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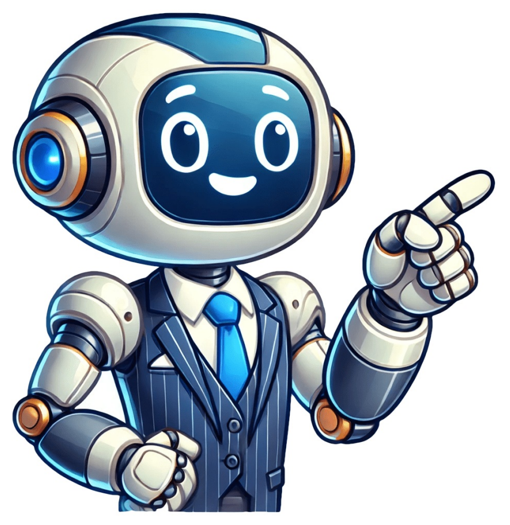

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In this solid form, methane molecules are held together by intermolecular forces, such as Van der Waals forces, to form a solid structure.Force of attraction or repulsion between molecules and neighboring particlesAn intermolecular force (IMF; also secondary force) is the force that mediates interaction between molecules, including the electromagnetic forces of attractionor repulsion which act between atoms and other types of neighbouring particles (e.g. atoms or ions). Intermolecular forces are weak relative to intramolecular forces the forces which hold a molecule together. For example, the covalent bond, involving sharing electron pairs between atoms, is much stronger than the forces present between neighboring molecules.[1] Both sets of forces are essential parts of force fields frequently used in molecular mechanics.The first reference to the nature of microscopic forces is found in Alexis Clairaut's work Thorie de la figure de la Terre, published in Paris in 1743.[2] Other scientists who have contributed to the investigation of microscopic forces include: Laplace, Gauss, Maxwell, Boltzmann and Pauling.Attractive intermolecular forces are categorized into the following types:Hydrogen bondingIondipole forces and ioninduced dipole forceCation, and bondingVan der Waals forces Keesom force, Debye force, and London dispersion forceCationcation bondingSalt bridge (protein and supramolecular)Information on intermolecular forces is obtained by macroscopic measurements of properties like viscosity, pressure, volume, temperature (PVT) data. The link to microscopic aspects is given by virial coefficients and intermolecular pair potentials, such as the Mie potential, Buckingham potential or Lennard-Jones potential.In the broadest sense, it can be understood as such interactions between any particles (molecules, atoms, ions and molecular ions) in which the formation of chemical (that is, ionic, covalent or metallic) bonds does not occur. In other words, these interactions are significantly weaker than covalent ones and do not lead to a significant restructuring of the electronic structure of the interacting particles. (This is only partially true. For example, all enzymatic and catalytic reactions begin with a weak intermolecular interaction between a substrate and an enzyme or a molecule with a catalyst, but several such weak interactions with the required spatial configuration of the active center of the enzyme lead to significant restructuring changes the energy state of molecules or substrate, which ultimately leads to the breaking of some and the formation of other covalent chemical bonds. Strictly speaking, all enzymatic reactions begin with intermolecular interactions between the substrate and the enzyme, therefore the importance of these interactions is especially great in biochemistry and molecular biology,[3] and is the basis of enzymology).Main article: Hydrogen bondA hydrogen bond refers to the attraction between a hydrogen atom that is covalently bonded to an element with high electronegativity, usually nitrogen, oxygen, or fluorine, and another highly electronegative atom.[4] The hydrogen bond is often described as a strong electrostatic interaction. However, it also has some features of covalent bonding: it is directional, stronger than a van der Waals force interaction, produces interatomic distances shorter than the sum of their van der Waals radii, and usually involves a limited number of interaction partners, which can be interpreted as a kind of valence. The number of hydrogen bonds formed between molecules is equal to the number of active pairs. The molecule which donates its hydrogen is termed the donor molecule, while the molecule containing lone pair participating in H bonding is termed the acceptor molecule. The number of active pairs is equal to the common number between number of hydrogens the donor has and the number of lone pairs the acceptor has.Hydrogen bonding in waterThough both are not depicted in the diagram, water molecules have four active bonds. The oxygen atoms two lone pairs interact with a hydrogen each, forming two additional hydrogen bonds, and the second hydrogen atom also interacts with a neighbouring oxygen. Intermolecular hydrogen bonding is responsible for the high boiling point of water (100C) compared to the other group 16 hydrides, which have little capability to hydrogen bond. 