MATERIAL INTERACTIONS

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Why can't you make pots with garden soil? Are you doomed to have straight hair all your life? What is artificial silk? Find out the answers here.

Interactions between four fundamental forces are known to describe the physical universe. Of these, physicists attribute interactions between atoms to the action of electromagnetic forces. Chemists, on the other hand, think of these same electron–nucleus interactions in terms of many other forces, depending on the strength and arrangement of the bonds they form. Thus, in chemistry, it is the combination of these subtler forces that shapes the properties of materials. These interactive forces allows us to understand why there are so many different kinds materials, all with different properties, and undergoing so many reactions, that allow all life, including us, to eat, grow and reproduce. They enable chemists to not only explain why a diamond is one of the hardest substances on Earth, but also to make other materials that are equally hard.

What are these chemical interactions that shape our material world? While, many of these interactions are strong and directed, and are called bonds; there are others that are simply referred to as non-bonded interactions. Let us take a look at some of these interactions, exploring how a combination of forces can explain the properties of substances, both natural and human-made. **The description given here is necessarily very simple and any high school or college text will give more details.**

Covalent bonding

Electrons are attracted by nuclei. When two atoms come together, the nucleus of each attracts the electrons of the other, and so the atoms are stuck together or bonded. When the two atoms are identical, as in H_2, the electrons are shared equally and the

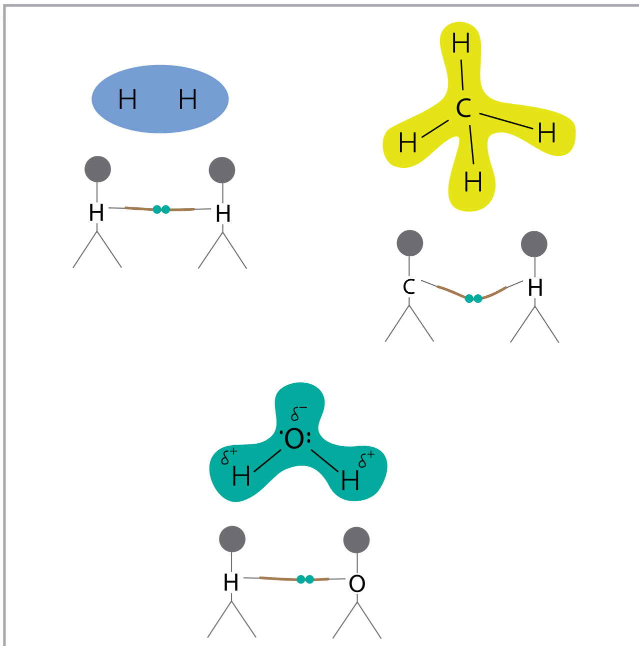


Figure 1. Structures showing dipoles formed by unequal sharing of electrons.

bond is called non-polar (refer Fig. 1a). This can also happen when the atoms are not identical but have the same pulling power as each other, as in CH_4 (refer Fig. 1b). When the atom of one element has a greater attraction for electrons, it can pull the shared pair of electrons toward itself, making a polar covalent bond, as in H_2O (refer Fig. 1c). These bonds are arranged so that the electron clouds are as far away from each other as possible. This leads to different geometries in molecules, as we will find out when considering different substances (refer Fig. 2). When the difference in pulling power is very large, one atom can pull away the shared electron completely, becoming negatively

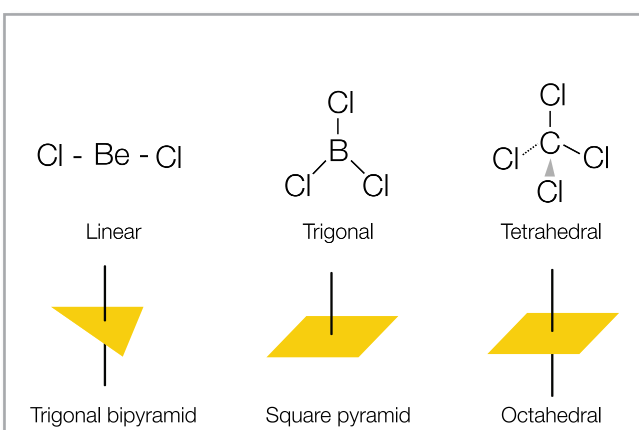


Figure 2. Shapes molecules adopt when there are different numbers of electron pairs.

