

Physical Adsorption Forces

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This assignment gives a short description of the forces responsible for the process of Physical Adsorption. The fundamental interacting force of physisorption is the van der Waals force.

Physical Adsorption Forces

Physical Adsorption or Adsorption is the attraction of atoms or molecules from an adjacent gas or liquid to an exposed solid surface. Such attraction forces (adhesion or cohesion) align the molecules into layers ("films") onto the existent surface. Since such surface films exist there must be some stabilizing interactions leading to such a state of gas/liquid atoms on solid surface.

The formation of surface films may be driven by

- **long range weak forces** which are present between two polar molecules, a polar and a non polar molecule and even between two non polar molecules. These forces are collectively called the van der waal forces and is of three types due to a specific type of interaction between molecules.
- **short range strong ionic or metallic forces** which may finalize the setting of new layers onto the solid surface (without generating new chemical species) — as salt deposits (crystalline growth) from super-saturated solutions OR as metal vapor deposition onto metallic surfaces.

Covalent forces at solid surfaces will always create new chemical species because the formation of covalent solids involves energy transfers that penetrate deep into the bulk and are far beyond the surfaces. These are valence electron rearrangements (phase transitions) at the whole scale of the involved bulk.^[1]

Van der waal Forces^[2]

The van der Waals force (or van der Waals interaction), named after Dutch scientist Johannes Diderik van der Waals, is the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules. The term includes:

- Force between two permanent dipoles (Keesom force).

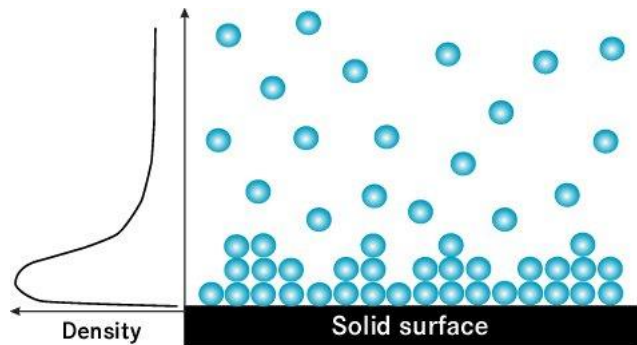


Figure 2: Triple layer adsorption on a solid surface and representation of the density distribution

- Force between a permanent dipole and a corresponding induced dipole (Debye force).
- Force between two instantaneously induced dipoles (London dispersion force).

Van der Waals forces are relatively weak compared to normal chemical bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics. Van der Waals forces define the chemical character of many organic compounds. They also define the solubility of organic substances in polar and non-polar media.

- All van der Waals forces are anisotropic (except those between two noble gas atoms), which means that they depend on the relative orientation of the molecules.
- The Lennard-Jones potential is often used as an approximate model for the isotropic part of the total (repulsion plus attraction) van der Waals force as a function of distance.
- Van der Waals forces are responsible for certain cases of pressure broadening (van der Waals broadening) of spectral lines and the formation of van der Waals molecules

Keesom Interaction^[3]

Keesom interaction is the interaction between two polar molecules (two dipoles). The potential energy of interaction is a complicated function of their relative orientation. It has the following properties:

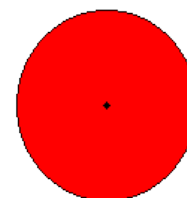
- In a fluid of freely rotating molecules, the interaction energy between dipoles should average to zero because forces will be present in all directions and average is zero.
- However the potential energy is a function of relative orientation and molecules are actually not completely free to rotate. There comes a non zero average interaction between polar molecules.
- The potential energy comes out as $-C/r^6$
- The negative sign indicates the interaction is attractive.
- The constant C depends on dipole moments, permittivity of the medium and Temperature.
- Inverse dependence of C on temperature indicates that greater thermal motion overcomes the mutual orientating effects of the dipoles at higher temperatures.
- The dependence on inverse 6th power of distance arises from the inverse 3rd power of the interaction potential energy weighted by the energy in the Boltzmann term, which is also proportional to the inverse 3rd power of distance.
- Such interactions are present in a HCl molecule as shown.



