

1 A brief review of how atoms and molecules interact (Is-draelachvili)

In the course on solid state physics, you will learn how atoms and molecules, arranged in ordered structures, behave. You will learn the mechanical and electronic properties of these crystals which will be then used as a basis to understand more elaborated solid-state phenomena. In this course, a new course in our curriculum, we will attempt to also move from the behavior of isolated atoms and molecules to their collective properties, building on the elements you have learned in your previous classes. Differently from solid-state, we will be focusing on essentially all the materials which surround you (and which compose yourself !) which are not solid.

Let us start from a classification of the interactions between atoms and/or molecules. In your "Struttura della Materia (Fisica Atomica)" class last year you have learned the the solution of quantum mechanical calculations based on the Schroedinger equation provide in principle the electronic distribution (the charge density) for fixed nuclei positions. The resulting charge distribution can then be analyzed to predict the interactions between different atoms/molecules.

As a frame for looking at the way atoms, molecules, macromolecules and particles interact and the relative importance of such interactions, we start by reviewing them.

1.0.1 R-dependence of interatomic forces

Suppose the attractive potential between two molecules or particles to be of the general form $w(r) = -C/r^n$, where n is an integer. Now consider a region of space where the number density of these molecules is ρ . This region can be a solid, a liquid, a gas, or even a region in outer space extending over astronomical distances. Let us add all [the interaction energies of one particular molecule with all the other molecules in the system. The number of molecules in a region of space between r and $(r + dr)$ away will be $\rho 4\pi r^2 dr$ (since $4\pi r^2 dr$ is the volume of a spherical shell of radius r and thickness dr , i.e., of area $4\pi r^2$ and thickness dr). The total interaction energy of one molecule with all the other molecules in the system will therefore be given by

$$\text{total energy} = \int_{\sigma}^L w(r) \rho 4\pi r^2 dr = -4\pi C \rho \int r^{2-n} dr = \frac{-4\pi C \rho}{(n-3)\sigma^{n-3}} \left[1 - \left(\frac{\sigma}{L} \right)^{n-3} \right]$$

where σ is the diameter of the molecules and L is the size of the system (e.g., the dimensions of a solid or the size of the box containing a gas). We can see that since σ must be smaller than L (i.e., $\sigma/L < 1$), large distance contributions to the interaction will disappear only for values of n greater than 3 (i.e., for $n = 4, 5, 6, \dots$). But for n smaller than 3, the second term will be greater, and the contribution from more distant molecules will dominate over that of nearby molecules. In such cases the size of the system must be taken into account, as occurs for the gravitational force where $n = 1$, and where distant planets, stars, and even

galaxies are still strongly interacting with each other. In later chapters we shall see that theoretical derivations of intermolecular force potentials do indeed predict that n always exceeds 3 asymptotically, and it is for this reason that the bulk properties of solids, liquids and gases do not depend on the volume of material or on the size of the container (unless these are extremely small) but only on the forces between molecules in close proximity to each other. Important long-range intermolecular forces also exist, especially between macroscopic particles and surfaces, but their effective range of action rarely exceeds 100 nm.

1.1 COVALENT OR CHEMICAL BONDING FORCES

When two or more atoms come together to form a molecule, as when two hydrogen atoms and one oxygen atom combine to form a water molecule, the forces that tightly bind the atoms together within the molecule are called covalent forces, and the interatomic bonds formed are called covalent bonds. Closely allied to covalent bonds are metallic bonds. In both cases the bonds are characterized by the electrons being shared between two or more atoms so that the discrete nature of the atoms is lost. Depending on the position an atom (or element) occupies in the periodic table, it can participate in a certain number of covalent bonds with other atoms. This number or stoichiometry is known as the atomic valency; for example, it is zero for the inert gases (e.g., argon) which cannot normally form divalent bonds with other atoms, one for hydrogen, two for oxygen, three for nitrogen and four for carbon. A further characteristic of covalent bonds is their directionality, that is, they are directed or oriented at well-defined angles relative to each other. Thus, for multivalent atoms, their covalent bonds determine the way they will coordinate themselves in molecules or in crystalline solids to form an ordered three-dimensional lattice. For example, they determine the way carbon atoms arrange themselves to form the perfectly ordered diamond structure. Covalent forces are of short range, that is, they operate over very short distances of the order of interatomic separations (0.1-0.2 nm). Table 3.1 shows the strength of some common covalent bonds. As can be seen they are mainly in the range 100-300 $k_B T$ per bond (200-800 kJ/mol), and they tend to decrease in strength with increasing bond length — a characteristic property of most intermolecular interactions.