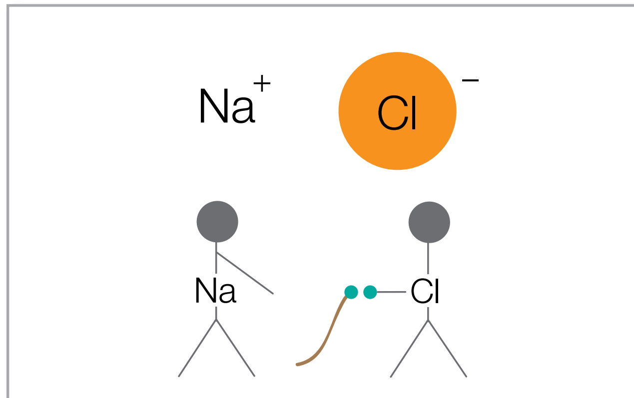


Figure 3. Formation of Sodium Chloride.

charged, an **anion**. The other atom has one less electron, is positively charged, and is called a **cation** (refer Fig. 3).

Ionic bonding

Ionic lattices are formed when the positive charge on a cation attracts negatively charged ions around itself and vice versa (refer Fig. 4). How ions arrange themselves in this lattice depends on their charge and size, but they are held together by a strong attraction. In ionic compounds, i.e., those made up of only ions, the strength of these interactions determine a variety of physical properties, such as melting points and solubility in water.

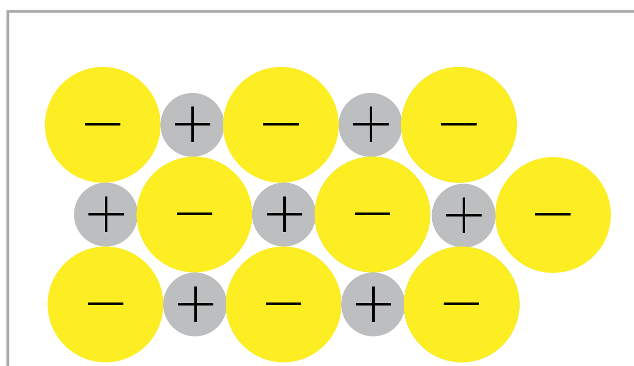


Figure 4. Arrangement of Na+ Cl- ions in sodium chloride crystals.

Metallic bonding

Elements that hold their electrons very loosely form metallic bonds. A metal consists of an array of positive ions surrounded by a 'sea' of electrons (refer Fig. 5). Since these electrons are loosely held, they can move and rearrange themselves, making the metals they are part of capable of conducting electricity, and also malleable and ductile (refer Fig. 6).

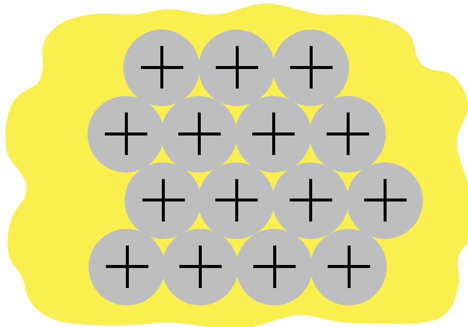


Figure 5. Metallic bonding.

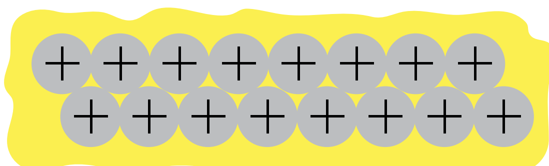


Figure 6. Metal after hammering.

Non-bonded interactions

If bonds were the only interactions between particles, all substances would be either solids or gases! Atoms/ ions forming a large array, held together by covalent, ionic or metallic bonds, would be solid at room temperature. Alternatively, atoms in small molecules like methane or water would be gases - with no forces holding these molecules together, they would be free to move away from each other. But water is a liquid at room temperature. What forces hold the water molecules together such that they are free to move but not escape from each other? These forces, collectively called non-bonded interactions, are of several kinds.

How do non-bonded interactions arise? Any atom or molecule has a cloud of electron charge around it, which fluctuates, creating a momentary dipole in the molecule. This dipole can induce a dipole on a neighbouring molecule, causing the two molecules to stick together for a brief period of time (refer Fig. 7). This force is called **instantaneous dipole-induced dipole** interaction, or dispersion force, and is very weak. However, the more electrons there are in a molecule, the stronger these forces are, especially when they act cumulatively (with energies <10kJ/mol.).

