Drops and Puddles: An Introduction to Interparticle Attractions

Recently available and inexpensive equipment can alter the presentation of a formerly descriptive part of the chemistry syllabus. The microscale balances described on page 38 of the book and pipettes on page 15 allow every pair of students to investigate interparticle attractions.

The existence of dipoles in liquids

A very popular and important demonstration shows that an electrostatic charge (made by rubbing an acrylic rod with a wool cloth) can deflect certain liquids from a burette (see Figure 1). As a class activity, this can be a difficult to organise with regard to equipment and odours from organic liquids. Students can carry this experiment out at home with water from a tap, using a balloon or a comb rubbed on a woolly jumper. However, the effect can be seen in drops of liquid on the end of a transfer pipette and in the puddles or droplets that form on a plastic surface, but it works better on a leaf!

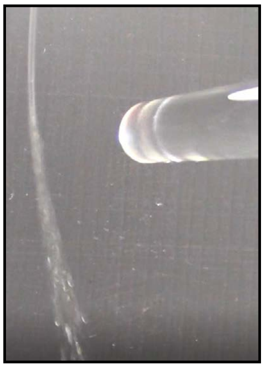

Figure 1: Deflecting water

Activity: Deflecting drops and wobbling puddles on leaves[1]

Outline requirements

- Water
- Ethanol
- Ethyl ethanoate
- Nasturtium leaf
- 1 cm^3 transfer pipette or a 1 cm^3 syringe with a blunt needle
- Polypropylene folder
- Retort stand and claw clamp (see Figure 5.1 in the book)
- Comb, balloon, acrylic rod
- Woollen cloth, although a jumper will do

Outline method

Deflecting drops

1. Fill the pipette with water to the 1 cm^3 mark.
2. Clamp it vertically.
3. Turn the clamp gradually to suspend a drop of water at the tip of the pipette.
4. Rub the rod on cloth, comb your hair, or run the balloon over your clothes (particularly wool) and bring the rod or comb close to the drop. The drop is attracted to the charged object.
5. Try it with ethanol or ethyl ethanoate.

Figure 2 illustrates the effect, where you can see the effect of the charge on the red comb as it approaches the suspended water drop. With ethanol, the effect is present but not as pronounced.

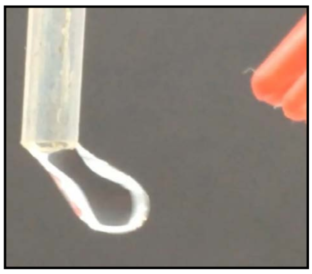

Figure 2: Deforming a drop at the end of a pipette

Wobbling puddles

1. Lay the leaf on a tile or the polypropylene folder on the bench.
2. Add water to the surface of each to form the hemispherical puddle.
3. Rub the rod on cloth, comb your hair, or run the balloon over your clothes (particularly wool) and bring it close to the puddle.

Figure 3 shows the distortion in the shape of the water drop on the plastic surface and on the leaf.

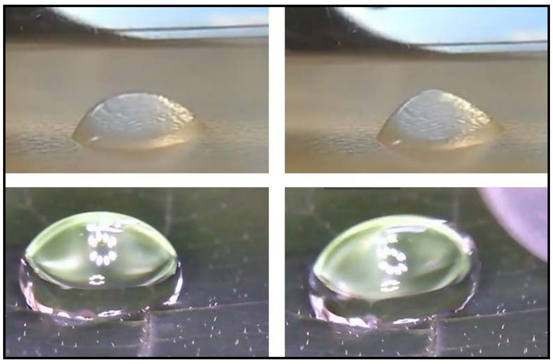

Figure 3

The lower of two photographs in Figure 3 shows the increased contact angle of the droplet on the Nasturtium leaf, which has increased from about 90° on plastic to 110° on the leaf. Bring a 'charged' comb or even the bulb end of a transfer pipette and the droplet wobbles. In the photographs, you can see the small 'hairs' on the leaf, which contain hydrocarbon-based oils that 'lift' the water off the surface, causing the contact angle to increase. There are important engineering connections. Surface coatings, which increase the contact with water, are used to reduce the water drag on boats, protect surfaces and equipment exposed to fresh or salt water, and build materials so that they remain clean with little maintenance and better protected from wear from the weather, and textiles that are resistant to staining and/or remain dry when submerged in water. Synthetic coatings often contain polysilicone, which may have an environmental impact. I once tried to make a polysilicone surface, but the water puddles were so mobile that I could not do anything with them. Yes, experiments fail but, at the same time, increase knowledge.