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.[5]Main article: Salt bridge (protein and supramolecular)The attraction between cationic and anionic sites is a noncovalent, or intermolecular interaction which is usually referred to as ion pairing or salt bridge.[6]It is essentially due to electrostatic forces, although in aqueous medium the association is driven by entropy and often even endothermic. Most salts form crystals with characteristic distances between the ions; in contrast to many other noncovalent interactions, salt bridges are not directional and show in the solid state usually contact determined only by the van der Waals radii of the ions.Inorganic as well as organic ions display in water at moderate ionic strength I similar salt bridge as association G values around 5 to 6 kJ/mol for a 1:1 combination of anion and cation, almost independent of the nature (size, polarizability, etc.) of the ions.[7] The G values are additive and approximately a linear function of the charges, the interaction of e.g. a doubly charged phosphate anion with a single charged ammonium cation accounts for about 2x5 = 10 kJ/mol. The G values depend on the ionic strength I of the solution, as described by the Debye-Hckel equation, at zero ionic strength one observes G = 8 kJ/mol.Dipoledipole interactions (or Keesom interactions) are electrostatic interactions between molecules which have permanent dipoles. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. These interactions tend to align the molecules to increase attraction (reducing potential energy). An example of a dipoledipole interaction can be seen in hydrogen chloride (HCl): the positive end of a polar molecule will attract the negative end of the other molecule and influence its position. Polar molecules have a net attraction between them. Examples of polar molecules include hydrogen chloride (HCl) and chloroform (CHCl3). H + Cl H + Cl {\displaystyle {\overset {\color {Red}\delta +}{{\ce {H}}}}-{\overset {\color {Red}\delta -}{{\ce {Cl}}}}\cdots {\overset {\color {Red}\delta +}{{\ce {H}}}}-{\overset {\color {Red}\delta -}{{\ce {Cl}}}}} Often molecules contain dipolar groups of atoms, but have no overall dipole moment on the molecule as a whole. This occurs if there is symmetry within the molecule that causes the dipoles to cancel each other out. This occurs in molecules such as tetrachloromethane and carbon dioxide. The dipoledipole interaction between two individual atoms is usually zero, since atoms rarely carry a permanent dipole.The Keesom interaction is a van der Waals force. It is discussed further in the section "Van der Waals forces".Iondipole and ioninduced dipole forces are similar to dipoledipole and dipoleinduced dipole interactions but involve ions, instead of only polar and non-polar molecules. Iondipole and ioninduced dipole forces are stronger than dipoledipole interactions because the charge of any ion is much greater than the charge of a dipole moment. Iondipole bonding is stronger than hydrogen bonding.[8]An iondipole force consists of an ion and a polar molecule interacting. They align so that the positive and negative groups are next to one another, allowing maximum attraction. An important example of this interaction is hydration of ions in water which give rise to hydration enthalpy. The polar water molecules surround themselves around ions in water and the energy released during the process is known as hydration enthalpy. The interaction has its immense importance in justifying the stability of various ions (like Cu2+) in water.An ioninduced dipole force consists of an ion and a non-polar molecule interacting. Like a dipoleinduced dipole force, the charge of the ion causes distortion of the electron cloud on the non-polar molecule.[9]Main article: van der Waals forceThe van der Waals forces arise from interaction between uncharged atoms or molecules, leading not only to such phenomena as the cohesion of condensed phases and physical absorption of gases, but also to a universal force of attraction between macroscopic bodies.[10]The first contribution to van der Waals forces is due to electrostatic interactions between rotating permanent dipoles, quadrupoles (all molecules with symmetry lower than cubic), and multipoles. It is termed the Keesom interaction, named after Willem Hendrik Keesom.[11] These forces originate from the attraction between permanent dipoles (dipolar molecules) and are temperature dependent.