The second kind of non-bonded interaction is that of **dipole–dipole** interactions, shown by those molecules that have polar bonds. In a molecule that contains atoms with different electro-negativities, charges within molecules are polarised to form a dipole. The positive end of one molecule attracts the negative end of another molecule, causing them to cluster together (refer Fig. 8).

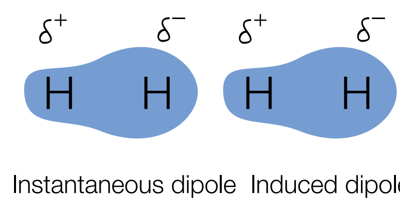


Figure 7. A fluctuation on the electron cloud of one molecule 'instantaneous dipole' causes a distortion on the neighbouring molecule 'induced dipole' leading to dispersion forces.

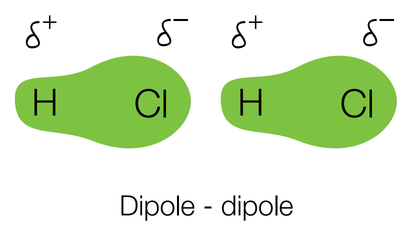


Figure 8. Attraction between opposite charges of two molecules causes them to stick together.

Box 1: The weakest interactions between particles (atoms and molecules) are called dispersion forces and require very little force to overcome them. But they exist between all substances and lots and lots of them can do wonders!

The house lizard, the gecko, can usually run upside down on a ceiling and hang there without falling. It seems to overcome the force of gravity for long periods of time, but can still unstick itself when it needs to run to catch an insect. Scientists, including Aristotle in the 4th century BCE, have long wondered how the gecko manages this feat. Turns out, geckos have special pads on their feet that, under greater magnification, are found to be made up of many (~500,000/foot) bristles. The ends of the bristles are further split into 100-1000 mini bristles, called spatulas, which make contact with surfaces like walls. It is through these numerous contact points, and the non-bonded force of attraction between them, that a gecko overcomes the force of gravity without using any energy or muscle power. In fact, as scientists who studied this found, even a dead gecko could stay stuck on the ceiling.

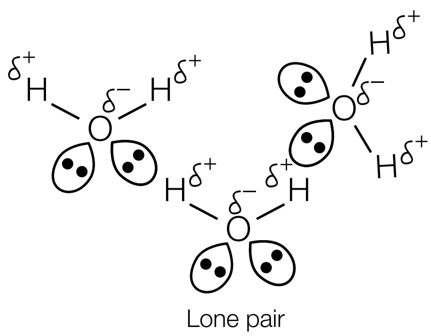


Figure 9. The positive charge on the hydrogen atom attracts the electron cloud of the oxygen lone pair, forming a hydrogen bond.

The third important non-bonded interactions are those mediated by **hydrogen bonds**. Hydrogen bonds are very special bonds, formed by molecules that have hydrogen bonded to a highly electronegative element such as fluorine, oxygen or nitrogen. These elements pull electrons away from the hydrogen atom, forming a polar bond. Because the hydrogen atom is very small, it can polarise the electrons on the neighbouring F, O or N atom forming a weak bond ~ 10-40 kJ/mol. (refer Fig. 9). Covalent bonds have energies between ~ 450-200 kJ/mol. Although hydrogen bonds are much weaker, they are strong enough to not only hold molecules together but also change their physicochemical properties. For example, the properties of water are largely ascribed to the hydrogen bonding between oxygen of one molecule and hydrogen of another molecule. Thus, hydrogen bonds play a very important role in all biological molecules, systems and processes.

Box 2: Hydrogen bonds
Many of us have had difficulty ironing creased cotton clothes. Cotton is made of cellulose, a polymer of glucose, and can form hydrogen bonds between strands, holding them together. It is very hard to iron out a crease, when a cotton cloth is dry; but when water is sprinkled on the cloth, the hydrogen bonds within the crease break, and are re-formed with water instead. Iron off the water, and the crease is gone. This is very similar to the way you can curl or straighten your hair after dampening it, but a humid day or a wetting will reverse the style.

Why are these bonded and non-bonded interactions that operate in the materials we see around us important? Let's start by looking at the earth beneath our feet, the structure of the soil minerals and their properties.