How dipoles arise in molecules

In both these activities, water is attracted to an electrostatic charge. It does not matter if the charge is positive or negative. In either case, the water molecules can rotate and be attracted to the charge; it is a position of lower potential energy. An explanation can be found in the structure of water.

Figure 4a illustrates how the bonding in the molecule is often represented. There is electrostatic attraction between the negatively-charged electrons in the bond and the positively-charged nuclei. There is also repulsion between the electrons and repulsion between nuclei in the bond. The structure is a final resolution of all these electrostatic effects. The electrons (red and black) in the final hydrogen-oxygen bond cannot be distinguished from each other.

However, the electrons in the bond are not evenly spaced between the oxygen and hydrogen atoms. The positively-charged nucleus in the oxygen atom exerts an attraction on the electrons in the bond, so the electrons are closer to the oxygen. This distortion causes the molecule to have a dipole with a slightly more positive side (δ+ve) (near the hydrogen atoms in the bond) and a slightly more negative side (δ-ve) (around the oxygen atoms). Figure 4b shows a line to represent the bond and the unevenness in the blue-red line illustrates the pull.

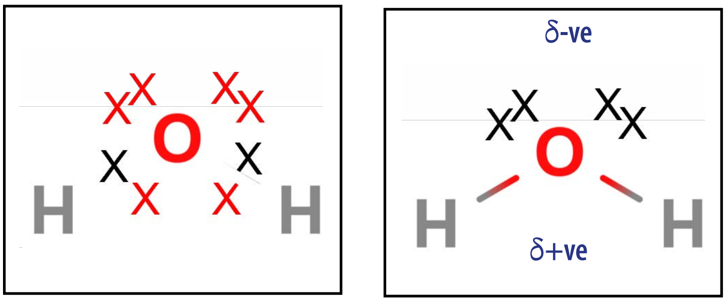

Figure 4a and 4b

Boiling points

The effect of the dipole on the properties of covalently bonded molecules is evident from their boiling points. The boiling point temperature depends on:

- the molar mass, as the heavier the molecule, the more energy is required. Table 1 shows the boiling points of straight chained alkanes whose dipole moment is almost zero;
- the intermolecular attractions, caused by the dipole, as extra energy is required to break the molecules apart.

Table 1: Boiling points of straight chained alkanes.

Alkane	Methane (CH_4)	Ethane (C_2H_6)	Propane (C_3H_8)	Butane (C_4H_{10})	Pentane (C_5H_{12})	Hexane (C_6H_{14})	Heptane (C_7H_{16})
Molar mass ($g\ mol^{-1}$)	16	30	44	58	72	86	100
Boiling Pt (°C)	-162	-89	-42	0	36	69	90

Figure 5 shows the structure of propanone (found in nail varnish remover). The molar mass is 58 g mol^{-1} (the same as butane), but its boiling point is higher, at 60°C. This is a consequence of a dipole and the attraction between molecules, which has to be broken so the molecules can separate in the gas phase.

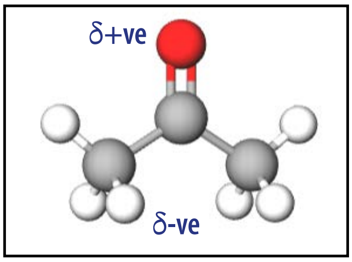

Figure 5

Water is odd!

- The boiling point is 100°C (higher than heptane), but has a molar mass of only 18 g mol^{-1}.
- The boiling points of the hydrides of the Group 16 (formerly Group 6) elements are -59.6°C for H_2S, -41.3°C for H_2Se and -2.2°C for H_2Te.

This also implies that there is another factor at work. There is an attraction between the molecules of water that is stronger than the expected dipole-dipole bond.

The hydrogen bond

Activity: The volume of drops from a plastic pipette

Outline requirements

- Water
- Ethanol
- 1 cm^3 transfer pipette.
- Balance
- Petri dish
- If preferred, retort stand and claw clamp (see Figure 5.1 in the book)

Outline method

1. Place the Petri dish on the balance.
2. Fill the pipette with ethanol to above the 1 cm^3 mark.
3. Switch the balance on and tare to zero.
4. Hold the pipette vertically and slowly squeeze 10 drops of ethanol into the Petri dish.
5. Note the reading on the balance.
6. Repeat steps 4 and 5 four more times so that you have added 50 drops.
7. Wash the pipette with water and the repeat procedure with water.
8. Make a table of 'number of drops', 'recorded mass' and the 'mass of 10 drops'.

