Van der Waals Forces

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Van der Waals is named after the Dutch physicist Johannes Diderik van der Waals. The importance of Van der Waals forces cannot be underestimated because it plays a fundamental role in physical chemistry, physics, and nanotechnology. To put it simply, Van der Waals forces are one of many different types of forces that hold matter together within a cell (1). However, compared to the ionic bonds that hold the crystal sodium chloride together or the covalent bonds in a diamond, they are weaker in electrostatic force. Van der Waals forces do have unique properties that make them the dominant force in certain situations (1).

Dispersion forces are considered a type of Van der Waals force because dispersion forces are the weakest of all intermolecular forces. The dispersion force is called the London dispersion force, and it is named after Fritz London, who first proposed its existence in 1930(5). London dispersion forces are intermolecular forces that occur between atoms and nonpolar molecules, resulting from the electrons' motion. However, van der Waals forces are described as a mixture of London dispersion forces which are instantaneously induced dipoles, Debye forces between the induced and permanent dipoles, and the Keesom force, which are between permanent molecular dipoles whose rotational orientations are averaged over time (3). The three most known van der Waals forces are the already discussed London dispersion forces, dipole-dipole, and Hydrogen bonding. The interactions between two atoms for van der Waals and London dispersion forces are that they only occur in molecules with permanent dipoles. Hydrogen bonding can only be bonded to oxygen or nitrogen (sometimes fluorine), and it has unique properties of high boiling point and surface tension. An example of a molecule that undergoes hydrogen bonding is water (H_2O).

Van der Waals forces have many different characteristics. Firstly, it is additive, which is just saying that many intermolecular interactions are joined together to form a singular force. Secondly, they are non-directional, which means they can attract molecules from all directions. Most importantly, they can only occur over a short range, and the interaction is more significant when the molecules are closer to one another.

Van der Waal forces are electrostatic forces that attract neutral molecules to one another in solids, liquids, and gases. When neutral particles collide with one another within a threshold distance, the electrons from one particle are pulled toward the nucleus of the other particle, which causes polarization (2). This is where the electron-deficient domain ($\delta+$) of one particle attracts the electron-rich domain ($\delta-$) of another particle (London dispersion force which is a process known as the Brownian motion (4).

Van der Waal forces have attractive interaction between atoms, resulting from induced dipoles, and repulsive interactions due to the overlap of the electron clouds between two atoms when they get past the threshold distance. "Van der Waals forces are nonspecific interactions that can form between any kinds of molecules, regardless of chemical structure" (Schwarzenbach et al., 2003) (6). Individual van der Waal bonds are

short-lived, but van der Waals bonding can achieve strong bonds If many bonds are formed across the substance and the surface, which has its advantages because at any given time van der Waals forces can prevent desorption. An example where this links with a real-life example would be the binding of a high molecular weight matter like protein to a surface (6).

The total energy of Van der Waals interactions

The total energy of Van der Waals forces can be approximated by the Lennard-Jones expression (Figure 1), where the x-axis is the distance (r) or y-axis energy potential (7). The commonly used expression for Lennard-Jones potential is given in figure 1 but can also be written as:

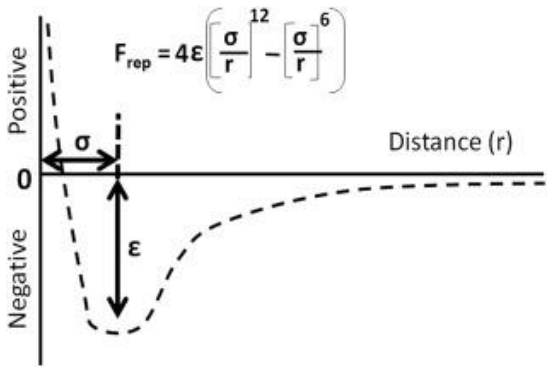

Figure 1: graph of Lennard-Jones potential function.

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Where V(r) is the energy potential, ε is the depth of the potential well (usually referred to as the "dispersion energy"), and the potential well is a region surrounding the local minimum of the potential energy, which can be thought of as a unit of energy. σ is the distance where the particle-particle potential energy V is zero (usually referred to as the "size of the particle") and is a unit of length, and r is the distance between the two centers of the molecules. To find the minima of the energy potential you set:

$$\frac{DV(r)}{dt} = 0$$

The Lennard-Jones potential has a minimum (7):

$$r = r_{min} = 2^{\frac{1}{6}}\sigma$$

where the potential energy has the value of (7):

$$V = -\varepsilon$$

The Lennard-Jones potential is a simplified model that describes the interactions between simple atoms and molecules. As seen in figure 1, when the two particles are at an infinite distance apart, the probability of the two particles interacting is minimal (at the lowest value). As the distance of separation decreases, the probability of the two particles interacting increases until it reaches a certain threshold where the two particles

reach the region of separation where the particles are bound together, and the potential energy decreases from zero to a negative value (7).
While the two particles have bounded, the distance between the centers will continuously decrease until it reaches equilibrium which is the separation distance where the minimum potential energy is reached.
Suppose the particles are pushed toward one another past. In that case, the region of separation (equilibrium distance) repulsion starts to occur because particles are too close to each other that their electrons are forced to occupy each other's orbitals (2).