How many ways can silica bond?

The basic component of soil is silica: SiO_2, in a giant covalent lattice, called quartz; where each silicon atom is covalently bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms. Quartz gets weathered or broken down by the action of wind and water into smaller pieces or sand. When these react with water, they result in the formation of silicate ions or SiO_4^{4-} that look like a tetrahedron (refer Fig. 10). Many of the earth's minerals are silicates that are linked together in different ways, through shared oxygen atoms, forming single or double stranded chains (refer Fig. 11a and 11b). Thus, for example, asbestos (refer Fig 12a) is made up of double stranded chains and peels off in strands; while mica (refer Fig12b) is made up of sheets (refer Fig. 12c) of the tetrahedra. The negative charge on silicate minerals is balanced by positive ions, like K^+, Mg^{2+}, Ca^{2+} and Al^{3+}, held by ionic interactions. As weathering continues, Al^{3+} replaces some of the silicon in the layers, converting sand into clay. The minerals in clay consist of two kinds of sheets held in layers - tetrahedral sheets mainly consisting of silicate tetrahedral; and octahedral sheets consisting of mainly of Al^{3+} surrounded by six OH^- ions (refer Fig. 13).

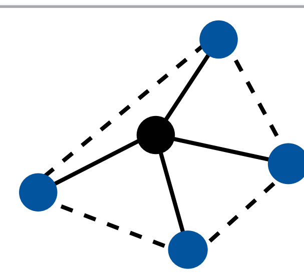


Figure 10. Silicon tetrahedron.

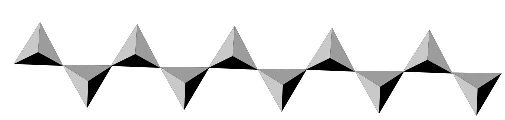


Figure 11a. Silicate Single strand.

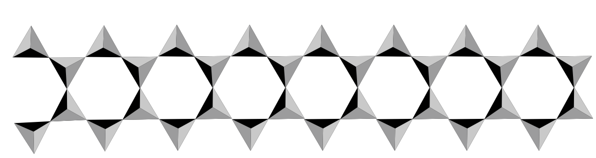


Figure 11b. Silicate double strand.

Figure 12a. Asbestos: fibres made of double stranded silicate chains. Source: Nikhil Fernandes.

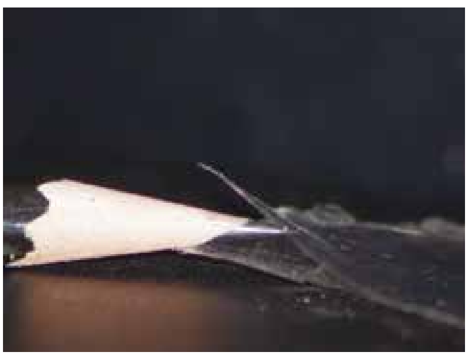


Figure 12b. Mica: made of sheets of silica tetrahedra. Source: Nikhil Fernandes.

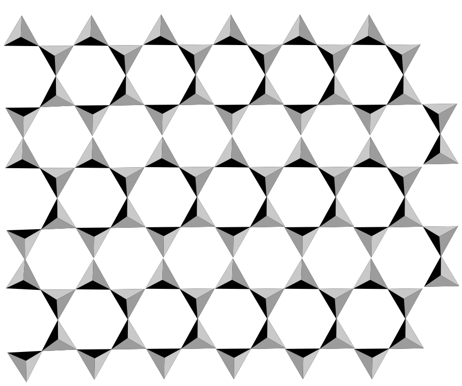


Figure 12c. Silicate sheet

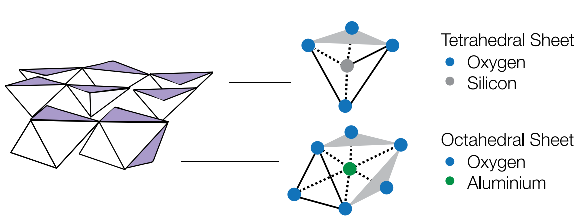


Figure 13. Layers of tetrahedral and octahedral sheets held together by shared oxygen atoms.