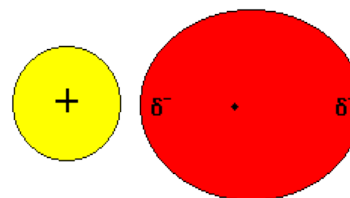
Debye Interaction or Dipole Induced Dipole Interaction^[4]

This interaction is the force between a permanent dipole and a corresponding induced dipole. It has the following properties:

- Non polar molecules acquire an induced dipole moment in an electric field and this induced moment is only temporary and disappears as soon as the field is removed. The field may be due to the presence of nearby dipoles.
- The average interaction energy comes out again as $-C/r^6$.
- The interaction is again attractive.
- The constant C however is not the same as Keesom interaction but depends on dipole moment of the permanent dipole, polarizability of the non polar molecule and permittivity of the medium.
- The constant is independent of temperature and hence thermal motion has no effect on the averaging process.
- The dependence on inverse 6th power of distance arises from the inverse 3rd power dependence of the field and the inverse 3rd power of dependence of the potential energy of interaction between permanent and induced dipoles.
- ***Ion Chromatography uses the principle of dipole induced dipole interactions to separate aromatics.***



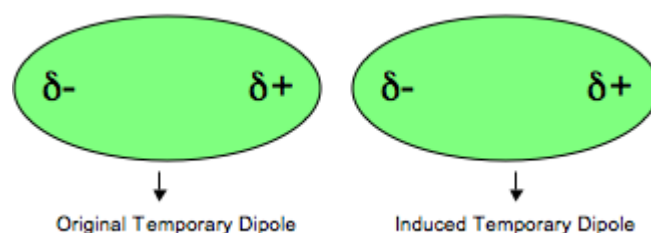
Spherical atom with no dipole. The dot indicates the location of the nucleus.



Upon approach of a charged ion, electrons in the atom respond and the atom develops a dipole.

London Dispersion Forces^[5]

London dispersion force is the interaction between two non polar molecules. The existence of such forces appears non-trivial however if we consider the probabilistic interpretation of the position of electrons around the nucleus, we can easily understand the origin of these forces. Since an electron has a probability to be found in a particular zone around the nucleus it is possible that at a certain instant the electron density is more skewed in a particular direction than the other. The resulting fluctuating instantaneous dipole can now induce dipole moment in the nearby non polar molecules resulting in a net interaction between them, and thus interaction does not average out to zero. This interaction has the following properties:



- Polar molecules can also interact by these forces but the time average of each fluctuating dipole corresponds to the permanent dipole.
- The interaction energy comes out again as $-C/r^6$.
- The negative sign indicates an attractive interaction.
- The constant C now depends on polarizability of the two fluctuating temporary dipoles, the ionisation energies of two molecules and relative permittivity of the medium.
- The interaction is dependent on the inverse 6th power of distance between the two interacting molecules.
- London forces become stronger as the atom or molecule in question becomes larger. This is due to the increased polarizability of molecules with larger, more dispersed electron clouds.
- ***Casimir effect is a consequence of London Dispersion Forces.***

The Total Attractive Interaction^[6]

For molecules where hydrogen bonding is not present we can calculate the total attractive interaction as the sum of the Keesom, Debye and London Dispersion interactions as $-C_6/r^6$.

- Here the total interaction will obviously be attractive hence a negative sign.
- The constant C_6 is a constant depending on the properties of interacting molecules.
- The total interaction is dependent of the 6th power of distance between interacting molecules.
- The important point here is that the above equation has **limited validity**.
- Because the above formulas are for dipole interactions which are dominant only if the average separation of the molecules is large. We should also consider higher order multipole interactions.
- Also the expressions have been derived assuming molecules can rotate reasonably freely. But in solids and rigid media interaction will be dependent only on 3rd power of distance as the Boltzmann averaging is irrelevant when molecules are trapped in a fixed orientation.
- Another error comes from the fact that energy of interaction of 3 or more molecules may not be the sum of pair-wise interaction energies alone.