These pipettes are made in their millions. Notice how consistent the drop masses are. The density of ethanol is 0.79 g cm^3 and for water 1.00 g cm^3 at room temperature and so using the formula Volume of drop = mass of drop/density, the volume of a single drop can be found. With the pipettes that I used, the volumes obtained were 0.02 cm^3 per drop for ethanol and 0.05 cm^3 per drop for water. The intermolecular attraction within water is much stronger than that for ethanol.

The activity can be extended to ethyl ethanoate, which is more dense than ethanol at 0.90 g cm^3. The clamp method has to be used, as there is no hydrogen bonding but only dipole-dipole attraction and the liquid is denser than ethanol. I found that the volume of one drop was 0.016 cm^3.

The hydrogen bond is rather more than a dipole-dipole attraction.

The electrons are fuzzy. And, as the 'cloud' is drawn into the bond and towards the oxygen, it leaves the hydrogen atom with a slightly positive charge that can attract the electron pair in the oxygen atom of an adjoining molecule (see Figure 6). This occurs with any hydrogen atom attached to nitrogen, oxygen and fluorine. This is the well-known hydrogen bond and it is responsible for not only the high boiling point of water, but also surface tension, viscosity, solvation properties and life itself as it runs though the double helix of DNA.

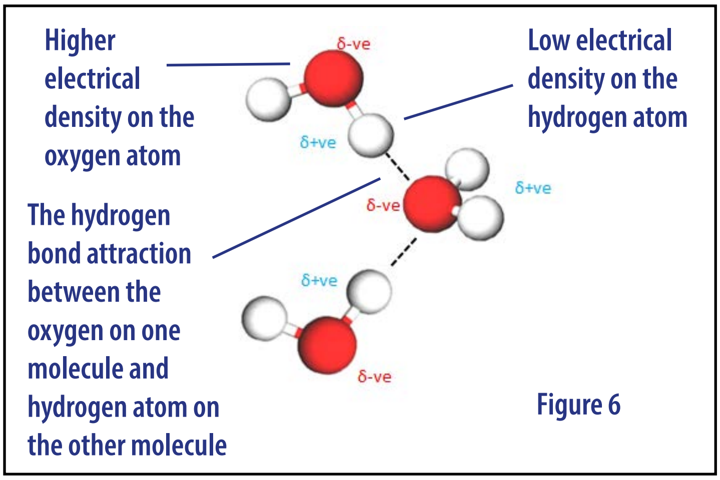

Figure 6

Surface tension

The molecules on the surfaces, without a full complement of surrounding molecules, are more strongly attracted to the adjoining molecules inside the drop. The 'skin' surrounding the water is shown to great effect when trying to add as much water as you can onto a coin before the 'skin' breaks (Figure 7).

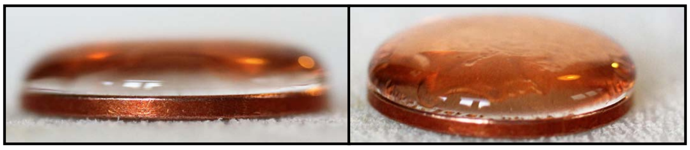

Figure 7: The 'skin' forming on a 2p coin.

Activity: How much liquid can be supported on a coin?

This lends itself to an investigation.

1. Is the mass different if other liquids than water are used?
2. Is the mass different if salts are dissolved in the water?
3. Is the mass different if different liquids such as ethanol are dissolved in the water?
4. Is the mass different if a detergent is added to the water?
5. Does the nature of the coin matter?

Outline requirements

- Water
- Ethanol
- Ethyl ethanoate
- 5M sodium chloride solution (Other liquids can be used, but some organic liquids do 'soften' plastics if left in contact with them for a long time)
- Soap
- Balance weighing to at least 2 dec places
- 1 cm^3 transfer pipette or a 1 cm^3 syringe with a blunt needle
- Small plastic Petri dish
- Paper towel
- 2p coin or other coins

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(Make sure that the benches are flat. A tile, small tray or heatproof pad with bits of Blu-tac underneath can help to provide a level surface)

If students find the use of a pipette or syringe difficult, the method shown in Figure 5.1 in the book works using a retort stand and claw clamp. The stand has to be placed just above the coin.

Outline method

1. Place the coin in the Petri dish and on the balance. Tare the mass on the balance.
2. Fill the 1 cm^3 pipette with water.
3. With the pipette **just above the coin**, deliver 1 drop at a time. You may need to refill the pipette.
4. As more water balances on the coin, be more careful adding the water. Suddenly the 'skin' will break and, at that point, record that mass on the balance.
5. Remove, empty and dry the Petri dish and the coin with a paper towel.
6. Repeat twice more to provide 3 readings and average the mass.

