Molecule Matters
van der Waals Molecules

1. History and Some Perspectives on Intermolecular Forces

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van der Waals introduced his equation of state in 1867 modifying the ideal gas equation. His equation had two constants a and b, which accounted for the fact that molecules have attractive forces and finite size. The constant a accounted for the attractive forces, the nature of which was not outlined by van der Waals. This series of articles will discuss about the nature of intermolecular forces.

1. Atomic Hypothesis

If one were to select a single most important discovery of science, the atomic hypothesis, i.e., that all things are made of atoms, would be a strong contender. Of course, atoms were postulated several thousand years ago in India, and Greek philosophers had discussed it as well. The renowned Tamil poet sage Thiruvalluvar's *Thirukural* (literal translation meaning honorable short verse) provides guidelines to be followed under all possible circumstances. It is more than 2000 years old and it remains and will remain relevant. It packs so much information in a couplet (two-line poem), that another renowned Tamil poet, Lady Auwaiyar, compared it to packing seven oceans into one atom (*anu* in Tamil, the word possibly having its origin in Sanskrit). What is interesting about Auwaiyar's couplet on Thirukural is

அணுவைத் துளைத்தேழ் கடலைப் புகுத்திக்
குறுகத் தறித்த குறள்.

Kural packs so much in a couplet that it is equivalent to piercing an atom and inserting the seven oceans into it.

that it talks about 'piercing an atom and inserting seven oceans into it'. However, it was only in the last century that indisputable experimental evidences for atoms were obtained. Today, atoms can be visualized with sophisticated microscopy techniques that are pushing the resolution of measurement to sub nanometer (Angstrom) level (1 nm = 10^{-9} m = 10 Å), the atomic dimension[1]. Atoms physisorbed on a surface can now be picked and moved around!

Figure 1. Structure of H_2O: red sphere represents oxygen atom and the grey ones represent hydrogen atoms.

2. Two Important Molecules: Water and DNA

Atoms have remained a domain of physics, rather than chemistry, as much as one can draw these artificial boundaries between disciplines. Atomic physics is a standard sub-division of physics and atomic chemistry does not exist. Chemistry is a molecular science. It is so much so that recently there was a suggestion that American Chemical Society be renamed Society for Molecular Science and Engineering [2]. Molecules, as we all are aware, are made up of atoms; different atoms combine only in select proportions and much of it was established by the turn of the 19th century by Joseph Proust [3] and John Dalton [4]. As we all know, water is a molecule made up of two hydrogen (H) and one oxygen (O) atoms and represented by the molecular formula H_2O and pictorially as in *Figure* 1.