Different types of clay have these layers arranged differently. Kaolinite, which is the clay used for making pots (refer Fig 14a), has a 1:1 structure - one tetrahedral sheet bonded to one octahedral sheet. These layers are held together tightly by hydrogen bonds between the OH of the octahedral sheet and the O of the tetrahedral sheet (refer Fig. 14b). These prevent water and cations from entering between the sheets and, therefore, do not allow the clay to expand very much. The small amount of water that does enter the clay, and rests between its crystals, allows it to be moulded into different shapes that hold (refer Fig 14c).

Figure 14a. Kaolinite clay can be made more pliable by wedging, where it is rolled into a tight spiral with a sort of kneading method, which removes air pockets. Source: Lalita Manjunath.

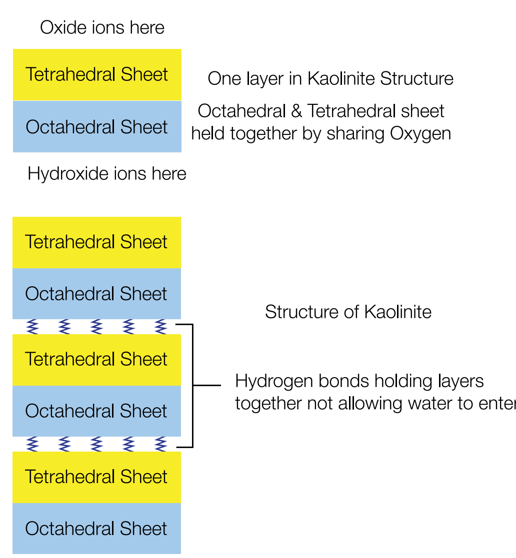


Figure 14b. The structure of Kaolinite shows tightly held layers, giving it characteristic modelling properties.

Figure 14c. The small amount of water that enters clay allows it to be moulded into pots. Source: Lalita Manjunath.

Figure 16. Soils containing expanding 2:1 clays crack and shrink when dry. Source: jackmac34, Pixabay. License: Public Domain. URL: https://pixabay.com/en/drought-earth-desert-aridity-711651/

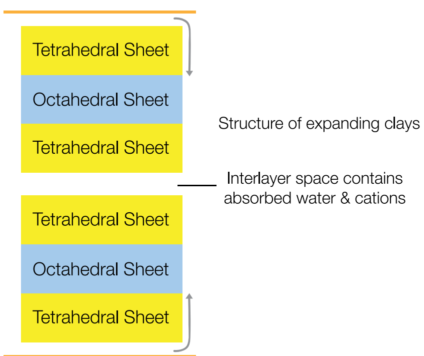


Figure 15. The structure of expanding clays – the lack of hydrogen bonds between layers allows water and ions to enter.

On firing the clay, this water is eliminated, but the layers are now held together by covalent bonds. These bonds are strong enough to prevent the clay from being recycled, and thus the moulded clay holds its shape permanently (refer Fig. 15).

Other clays that make up soil are 2:1 clays, where an octahedral sheet is sandwiched between two tetrahedral sheets. The tetrahedral sheets in these clays cannot bond together, but being negatively charged on the surface, allow water molecules and cations to move in between them, allowing these clays expand. These clays are like store-houses for plants, providing plant roots with water and minerals (refer Fig. 16).

Molecules of life

Nothing shows the role of these various interactions better than the structure of proteins. Proteins are polymers or long-chain molecules that are made up of smaller molecules, called amino acids, held together by covalent bonds. There are 21 such amino acids which combine in different ways to form proteins with diverse properties and functions.

This diversity can be seen by taking just two examples of proteins in the human body. One, called amylase, is a protein that is water-soluble and catalyses the digestion of starch; while another, called keratin, is tough, inert, water insoluble and forms the hair on our heads.

Activity - Hydrogen bonds and Disulfide Bridges in the Kitchen.

We 'see' hydrogen bonds forming and breaking when we iron out creases in damp cotton clothes. But another place to notice this is in making 'atta' for chapattis. Once I realised that this is what was happening, I notice it every time with interest!

Take flour in a vessel and run your fingers through it to get a feel of its temperature. Add water, again dropping it over your fingers. As you mix the flour and water together, the mix will feel perceptibly warmer. This is because energy is being released as the water forms hydrogen bonds with the –OH groups in starch.

Take a piece of this mixture and hold it under running water. It will wash away. Continue kneading and the dough will become elastic. Two types of proteins - gliadins and glutenins combine together to form gluten. This is a water-insoluble protein mass, held together by disulfide bridges, mostly made by the kneading action and the incorporation of air. If you now take a lump of atta and wash it under running water, the starch will wash away leaving behind the elastic gluten lump.