Repulsive Interactions^{[7][8][9]}

Van der waal forces are attractive forces which may result in three cases as explained above. However there also exists another type of interaction which is repulsive in nature and is a direct consequence of Pauli's exclusion principle. It is this interaction which prevents the complete collapse of matter to nuclear densities. This interaction has the following properties:

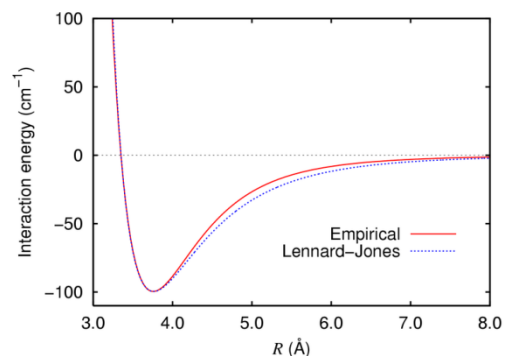
- The repulsive interactions can be thought of as resulting from the coulombic repulsions between electrons and nucleus of two molecules when they are brought near to each other.
- Note that electronic energies will also increase on moving closer and closer towards the nucleus. Thus, **the basic stability problem for an atom** was solved by the Heisenberg's Uncertainty Principle which gave an inequality saying that position measurement can be made more accurate only at the expense of making momentum measurement even lesser accurate. Hence there exists a finite lower bound to the energy and atoms are stable in that state. ^[x]
- Another interpretation of the repulsive interactions can be as a direct consequence of the **Pauli Exclusion Principle**, which states that any two particles are excluded from having the same set of quantum numbers. Thus the rule forbids the electrons from occupying the same quantum state **and electrons have to "pile on top** of each other" within an atom.
- Pauli's exclusion principle is responsible for the fact that ordinary bulk **matter is stable and occupies volume**. Atoms therefore cannot be squeezed too closely together.
- In conductors and semi-conductors, free electrons have to share entire bulk space. Thus, their **energy levels stack up, creating band structure** out of each atomic energy level. Many mechanical, electrical, magnetic, optical and chemical properties of solids thus are the direct consequence of Pauli exclusion.
- These repulsive interactions vary exponential with distance ($e^{-r_0/r}$) however due to ease and efficiency of using r^{12} the magnitude of these forces can also be considered as $(r_0/r)^{12}$.
- Obviously the forces become dominating when $r_0/r < 1$ that is when distance is smaller than critical distance r_0 .

Total Interactions^{[10][11]}

The net effect of the attractive and repulsive interactions can be easily understood in terms of a critical distance above which attractive forces will dominate and below which repulsive forces will dominate. Such a critical distance will exist because repulsive interactions depend roughly on the 12th power of distance and as such will rise rapidly at very small distances.

One model for total interaction is the **Lennard-Jones Potential**. It is given by

$$V = 4\epsilon \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right] \quad ; \epsilon \text{ is the depth of the potential well}$$



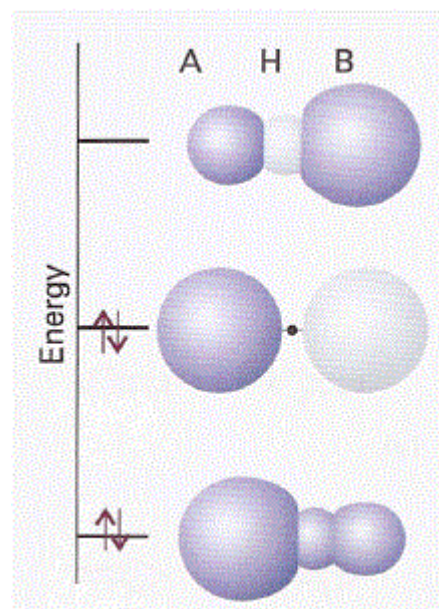
Another general equation for potential energy of total interactions is given by **Mie Potential**

$$V = [C_n/r^n - C_m/r^m]$$

Hydrogen Bonding^[12]

The types of forces described above are general in nature in the sense that these will exist for all molecules. However there exists one another interaction besides covalent and ionic bonds which is possessed only by molecules having a particular constitution. Hydrogen bonding has the following features:

- The name bonding is used to signify the strength of these forces. A hydrogen bond can be as strong as 155 kJ/mol in case of F-H...F. Thus these interaction lie somewhat between chemical bonds and van der Waal interactions.
- The interaction arises only in molecules where an entity of the type A-H...B is possible where A and B are highly electronegative atoms or species and B possesses a lone pair of electrons.
- Mostly nitrogen atom(N), oxygen atom(O) and fluorine atom(F) containing molecules show hydrogen bonding but is not restricted to only these.
- The interaction can be thought of as resulting from the attractive interaction between partial positive charge formed on Hydrogen due to electronegative A and the available lone pair of electrons of B.
- In terms of molecular orbital theory, since three atoms will form three molecular orbitals of different energy and these orbitals have to be filled by four electrons, two from the A-H bond and two from the lone pair of B. Out of three two orbitals will be filled by these electrons and a high energy orbital will remain vacant. Hence there is a net lowering of energy and interaction is stabilizing.
- Intermolecular hydrogen bonding is responsible for the **high boiling point** of water (100 °C) compared to the other group 16 hydrides that have no hydrogen bonds. Intramolecular hydrogen bonding is partly responsible for the secondary, tertiary, and quaternary structures of proteins and nucleic acids. It also plays an important role in the structure of polymers, both synthetic and natural.



Some Interesting Applications

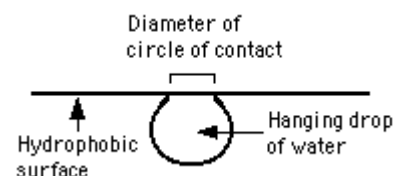
1. **Dry Glue**^{[13][14][15]}: The ability of geckos - which can hang on a glass surface using only one toe - to climb on sheer surfaces has been attributed to van der Waals force, although a more recent study suggests that water molecules of roughly monolayer thickness (present on virtually all natural surfaces) also play a role.

The toes of live Tokay geckos are highly hydrophobic, but adhered equally well to strongly hydrophobic and strongly hydrophilic, polarizable surfaces. This remarkable adhesive property of gecko setae is merely a result of the size and shape of the tips and may also be a result of the particular style of gecko movement. Gecko toes are pads covered with millions of the microscopic hairs that have even tinier split ends, called spatulae. This intricate design enables an electric force that attracts molecules to each other — the van der Waals force — to supply the energy to hold a gecko to a surface.



Researchers announced in a paper published in the June 18–22, 2007 issue of the Proceedings of the National Academy of Sciences that using this technique they have created a synthetic “gecko tape” with four times the sticking power of a natural gecko foot. Particularly effective has been a checkerboard carpet of this material, which can be peeled and re-adhered repeatedly without weakening.

2. **Measuring the magnitude of van der Waal forces**^[16]: If you sprinkle a few drops of water on a Teflon surface say a frying pan then water droplets move freely on the surface. But very small droplets stick to the surface of Teflon. Now we know that Teflon which is a polymer made of repeating- $\text{CF}_2\text{-CF}_2$ - units and is a very good non stick material. Which implies that the water droplets are not sticking on the surface but actually levitating because they can not stick.



Actually the water droplets are held on the surface of Teflon by van der Waal forces because if one goes on to flip the Teflon pan he will observe that small water droplets do not fall down. Since no other interaction other than van der Waal force is possible the magnitude of van der Waal force must be equal to the weight of the water droplet. Hence we can measure the magnitude of this force.

References

1. <http://en.wikipedia.org/wiki/Adsorption>
2. http://en.wikipedia.org/wiki/Van_der_Waals_force
3. Atkins' Physical Chemistry
4. Atkins' Physical Chemistry
5. Atkins' Physical Chemistry
6. Atkins' Physical Chemistry
7. Atkins' Physical Chemistry
8. http://en.wikipedia.org/wiki/Pauli_exclusion_principle
9. The stability of matter and quantum electrodynamics – Elliot H. Lieb
10. Atkins' Physical Chemistry
11. http://en.wikipedia.org/wiki/Lennard-Jones_potential
12. Atkins' Physical Chemistry
13. http://en.wikipedia.org/wiki/Dry_glue
14. <http://www.clemson.edu/newsroom/articles/2009/august/geckos.php5>
15. Evidence for van der Waals adhesion in gecko setae - Kellar Autumn
16. <http://www.science-projects.com/vdWForce.htm>