The molecule of life, DNA, on the other hand is made up of thousands of atoms of H, C, O, N and P. It is impossible and also meaningless to write a molecular formula or structure made up of atoms for DNA and biologists have better ways of representing DNA (see *Figure* 2). DNA exists as a double helix and the reader is referred to the book by Sinden for details [5]. There is a more important difference between single molecules of water and DNA. In water, oxygen is covalently bonded to the two hydrogen atoms and there are two O-H covalent bonds. A covalent bond between two atoms implies that
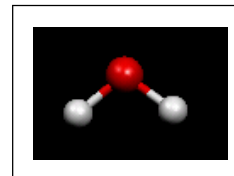
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Figure 2. The double helix of DNA is shown along with details of how the bases, sugars and phosphates connect to form the structure of the molecule. DNA is a double-stranded molecule twisted into a helix (think of a spiral staircase). Each spiraling strand, comprised of a sugar-phosphate backbone and attached bases, is connected to a complementary strand by non-covalent hydrogen bonding between paired bases. The bases are adenine (A), thymine (T), cytosine (C) and guanine (G). A and T are connected by two hydrogen bonds. G and C are connected by three hydrogen bonds. Moreover, the bases interact through π stacking schematically shown by the dashed line in color.
(Figure taken with permission from the following website: http://www.accessexcellence.org/RC/VL/GG/ dna_ molecule.php).
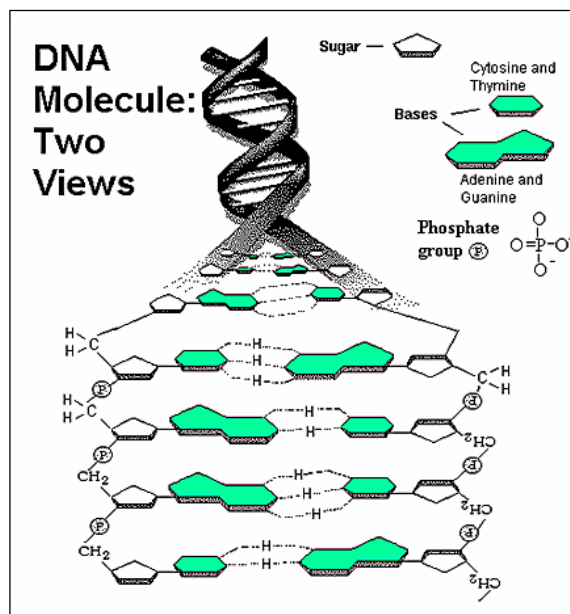
each atom contributes an electron and the two electrons remain largely between the two atoms holding them together. Though the two electrons with the same negative charge repel each other, they acquire opposite spins and share a spatial orbital located mostly in between the two atoms, holding the two nuclei together in a bond.

3. Intermolecular Interactions in Water and DNA

In DNA, we not only have numerous such covalent bonds but also have other interactions which are called hydrogen bonding and π–π interactions or π stacking (see *Figure* 2), the details of which we will address in this series of articles. These have been called non-covalent interactions in the literature to differentiate them from the covalent interactions mentioned above [6]. The DNA is one gigantic molecule (could be as long as 3 cm!) and molecular biology is an established field now. Hence the hydrogen bonding occurring in DNA can be loosely considered as intra-molecular hydrogen bonding. Hydrogen bonding occurs in water as well and in fact it is the hydrogen bonding that makes water what it is, i.e., the

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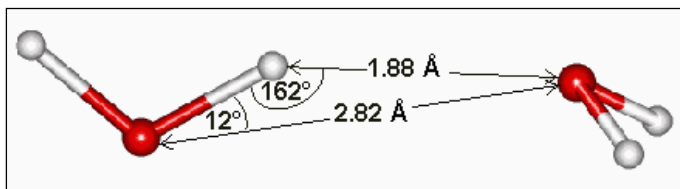
molecule without which life as we know would not exist. However, in water hydrogen bonding is intermolecular, i.e., hydrogen bonding links two molecules of water. In liquid and solid phases, each water molecule is typically hydrogen bonded to four water molecules forming a network. The structure of water dimer is shown in *Figure* 3 and that found typically in liquid water is shown in *Figure* 4.

4. van der Waals Equation

That intermolecular forces exist must be obvious, as without them all substances would have remained gases at all temperatures. Indeed, when cooled to lower temperatures all gases without exception condense to become liquids or solids. However, some gases become liquids at much higher temperatures than others. For example, water vapour condenses at 100 °C while hydrogen sulphide (H_2S) condenses at the much lower temperature of –60 °C. Evidently, the intermolecular forces
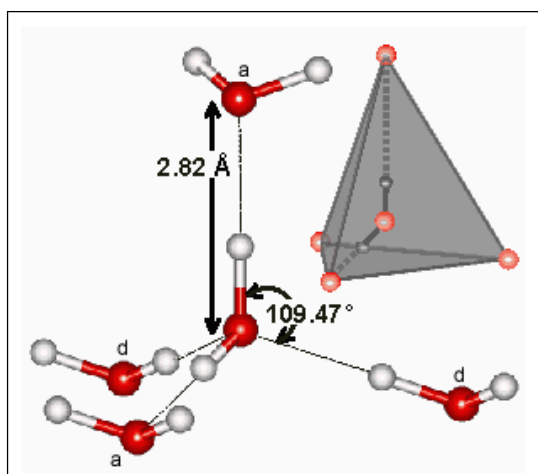

