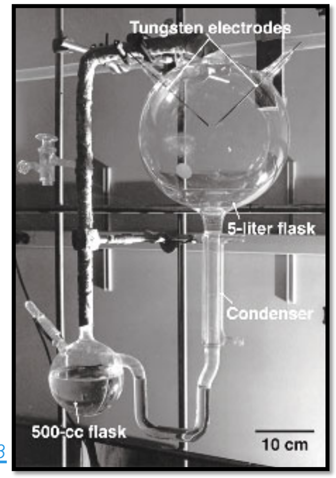
Miller and Urey (USA) reasoned that lightning and solar UV would provide the energy necessary for the neutral-neutral reactions and simulated these conditions in the lab.

The original Miller-Urey experiment

A classic molecular biology experiment

- Ingredients: H_2, ammonia (NH_3), methane (CH_4) gas in 5-liter flask, connected by condenser to the "ocean," consisting of water in the 500 cc flask.
- A high-voltage discharge (a continuous spark) simulated lightning and provided ultraviolet light as well.
- Ran like this for one week. The experiment was repeated several times with new glassware and electrodes.

Result: After one week, 10-15% of the carbon had become incorporated into a wide variety of **prebiotic molecules** including several amino acids, sugars, lipids, and other organic acids.



Miller 1953

Results of the original Miller-Urey experiment

Compound	Yield	Compound	Yield
Glycine	270	Iminoacetic-propionic acid	6
Sarcosine	21	Lactic acid	133
Alanine	145	Formic acid	1000
N-methylalanine	4	Acetic acid	64
Beta-alanine	64	Propionic acid	56
Alpha-amino-n-butyric acid	21	Alpha-hydroxybutyric acid	21
Alpha-aminoisobutyric acid	0.4	Succinic acid	17
Aspartic acid	2	Urea	8
Glutamic acid	2	N-methyl urea	6
Iminodiacetic acid	66		

Miller 1953, Miller & Urey 1959

Lots of formaldehyde (H_2CO), hydrogen cyanide (HCN), cyanopolyyne (HC_3N), and urea (NH_2CONH_2) formed in the gas and condensed into the "ocean."

Note that these are also seen in the ISM and/or meteorites.

The other molecules formed in the water with "wet chemical" reactions, among the formaldehyde, hydrogen cyanide, cyanopolyyne, and urea. A good example is the "Strecker synthesis" of the amino acids.

Modern "Miller-Urey" results

Alas, it is not so simple: it seems impossible that Earth's early atmosphere was *this* reducing.

- Gravity is insufficient to retain much hydrogen.
- Volcanism, heat, and solar UV light seem sure to have made the atmosphere oxidizing (opposite of reducing), producing lots of CO_2 and N_2, and vaporizing water. The atmosphere would have been more like that of Saturn's moon Titan.
- Formaldehyde, hydrogen cyanide, cyanopolyyne, and urea are not produced by reactions in a $CO_2/N_2/H_2O$ atmosphere.
- This has moved attention to volcanic vents, which can produce locally high concentrations of reducing gases like methane (CH_4) and ammonia (NH_3), and where lightning naturally occurs.

As long as the precursors formaldehyde, hydrogen cyanide, cyanopolyyne, and urea are supplied, interesting molecules get formed in the "ocean."

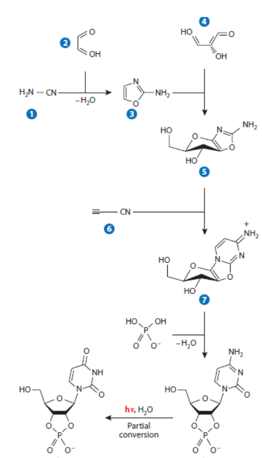
Modern Miller-Urey results

Hydrogen cyanide and ammonia have been shown to react with water to produce adenine, one of the **nucleobase** components of DNA and RNA (Oro 1961).

Two more nucleobases, cytosine and uracil, are made in water by reacting cyanopolyyne and urea (Robertson & Miller 1995).

The sugar ribose can be formed in high concentrations of formaldehyde: five formaldehyde molecules make one ribose (Reid & Orgel 1967). This works better in soil or clay than in water, though.

From these, entire **nucleotides** – combinations of nucleobases, ribose and phosphate from which RNA is built – form, all in the same "ocean" (Powner et al. 2009).



M-U formation of nucleotides (McCollum 2013)

Summary: synthesis of prebiotic molecules

Either by the slight reducing properties of the early atmosphere ***or*** by the reducing atmosphere near volcanic vents ***or*** by delivery *via* IDPs and meteorites of molecules formed in the reducing atmosphere of the ISM, it seems that the early Earth had supplies of formaldehyde, hydrogen cyanide, cyanopolyyne, and urea.