Proteins have complex structures that are assembled in three (or four) layers. The first, called a protein's primary structure, is the sequence of its amino acids held together by covalent bonds. This linear chain coils into sections of helices and sheets, held together by hydrogen bonds (refer Fig. 17). This is called its secondary structure. In its tertiary structure, protein molecules fold into various shapes using non-bonded interactions, ionic interactions, and a very special covalent bond called the disulfide bridge (refer Fig. 18). Consider milk. The proteins in milk are held in solution and will not settle down on keeping. Curdling the milk to make paneer breaks the tertiary and secondary structures of its proteins, precipitating them out. This happens because adding lemon juice or vinegar disrupts the ionic interactions and the hydrogen bonds within proteins, which can no longer interact with the water in milk in the way they originally did. When we eat paneer, digestive enzymes of our gastro-intestinal tract break the covalent bonds holding the primary structure of amino acids together.

It is these intricacies of folding that make amylase a compact molecule that can be held in solutions (like our saliva), while exposing a region that can accommodate its substrate starch molecules. If we change the secondary structure of amylase by heating or changing the pH of its environment, the amylase will not catalyse the reaction any more.

In contrast, the tertiary structure of keratin is made up of secondary structures of helices winding around each other, and held together by disulfide bridges. The number of these disulfide bridges in keratin varies from one individual to the other; and in general, the more their number, the curlier is one's hair! By dampening your hair and combing it out in the style you want, you can temporarily straighten curly hair or curl straight hair. By the time your hair dries, new

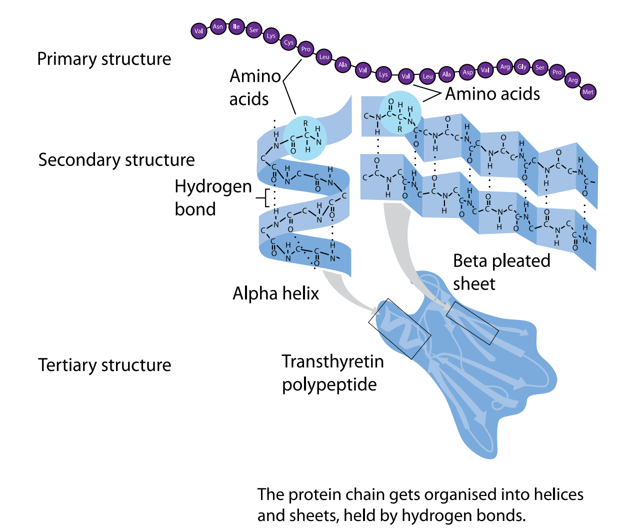


Figure 17. Levels of protein structure.

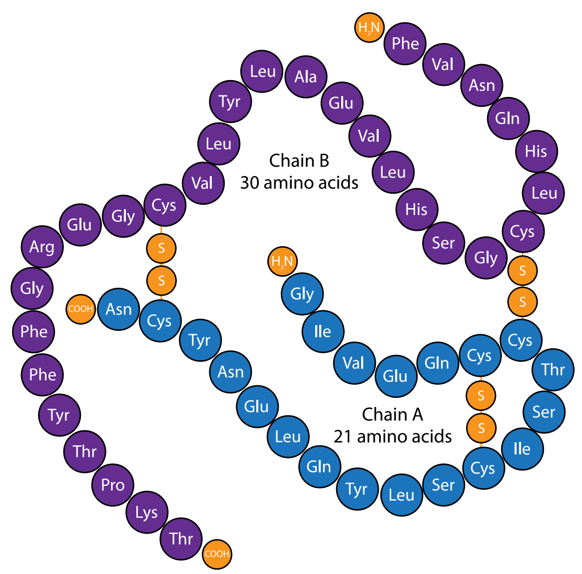


Figure 18. Disulfide bridges bring together different parts of a protein chain, giving rise to specific shapes.