[10]They consist of attractive interactions between dipoles that are ensemble averaged over different rotational orientations of the dipoles. It is assumed that the molecules are constantly rotating and never get locked into place. This is a good assumption, but at some point molecules do get locked into place. The energy of a Keesom interaction depends on the inverse sixth power of the distance, unlike the interaction energy of two spatially fixed dipoles, which depends on the inverse third power of the distance. The Keesom interaction can only occur among molecules that possess permanent dipole moments, i.e., two polar molecules. Also Keesom interactions are very weak van der Waals interactions and do not occur in aqueous solutions that contain electrolytes. The angle averaged interaction is given by the following equation: d 1 2 d 2 2 24 2 0 2 r 2 k B T r 6 = V , {\displaystyle {\frac {-d_{1}^{2}d_{2}^{2}}{24\pi ^{2}\varepsilon _{0}^{2}\varepsilon _{r}^{2}k_{\text{B}}Tr^{6}}}=V,} where d = electric dipole moment, 0 {\displaystyle \varepsilon _{0}} = permittivity of free space, r {\displaystyle \varepsilon _{r}} = dielectric constant of surrounding material, T = temperature, k B {\displaystyle k_{\text{B}}} = Boltzmann constant, and r = distance between molecules.The second contribution is the induction (also termed polarization) or Debye force, arising from interactions between rotating permanent dipoles and from the polarizability of atoms and molecules (induced dipoles). These induced dipoles occur when one molecule with a permanent dipole repels another molecule's electrons. A molecule with permanent dipole can induce a dipole in a similar neighboring molecule and cause mutual attraction. Debye forces cannot occur between atoms. The forces between induced and permanent dipoles are not as temperature dependent as Keesom interactions because the induced dipole is free to shift and rotate around the polar molecule. The Debye induction effects and Keesom orientation effects are termed polar interactions.[10]The induced dipole forces appear from the induction (also termed polarization), which is the attractive interaction between a permanent multipole on one molecule with an induced (by the former di/multi-pole) 31 on another.[12][13][14] This interaction is called the Debye force, named after Peter J. W. Debye.One example of an induction interaction between permanent dipole and induced dipole is the interaction between HCl and Ar. In this system, Ar experiences a dipole as its electrons are attracted (to the H side of HCl) or repelled (from the Cl side) by HCl.[12][13] The angle averaged interaction is given by the following equation: d 1 2 2 16 2 0 2 r 2 r 6 = V , {\displaystyle {\frac {-d_{1}^{2}\alpha _{2}}{16\pi ^{2}\varepsilon _{0}^{2}\varepsilon _{r}^{2}r^{6}}}=V,} where 2 {\displaystyle \alpha _{2}} = polarizability.This kind of interaction can be expected between any polar molecule and non-polar/symmetrical molecule. The induction-interaction force is far weaker than dipoledipole interaction, but stronger than the London dispersion force.Main article: London dispersion forceThe third and dominant contribution is the dispersion or London force (fluctuating dipoleinduced dipole), which arises due to the non-zero instantaneous dipole moments of all atoms and molecules. Such polarization can be induced either by a polar molecule or by the repulsion of negatively charged electron clouds in non-polar molecules. Thus, London interactions are caused by random fluctuations of electron density in an electron cloud. An atom with a large number of electrons will have a greater associated London force than an atom with fewer electrons. The dispersion (London) force is the most important component because all materials are polarizable, whereas Keesom and Debye forces require permanent dipoles. The London interaction is universal and is present in atom-atom interactions as well. For various reasons, London interactions (dispersion) have been considered relevant for interactions between macroscopic bodies in condensed systems. Hamaker developed the theory of van der Waals between macroscopic bodies in 1937 and showed that the additivity of these interactions renders them considerably more long-range.[10]Bond typeDissociation energy(kcal/mol)[15]Dissociation energy(kJ/mol)NoteIonic lattice2504000[16]110020000Covalent bond302601301100Hydrogen bond112450About 5kcal/mol (21kJ/mol) in waterDipoledipole0.5228London dispersion forces