With the liquid water supplied by meteorites serving as the solvent, the primary prebiotic molecules – the amino acids and the nucleoside bases – can be made without much trouble or imagination.

The next step is the polymerization of these monomers: the generation of long, much more complex molecules that can encode information.

Wet chemistry of amino acids

In water, important modifications are made to amino acids and nucleoside bases, owing to the **propensity of water to grab positive charges**.

When any acid dissolves in water, loosely-bound hydrogen nuclei attach themselves to water and leave their electrons behind. Example of hydrochloric acid:

$HCl + H_2O \rightarrow Cl^- + H_3O^+$ (in liquid water)

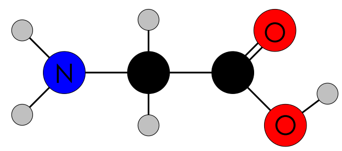
This would happen just as well in liquid ammonia, which shares this propensity with water:

$HCl + NH_3 \rightarrow Cl^- + NH_4^+$ (in liquid ammonia)

Wet chemistry of amino acids

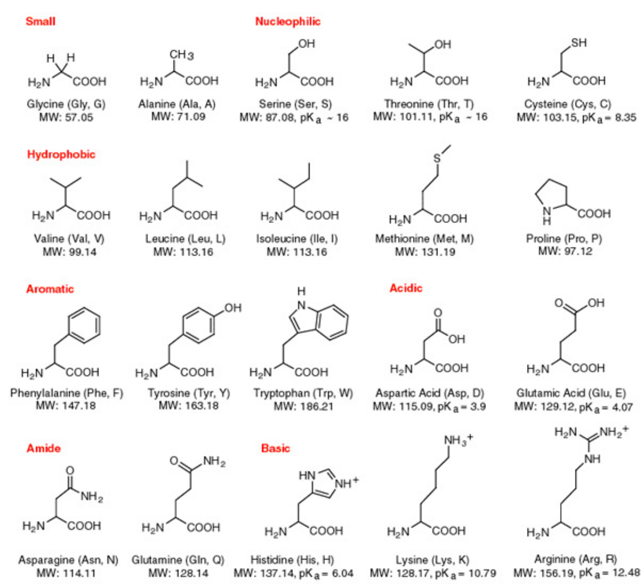
Amino acids express these tendencies on both of their ends: "amino" refers to the NH_2 group they all have at one end, and the H in the COOH organic-acid group they have at the other end is the one that comes off in the solution.

- Example: the simplest amino acid, glycine – NH_2CH_2COOH



Note the color code, which we will use from here on.

The cool thing about them is that **the NH_2 group on the end has the same propensity to grab positive ions as ammonia does in liquid**.

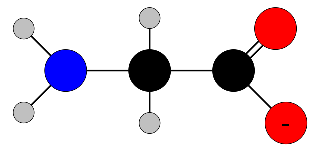


Amino acids

Wet chemistry of amino acids

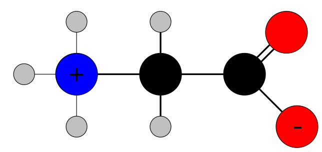
In an aqueous solution, the H in the COOH group is swiped by a water molecule…

$NH_2CH_2COOH + H_2O \rightarrow NH_2CH_2COO^- + H_3O^+$



And the amino group acquires an H^+ from a H_3O^+ (hydronium) ion:

$NH_2CH_2COO^- + H_3O^+ \rightarrow (NH_3)^+CH_2COO^- + H_2O$

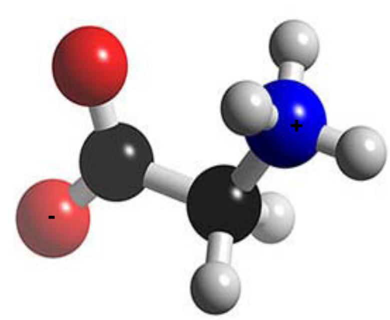


Wet chemistry of amino acids

This is a general and key property of amino acids in solution: there is a positive electrical charge localized on one end (the amino group) and a negative charge on the other end, with the molecule being electrically neutral.

These molecules are called **zwitterions** by biochemists. All amino acids are zwitterions when dissolved in water.

Zwitterions can thus undergo **ion-molecule** chemical reactions with each other, plus-end to minus-end. This is the same class of reactions as in molecular synthesis at low T in the interstellar medium.