One among the many interactions that hold the structure of a protein together is the disulfide bridge. The amino acid cysteine contains the –SH group. Two –SH groups can link together and get oxidised to form –S-S-, the disulfide bridge. This brings different parts of the protein strands together, giving a specific shape to the protein. Hair contains a lot of cysteine - the number of disulphide bridges a strand forms decides whether your hair is curly, wavy or straight. While you can temporarily change your hairstyle by putting rollers on damp hair, a more permanent change will require a change in its existing disulfide bridges. To do this, a reagent called ammonium thioglycolate, containing a –SH group, is applied to hair to break its existing disulfide bridges. This allows you to set your hair in a style of your choice. Once new bridges are formed by oxidation, the reagent is washed off. Your hair is now the way you want it! Of course, when new hair grows, it will be what it was before you styled it - unfortunately, you cannot change your genes.

hydrogen bonds are formed within the keratin, which will persist (and allow you to retain your new hair style), till your hair is dampened again, or the air gets damp. To get a more lasting 'perm', the disulfide bridges within hair have to be broken using sulfur compounds, and reformed in the required style. While this perm stays permanently, as your hair grows, it comes out in the way it is naturally.

Designer molecules

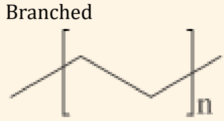
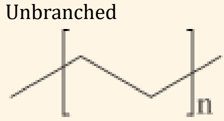
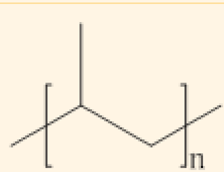
As if the variety and number of proteins in the natural world are not mind-boggling enough, we are now able to synthesize many artificial polymers with exactly the properties we want.

The first plastics were formed by accident. We are all familiar with polythene, PVC, Teflon and polystyrene (popularly known as Thermocole). While all of them have different properties and uses, their basic structure is the same with only their side-chains being different (refer Table 1). In poly-ethene and poly-propene, the main forces of attraction are non-bonded interactions between the long chains. So these plastics are soft, soften with heat, and are mainly used for plastic bags. In contrast to low-density polythene (LDPE), with its loosely packed branched chains, synthetic high-density polythene (HDPE) has more compactly packed side-chains, giving it higher melting points and making it stronger. The side-chains of PVC or polyvinyl chloride are held together by strong polar bonds, making PVC harder. Similarly, the strong covalent carbon fluorine bonds in Teflon (poly-tetra-fluoroethene) make it quite inert. Since fluorine holds its electrons quite tightly, the dispersion forces in Teflon are weak, giving it its ability to act as a non-stick coating in cookware.

How can one change the properties of a polymer? Broadly, there are three ways of doing this:

- By changing its side chains – more polar side-chains bring greater interactivity.
- By changing the length of the chain – longer chains have stronger intermolecular forces.
- By changing the orientation of the side groups – helping the chains pack better.

A polymer similar in structure to polythene is poly-ethenol. Polyethenol has many hydroxyl (–OH) groups in its side chain. When 99-100% of the polymer is made up of –OH groups, it becomes insoluble, with hydrogen bonds forming between the side-chains. As the percentage of –OH group's drops, the polymer becomes soluble in water, since the gaps between its side-chains allow water molecules to penetrate and react with the polymer. Making use of this property, poly-ethenol is used to make hospital laundry bags. When infected clothing is put into these bags and

POLYMER	COMMON NAME	STRUCTURE	FORCES BETWEEN CHAINS	PROPERTIES	USES
Polyethene Low Density	Polythene LDPE	Branched 	Dispersion forces	Inert, softens with heat, can be moulded	Plastic bags, wrapping
Polyethene HDPE	Polythene HDPE	Unbranched 	Dispersion forces. Chains pack closer	Softens at higher temperature than LDPE. Inert	Bottles, Pipes, Lab beakers etc.
Polypropene	Poly-propylene		Dispersion forces.	Higher softening point since forces are larger. Inert	Furniture, pipes, Lab equipment that can be sterilised. Hinges for pop up lids