Table 2. One set of results

Liquid	Molar mass (g mol^{-1})	Density (g cm^3)	Mass of liquid on coin (g)	Volume (cm^3)	Amount (mol)
Water	18	1.00	1.89	1.89	0.105
Ethanol	46	0.79	0.46	0.58	0.010
Ethyl ethanoate	88	0.9	0.63	0.70	0.007
5M salt solution		1.2	2.45	2.01	

When sodium chloride dissolves in water, density of the solution increases with a contraction in volume. The surface tension also increases. This is an introduction to the ion-dipole attraction, another interparticle attraction. It is more commonly called 'solvation of ions'.

If sodium chloride solution is boiled and the water removed, sodium chloride crystals will form. The attraction between positive and negative ions in crystals can be considered as the strongest interparticle attraction known.

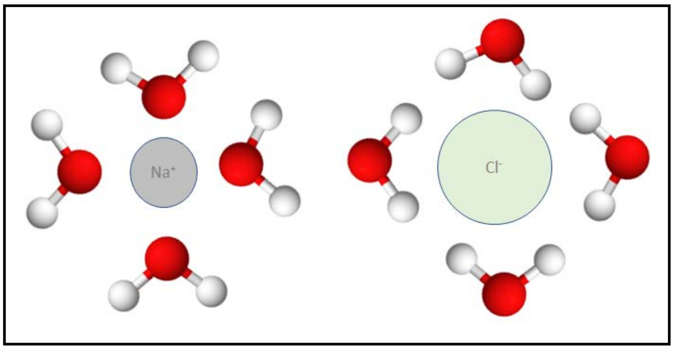

Figure 8

London dispersion forces

London dispersion forces are the weakest forces. The electron is not a hard sphere but a fuzzy shape of negative electrical charge. The charge is not distributed evenly all the time, but is constantly shifting position so that, over time, it appears to be distributed evenly. The movement of the electrons in adjoining or colliding molecules sets up a temporary positive and negative charged region in the molecules. Figure 9 is an attempt to show this by combining a ball and stick model of heptane inside an electron cloud version. The constant movement of electrons sets up a dipole between an adjoining molecule for a fraction of a second but, in the next fraction, the dipole has moved.

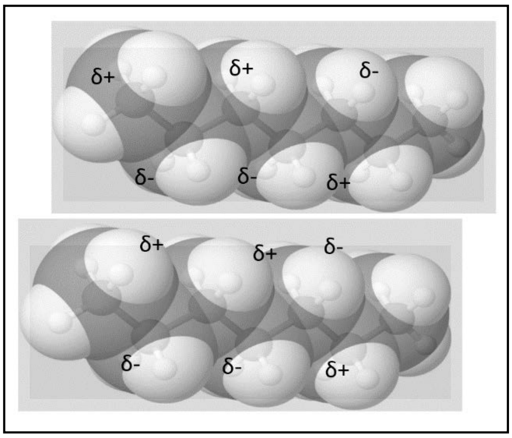

Figure 9

The comparative force between these interparticle forces is shown in Figure 10.

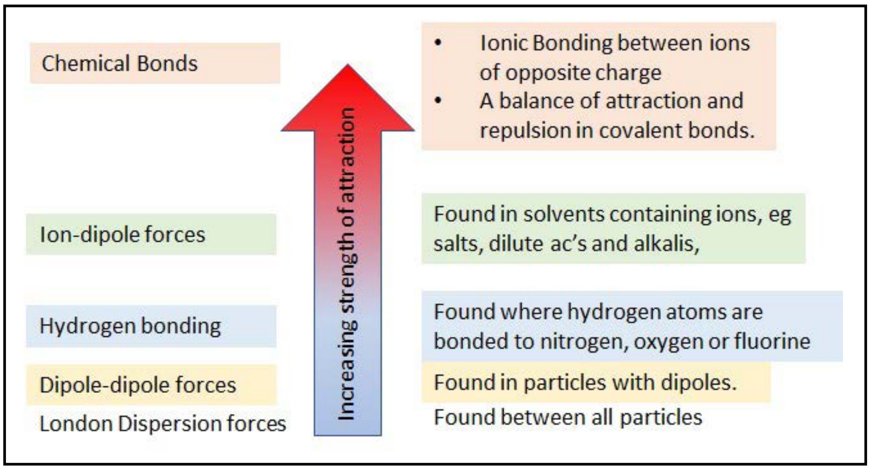

Figure 10

Footnote

[1]See www.youtube.com/watch?v=BoVoDYzVHVs and https://www.youtube.com/watch?v=AvLSpxrKkk

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