Van der Waals interactions

Van der Waals forces come from weak attraction forces between two atoms from atomic or molecular dipoles. The weak forces lead to a weak and short-range force. The form of Van der Waals interactions is usually a repulsive interaction and the London dispersion force energy of the dipole-dipole interaction. The interactions can be modeled by using the functions below:

$$Repulsion\ energy\colon be^{-\alpha r}\ or\ \frac{b}{r^n}$$

$$Attractive\ potential\colon\ -\frac{a}{r^6}$$

"Where n is often given as 12 as in the Lennard-Jones potential" (Douglas et al.,1993) (8). The sum to find all the pairwise forces acting between the two bodies is required to calculate the surface force between the two bodies (8). To calculate the net force between the two flat plates would be:

$$F = -\frac{A_H}{6\pi d^3}$$

"Where AH is the Hamaker constant and d is the separation between 2 surfaces" (Horn, 1990; Wan et al.,1992). The Hamaker constant completely depends on the medium of contact. Assuming constant separation between two surfaces d_0. Wv, which is the specific interaction energy per unit area, is (8):

$$W_v = \int_{d_0}^{\infty} \frac{A_H}{6\pi x^3}\,dx = \frac{A_H}{12\pi(d_0)^2}$$

A typical value of Wv due to van der Waals would be <0.01 Jm-2. With the given expressions and functions, it is possible to model the repulsion energy and the attractive potential energy while finding the net force and specific interaction of the forces due to van der Waals forces (8).

Interfacial phenomena

Van Der Waals can be categorized into three different forces, which are Keesom, Debye, and London, and using figure 2 (below), the different forces are shown how the two different particles interact with one another.

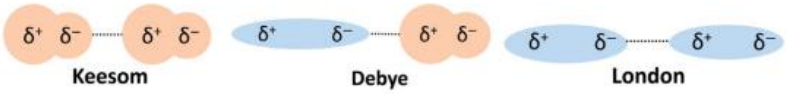

Figure 2 how the interactions for different van der Waal forces work

As seen in figure 2, Keesom forces are when two polarized molecules interact due to their difference in charge distribution. For Debye forces, the molecule with a permanent dipole induces charge distribution to neighbor particles that do not have any dipole moments. London forces mainly focus on molecules that do not have permanent dipoles. So, the fluctuations in the electron cloud would lead to temporary changes to the charge, which leads to a charge redistribution to nearby molecules, and it can be modeled using the expression below (4).

$$U(r) = -\frac{C}{r^6}$$

Where C is a constant that depends on the component and r is the intermolecular distance (4).

There exists another force between electron-poor and rich atoms called dipole-dipole interactions, where the effect of the bond decrease as the length increases. Thus, it would change depending on the state of the matter. Especially when it goes from vapor to liquid or solid. Coulombic forces also develop in charged atoms to find the nature (attraction or repulsion), and the magnitude depends on the sign (positive or negative), charge, distance, and separation. So, an expression to find the magnitude for two oppositely charged ions would be:

$$(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2}$$

Where Q is the charge, r is the distance between them from the center of the atom, and ϵ_0 is the dielectric constant (4).

Van der Waals forces play a significant part in the real world and have many real-life applications that are commonly used. From the research conducted, there is an ideal distance where the two molecules should be for interaction to occur. The amount of energy for each type of van der Waals force can be calculated, and the attraction forces, repulsion forces, and charge redistribution can be modeled to find how they differ from different distances. Van der Waals is significant in real-life examples for many different species. An example would be in animals would be that spiders and geckos use van der Waals to scale up smooth surfaces, and for some animals, it is used to walk on water. Van der Waals forces also play a vital role in protein structures, especially in folding and stabilizing the structure. They are also crucial in polymer formations, physical chemistry, and nanotechnology. These are just a couple of real-life examples of van der Waals that occur in our everyday lives.

Annotated bibliography

(1)

"Van Der Waals Forces." *Encyclopædia Britannica*, Encyclopædia Britannica, Inc., https://www.britannica.com/science/van-der-Waals-forces

(2)

Ashok K.Singh PhD, et al. "Structure, Synthesis, and Application of Nanoparticles." *Engineered Nanoparticles*, Academic Press, 12 Feb. 2016, https://www.sciencedirect.com/science/article/pii/B9780128014066000029.

(3)

Tadmor, Rafael. *The London-Van Der Waals Interaction Energy between ... - Iopscience*. https://iopscience.iop.org/article/10.1088/0953-8984/13/9/101

(4)

Hadjittofis, E, et al. "Interfacial Phenomena." *Developing Solid Oral Dosage Forms (Second Edition)*, Academic Press, 6 Jan. 2017, https://www.sciencedirect.com/science/article/pii/B978012802447800008X.

(5)

Libretexts. "London Dispersion Interactions." *Chemistry LibreTexts*, Libretexts, 27 Feb. 2022, https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/Atomic_and_Molecular_Properties/Intermolecular_Forces/Specific_Interactions/London_Dispersion_Interactions.

(6)

Keil, R G, and L M Mayer. "Mineral Matrices and Organic Matter." *Treatise on Geochemistry (Second Edition)*, Elsevier, 6 Nov. 2013, https://www.sciencedirect.com/science/article/pii/B978008095975701024X.

(7)

Schwerdtfeger, Peter, et al. *ACS Publications: Chemistry Journals, Books, and References* https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22%22&field2=AllField&text2=&publication=&accessType=allContent&Earliest=&ref=pdf.

(8)

Kuech, T F. “Integration of Dissimilar Materials.” *Comprehensive Semiconductor Science and Technology*, Elsevier, 4 Feb. 2011, https://www.sciencedirect.com/science/article/pii/B9780444531537001061.