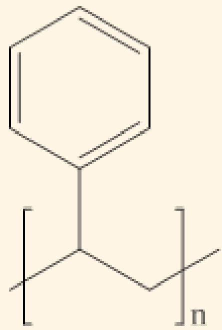
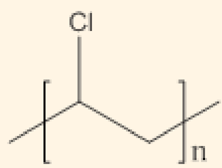
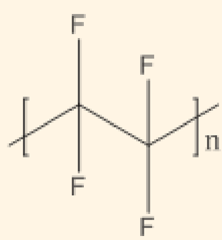
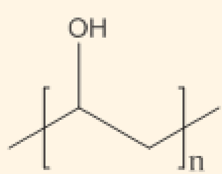
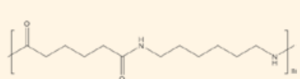
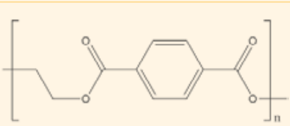
POLYMER	COMMON NAME	STRUCTURE	FORCES BETWEEN CHAINS	PROPERTIES	USES
Polystyrene Hard and foam	Thermo-cole, Styrofoam		Dispersion forces	Hard, and tough, can be formed into a lightweight foam	Packing material, insulation, lab equipment
Polychloroethene	Poly vinyl chloride PVC		Dipole-induced dipole	Hard and strong	Pipes, wire coatings
Polytetrafluroethene PTFE	Teflon		Dipole- dipole between chains	Inert, High melting, non-stick since electrons are held tightly by fluorine so does not interact with other molecules*	Coatings for pans, valves, lubricant
Polyethenol	PVOH		Hydrogen bonding	Depends on % of –OH groups: >99% insoluble in water, 99-90% soluble in hot/ warm water. < 90% soluble in cold water	Hospital laundry bags. Surgical stitches
Polyamides	Nylon		Hydrogen bonding	Strong, high melting, resistant to decay, can be moulded	Clothes, ropes Machine parts
Polyetheleneterephthalate Polyesters	Terylene, PET,		Hydrogen bonding	Strong, high melting	Clothes, films (Mylar), bottles

Table 1. Polymers are long chain molecules with differing side groups. Interactions between the chains increase with size and with the structure, changing the properties. *Since fluorine holds on to its electrons very tightly, dipoles don't get induced very readily, so dispersion forces are weak. Even a gecko will not stick to Teflon.

loaded into washing machines, the bags will dissolve, releasing clean clothes.

Chemists have also tried to mimic natural polymers like silk, wool and rubber. Silk and wool are made up of proteins, and nylons and polyesters are their equivalent synthetic versions. These synthetic polymers can be drawn into fibres, and woven into cloth. These properties are partly due to the chemical nature of the molecule, and partly due to the way it is processed.

Similarly, chemists have played around with molecules to get Kevlar (strong and lightweight), PHA (fire resistant) and polycarbonates (replacement for glass).

Conclusion

We live in an age where we can design new materials using our knowledge of molecular interactions. Many recent efforts in this field, for example, are aimed at making bio- and photo-degradable synthetic polymers.

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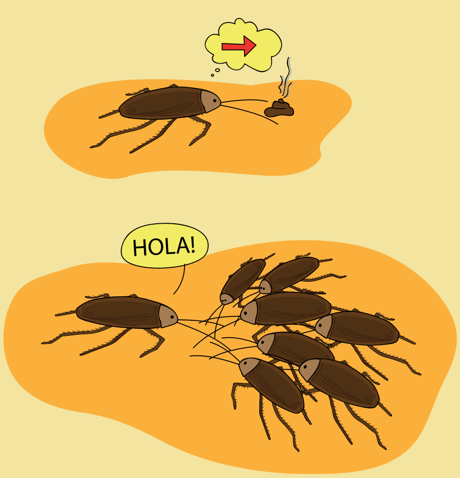
Poop Helps Insects Socialise

– Vignesh Narayan

"Man is a social animal" said Aristotle, the philosopher who lived 2300 years ago. What he did not know, and what scientists today have found out is that insects too are social animals. This is why if you find one cockroach in your house, chances are that there are a hundred more hidden from view. What has puzzled entomologists (people who study insects) is how these insects communicate with each other.



Cockroach biologists (yes, there are some!) have come up with the answer. Cockroaches, they say, are attracted to poop. Apparently, the tendency of cockroaches to aggregate together is because of their attraction to volatile fatty acids that bacteria present in the faeces produce. When cockroaches were hatched and raised in germ-free cages, they turned out to be very solitary folks, hardly even stopping to rub antennae. These socially awkward cockroaches regained their camaraderie and group clustering when the bacteria were re-introduced into their cages.

In fact, other insects also communicate by using bacteria that give off certain odours and chemicals. Locusts play host to a specific kind of microbe that helps them aggregate and form a swarm. Some animals too, like the hyena, have bacteria in their scent glands which help them tell relatives from non-relatives.

So next time you're looking for someone in a crowded room, close your eyes and give the air a good sniff!

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