What is special about ion-molecule chemical reactions as compared to neutral-neutral (n-n) reactions?

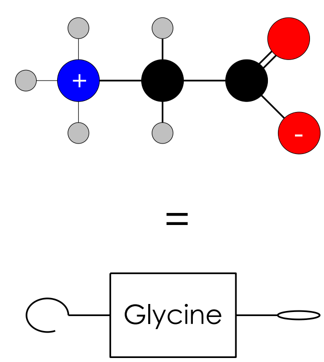
Question

A. They have no energy barrier, and the n-n reactions do.
B. They are much rarer under most conditions because high degrees of ionization are rare.
C. They heat their surroundings much less than n-n reactions do.
D. They only work in the interstellar medium, and n-n reactions only work elsewhere.

Wet chemistry of amino acids

That the electrical charges are localized on these groups rather than shared among the atoms of the molecule as, for example, the electrons are among a benzene ring, means that the amino ends of amino acids will be electrically attracted to the acid ends of other molecules.

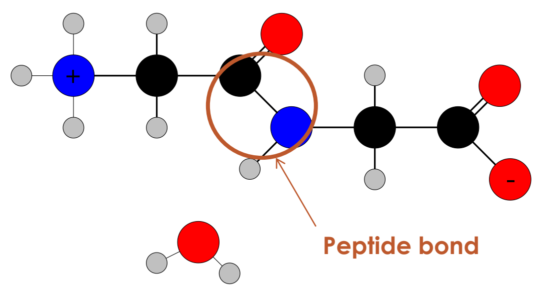
It is as if each amino acid has hook and eye connectors on opposite ends.



Wet chemistry of amino acids

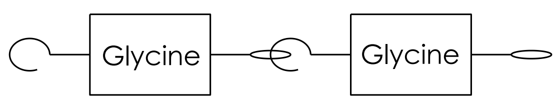
The electrostatic attraction between hook and eye can lead to chemical bonds, creating a longer zwitterion and a spare water molecule. Example of two glycines:

$$2[(NH_3)^+CH_2COO^-] \rightarrow (NH_3)^+CH_2CONHCH_2COO^- + H_2O$$

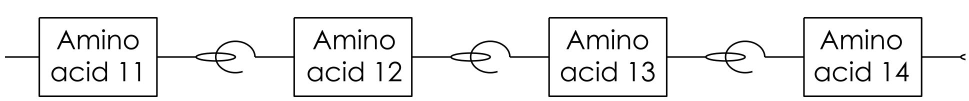


Wet chemistry of amino acids

Or, using our hook and eye shorthand, and noting that a spare water molecule is generated every time a hook and eye connect:



Obviously, this can be repeated *ad nauseam*, and it does not need to be the same amino acid every time. A long-chain **polymer** has been created from amino-acid **monomers**.

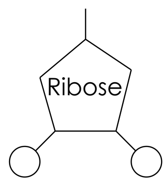


A polymer of amino acids is generally called a **protein** (or a polypeptide).

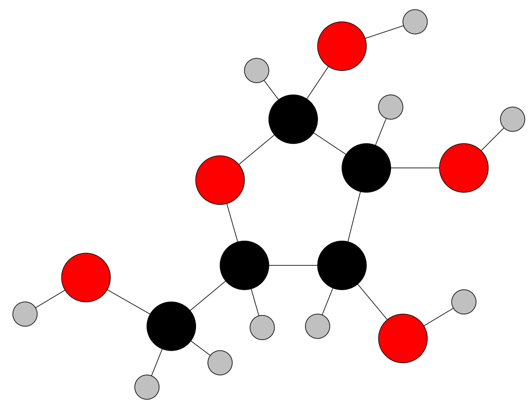
Other monomers: wet chemistry of ribose

Ribose ($C_5H_{10}O_5$) is a sugar that is made in the "ocean," or even better on dry land, by formaldehyde either delivered or made by Miller-Urey means.

Some of the dangling OH groups are good at making bonds in much the same way as the dangling OH in glycine. A shorthand schematic:



Glycine-like "eyes" ⟶



Other monomers: phosphoric acid

Phosphoric acid (H_3PO_4) can also be made in electrical discharges in a reducing atmosphere if there is any phosphorous around. (There is never much.)

In solution, $H_2O + H_3PO_4 \rightarrow H_3O^+ + H_2PO_4^-$

The two dangling OH groups of $H_2PO_4^-$ (phosphate ion) are good at making bonds with the "eyelet" groups on sugars in much the same way that the "hook" groups do in amino acids. The phosphate ion hook plus sugar eye lead to a bond that, like a peptide bond, releases a water molecule.