Figure 4. Typically each water molecule has four hydrogen bonds in liquid and solid phases of water as shown by the dotted lines forming an extended network. The oxygen atoms form a tetrahedron with one at the center and the other four at the corners as shown in the inset. In ice the hydrogen bonds lead to a rigid structure. However, in liquid water these hydrogen bonds can be broken and formed easily and it is important to realize that a static structure cannot represent the liquid water at all.

in water are much stronger than those in hydrogen sulphide. Intermolecular forces lead to deviation from the ideal gas law, which was put forward by Clapeyron in 1834 [7]. The ideal gas law assumes that molecules are point masses and they do not interact with each other. It relates the pressure (P), volume (V) and temperature (T) of n moles of a gas through the gas constant R as $PV = nRT$. van der Waals realized that the finite size of the molecules and intermolecular attraction would cause deviation from ideal gas behaviour. The finite size of the molecules reduces the available volume in a container. Intermolecular attraction reduces the pressure exerted by the molecules on the walls of a container, as they are pulled towards each other by this attraction. Hence, the real volume is less than that of the container and the real pressure would have been more than what is measured but for the intermolecular attraction. Based on these empirical reasons, van der Waals proposed the equation named after him, in 1867 in his PhD thesis [8].

$$\left(P \ + \ \frac{a}{n^2 V^2} \right) (V \ - \ nb) \ = \ nRT \ .$$

The constant a depends on the intermolecular potential which controls the intermolecular interaction and b is the excluded volume from the container that is not available for the gas molecules to occupy due to the finite size of the molecule.

5. van der Waals Molecules

The term 'van der Waals molecules' is used to describe the weakly-bound complexes that are bound by 'van der Waals' forces. This statement has a circuitous logic and one of the main reasons is that van der Waals did not spell out the nature of the intermolecular forces he invoked to account for the deviation from ideal gas law. Hence, all intermolecular forces can be safely considered to be van der Waals forces. However, one must add that there is no unanimous view about what is meant

by van der Waals forces [9]. In this series of articles, we take van der Waals forces to imply all intermolecular forces. Among chemists, recently another term is becoming popular and that is 'closed-shell interaction', first proposed by Bader [10].

As mentioned above, a covalent bond is formed when an electron from each atom is shared to form the bond. The H_2 molecule formed by the two H atoms is a classic example for a covalent bond. This is called 'shared-shell interaction'. In an 'ionic bond' such as found in KCl (in the gas phase), an electron from potassium is transferred to Cl and so we have K^+ and Cl^- forming KCl molecule. Both K^+ and Cl^- have closed shells of electrons and an ionic bond would be a closed-shell interaction. Of course, both of these are intra-molecular interactions. Ionic bonding could be found not only between two atoms, but also between two groups of atoms such as in ammonium nitrate NH_4NO_3, having the positive ammonium ion and the negative nitrate ion. In van der Waals molecules we neither have two electrons from two atoms forming a bond or an electron from one transferred to another. van der Waals molecules also have a closed-shell interaction, as the electrons from both the interacting molecules are largely retained within themselves and still they experience an attractive interaction. Thus when these interactions result in condensation of a molecule, the identity of the molecule within its liquid and solid phases remains intact. Hence the name closed-shell interaction.

## 6. Nature of van der Waals Forces

6.1 *Dipole-Dipole Interaction*

What is the nature of van der Waals forces? According to Debye [11], only in the beginning of the 20th century (several decades after the van der Waals equation) did physicists start wondering about the interpre-

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Figure 5. Structure of (LiF)₂ is experimentally observed to be cyclic as shown in the right-hand side where the two dipoles are oriented anti-parallel. δ+/δ– represent a partial positive/negative charge.
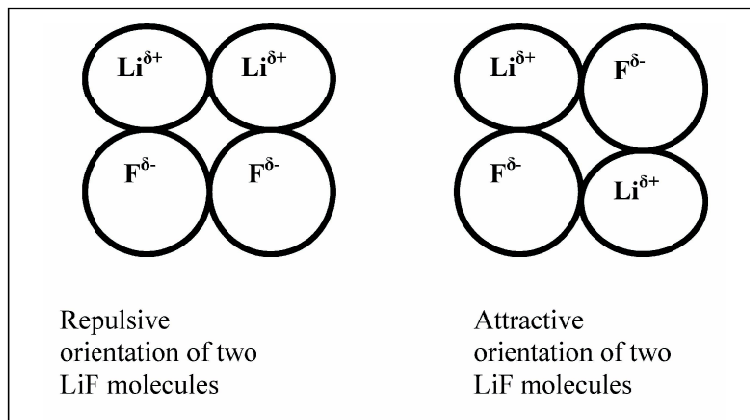
tation of van der Waals' universal molecular attraction. Though molecules do not have any net positive or negative charge, it was realized that they could be rigid assembly of charges with no resultant net charge. We could have a partial +ve charge in one end and an equivalent negative charge in another end creating a dipole moment as shown for the molecule LiF in *Figure* 5. The lithium atom carries a partial positive charge in this molecule ($\delta+$) and the fluorine atom carries an equivalent negative charge ($\delta-$). If another LiF molecule comes near, it would preferentially align in such a way that there is a net attraction as shown in *Figure* 5. The dipoles are oriented anti-parallel for net attraction. At a high enough temperature, LiF molecules could rotate freely leading to all possible mutual orientations and hence no net attraction. At lower temperatures, orientations with negative potential energy would be preferred. W H Keesom in 1912 considered this scenario and derived an expression for attraction between two dipoles [12]. This attraction is electrostatic in nature and it is part of electrostatic interactions – specifically a dipole-dipole interaction.

6.2 *Higher and Induced Moments*

Molecules that do not have an electric dipole moment (such as CH_4, C_6H_6 and CO_2) also condense at low temperatures. Hence, intermolecular forces must exist
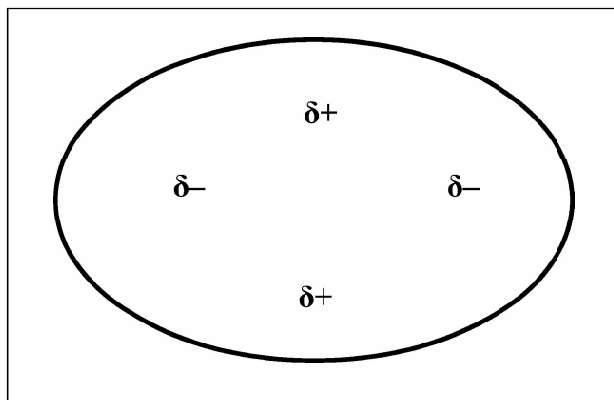
for non-polar molecules as well. These molecules could have higher moments, i.e., both C_6H_6 and CO_2 have a quadrupole moment with two partial positive and two equivalent negative charges arranged alternately, leading to a net resultant zero charge *(Figure* 6). CH_4 has an octupole moment, naturally involving eight alternating positive and negative charges. These can easily be visualized as a tetrahedron having all its four corners carrying a partial positive charge and all the four face centres carrying an equivalent negative charge (see *Figure* 4 inset for tetrahedron structure). However, the interactions from quadrupole and octupole moments, though real, are much weaker.

Debye realized that the molecules are not static and the charge distribution within the molecules could be deformed. A non-polar molecule could be polarized by interaction with a charge or a dipole and this can lead to a net attractive interaction. If the polarizing source is a dipole, this interaction would be called a 'dipole-induced dipole interaction'. Debye derived an expression for the potential energy for this dipole-induced dipole interaction in 1920 [13]. A complex formed between the inert gas Ar and HF, which could be written as ArHF is a classic example for this interaction. Naturally, the induced moments could also be of higher order such as quadrupole, octupole, etc.

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6.3 *Dispersive Forces*

Electrostatic interactions between permanent and induced multipole moments could explain the intermolecular forces to a large extent. However, they could not explain why rare gas atoms such as Ar and He condense. These have spherical charge distributions. In 1923, London came up with an explanation for the interaction between two rare gas atoms [14]. He reasoned that these atoms should have an instantaneous distribution of charges that is not spherical, though on average it would be spherical. Thus an instantaneous dipole moment in an Argon atom can interact with that of a neighbouring Ar atom. These instantaneous dipole moments need to be correlated for a net attractive interaction. The forces that arise from the correlation of instantaneous dipoles are called 'London dispersive forces'.

If an atom can have an instantaneous dipole moment, there is no reason why a molecule cannot. Clearly, all molecules can have attraction from electrostatic (interaction between permanent multipole moments), inductive (interaction between permanent and induced multipole moments) and dispersive (interaction between instantaneous multipole moments) forces. While these forces can be attractive or repulsive depending on the orientation (see *Figure* 5), as the molecules approach each other, strong repulsive forces between them start dominating due to the overlap of the electron cloud around them. This explains why the molecules do not coalesce into each other but retain their identity by keeping a distance between them even when they are condensed into liquids or solids. The optimum distance between them is where the net binding energy is the highest for a given molecule.

6.4 *Hydrogen Bonding*

Though van der Waals forces operate in both condensed

and gas phases, van der Waals molecules typically refer to the weakly-bound complexes formed at very low temperatures in a supersonic expansion. The binding energy is typically very low ranging from as low as 1 kJ mol^{-1} to about 42 kJ mol^{-1}, though there is no hard and fast rule about these limits. Clearly the van der Waals molecules are bound because of electrostatic, inductive or dispersive forces and more often due to a combination of all these forces.

What is the nature of the intermolecular forces in water, i.e., what is hydrogen bonding? A look at the structure of $(H_2O)_2$ and comparison with that of $(LiF)_2$ gives an important clue! It is not simple electrostatic interaction. If it were, the water dimer would have had a structure in which the dipole moments of the two H_2O molecules are anti-parallel. In water dimer we have one H atom from the first water molecule, which has a net partial positive charge pointing towards the electron rich region in the other water molecule, i.e., towards the lone pair of electrons in the oxygen atom. One could compare $(LiF)_2$ with $(HF)_2$; observations are similar. The HF dimer has F-H...F linear and the LiF dimer is cyclic. Clearly the dipole-dipole interaction dominates the latter and something more is involved in the former, i.e., hydrogen bonding. Buckhingham had shown some time ago that the inclusion of multipole moments of H_2O and HF in the intermolecular interaction would lead to the experimentally observed linear structures for the respective dimers [15]. However, there have been several crucial experimental evidences in the last decade which point to the partly covalent nature of hydrogen bonding, though it would contribute only to a small extent (about 5–10 %) in the total interaction [16]. Thus hydrogen bonding involves all the intermolecular forces discussed above and in addition the chemical forces in the form of a partial covalent bond.

7. Conclusion

Clearly hydrogen bonding could be considered as part of the van der Waals forces, though it is not a widely accepted view among chemists. In the subsequent articles in this series, we plan to present some examples of van der Waals molecules. One example each for systems with predominantly dipole-dipole, dipole-induced dipole, dispersion and hydrogen bonding interactions will be discussed in detail. For completeness, it is also planned to include one example each for covalent and ionic bonding within a molecule. These articles will appear in the forthcoming issues.

Suggested Reading

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