1.2 PHYSICAL FORCES: COULOMB INTERACTIONS

The potential energy for the Coulomb interaction between two charges Q_1 and Q_2 is given by

$$w(r) = \frac{Q_1 Q_2}{4\pi\epsilon r} = \frac{z_1 z_2 e^2}{4\pi\epsilon r}$$

where ϵ is the permittivity or dielectric constant of the medium and r the distance between the two charges. The expression on the right is commonly used for ionic interactions, where the magnitude and sign of each ionic charge is given in terms of the elementary

charge ($e = 1.602 \times 10^{-19} C$) multiplied by the ionic valency z . For example, $z = q = 1$ for monovalent cations such as Na^+ , $z = -1$ for monovalent anions such as Cl^- , $z = 2$ for divalent cations such as Ca^{2+} , etc.

Let us put the strength of the Coulomb interaction into perspective. For two isolated ions (e.g., Na^+ and Cl^-) in contact, r is now the sum of the two ionic radii (0.276 nm), and the binding energy $w(r)$ is

$$w(r) = \frac{-(1.602 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12})(0.276 \times 10^{-9})} = 8.4 \times 10^{-19} J$$

In terms of the thermal energy $k_B T = (1.38 \times 10^{-23})(300) = 4.1 \times 10^{-21} J$ at 300K, this energy turns out to be of order 200 $k_B T$ per ion pair in vacuum. viz. similar to the energies of covalent bonds. Only at a separation r greater than about 56 nm will the Coulomb energy fall below $k_B T$. We have thus established that the Coulomb interaction is very strong and of long range.

One very important aspect of Coulomb forces concerns the range of the interaction. The inverse-square distance dependence of the Coulomb force, the same as for the gravitational force, appears to make it very long ranged, in apparent contradiction with the statement that all intermolecular force laws must fall with distance faster than $1/r^4$ ($1/r^3$ for the energy). Since positive ions always have negative ions nearby, whether they are in a lattice or in solution, the electric field becomes screened and decays more rapidly away from them than from a truly isolated ion. We shall see that at large distances the decay is always exponential with distance, thus making all Coulomb interactions between ionic crystals, charged surfaces, and dissolved ions of much shorter range (though still of much longer range than covalent forces).

1.3 Are gravitational forces relevant ?

Let's try to do the same estimate for gravitational forces. The sodium mass is 23 atomic units, while the chlorine mass is 35.4 atomic units. The gravitational constant is $G = 6.67 \times 10^{-11} m^3/Kg/s^2$. Then

$$w(\sigma) = -G \frac{m_{Na} m_{Cl}}{\sigma} = 6.67 \times 10^{-11} \frac{23 \times 10^{-3}}{6.023 \times 10^{23}} \frac{35.4 \times 10^{-3}}{6.023 \times 10^{23}} \frac{1}{0.276 \times 10^{-9}} J = 5.4 \times 10^{-52} J$$

Comparing this number with the corresponding one for the electrostatic interaction clearly show that at atomic level gravitational forces are irrelevant.

1.4 POLAR MOLECULES

Most molecules carry no net charge, but many possess an electric dipole. For example, in the HCl molecule the chlorine atom tends to draw the hydrogen's electron towards itself, and this molecule therefore has a permanent dipole. Such molecules are called

polar molecules. The dipoles of some molecules depend on their environment and can change substantially when they are transferred from one medium to another, especially when molecules become ionized in a solvent. For example, the amino acid molecule glycine contains an acidic group on one side and a basic group on the other. In water this molecule exists as a dipolar molecule in the following form: basic acidic

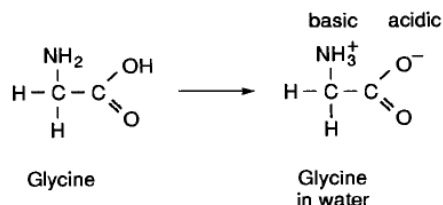


Figure 1:

Such dipolar molecules in water are also referred to as zwitterions (molecules ionized simultaneously in two different sites). Quite often the magnitude of the positive and negative charges on zwitterions are not the same, and these molecules therefore possess a net charge in addition to a dipole. Such molecules are then referred to as dipolar ions. It should already be apparent that the interactions and the solvent effects of polar molecules can be very complex. The dipole moment of a polar molecule is defined as

$$\mu = ql$$

where l is the distance between the two charges $+q$ and $-q$. Thus, for two electronic charges $q = e$ separated by $l = 0.1\text{nm}$, the dipole moment is $u = (1.602 \cdot 10^{-19})(10^{-10}) = 1.602 \cdot 10^{-29}\text{Cm} = 4.8D$. The unit of dipole moment is the Debye, where $1 \text{ Debye} = 1D = 3.336 \cdot 10^{-30}\text{Cm}$. Small polar molecules have moments of the order of $1D$. [Historically D was defined as the dipole moment resulting from two charges of opposite sign but an equal magnitude of 10^{-10} electrostatic units separated by 1 \AA]. Permanent dipole moments only occur in asymmetric molecules and thus not in single atoms. For isolated molecules, they arise from the asymmetric displacements of electrons along the covalent bonds, and it is therefore not surprising that a characteristic dipole moment can be assigned to each type of covalent bond. These values are approximate but very useful for estimating the dipole moments of molecules and especially of parts of molecules by vectorial summation of their bond moments. For example, the dipole moment of gaseous H_2O , where the HOH angle is

$$\theta = 104.5$$

may be calculated (knowing that the dipole moment of an OH group is $\mu_{OH} = 1.51 \text{ D}$) from

$$\mu_{H_2O} = 2 \cos(\theta/2)\mu_{OH} = 2 \cos(52.25^\circ)1.51 = 1.85D$$

1.5 ION-DIPOLE INTERACTIONS (4.2 Isd)

The second type of electrostatic pair interaction we shall consider is that between a charged atom and a polar molecule, for example, between Na^+ and H_2O . As an illustrative example we shall derive the interaction potential for this case from basic principles. Figure 4.1 shows a charge Q at a distance r from the centre of a polar molecule of dipole moment μ subtending an angle θ to the line joining the two molecules. The length of the dipole is l .

Since the electric field of the charge acting on the dipole is $E(r) = Q/4\pi\epsilon r$, we see that in general the energy of a permanent dipole μ in a field E may be written as

$$w(r, \theta) = -\mu \cdot \mathbf{E} = -\mu E(r) \cos \theta. \quad (1)$$

Equation gives the energy for the interaction of a charge Q and a 'point dipole' μ (for which $l = 0$) in a medium. Thus, when a cation is near a dipolar molecule maximum attraction (i.e., maximum negative energy) will occur when the dipole points away from the ion ($\theta = 0$), while if the dipole points towards the ion ($\theta = 180^\circ$) the interaction energy is positive and the force is repulsive. Figure 4.2 shows how the energy varies with distance for a monovalent cation ($z = +1$) interacting with a dipolar molecule of moment 1D in vacuum. The solid curves are based on the exact solution calculated from the two charges positions, while the dashed curves are for the point-dipole approximation, which shows itself to be surprisingly accurate down to fairly small separations. Only at ion dipole separations r below about $2l$ does the approximate equation deviate noticeably ($>10\%$) from that obtained using the exact formula. Thus, if the dipole moment arises from charges separated by less than about 0.1 nm, the point dipole approximation will be valid at all physically realistic intermolecular separations. However, for greater dipole lengths — as occur in zwitterionic molecules—the deviations may be large, thereby requiring that the energy be calculated in terms of the separate Coulombic contributions. In such cases the interactions are always stronger than expected from the point dipole approximation, as can be inferred from Fig. 4.2. It is also evident from Fig. 4.2 that the ion-dipole interaction is much stronger than $k_B T$ at typical interatomic separations (0.2-0.4 nm). It is therefore strong enough to bind ions to polar molecules and mutually align them. Let us calculate the vacuum interaction between some common ions and water molecules. We shall assume that the water molecule may be treated as a simple spherical molecule of radius 0.14 nm with a point dipole of moment 1.85 D. This is a gross oversimplification: the distribution of charges in a water molecule is much more complex than for a simple dipole, as will be discussed later. But for our present purposes, we may ignore this complication. Thus, for the monovalent ion Na^+ ($z = 1$, $a = 0.095$ nm) near a water molecule ($a = 0.14$ nm, $\mu = 1.85$ D), the maximum interaction energy will be given by

$$w(r, \theta = 0) = \frac{(1.60210^{-19})(1.85 \cdot 3.336 \cdot 10^{-30})}{4\pi(8.854 \cdot 10^{-12})(0.235 \cdot 10^{-9})^2} = 1.6 \cdot 10^{-19} \text{ J} = 39 k_B T \text{ or } 96 \text{ kJ mol}^{-1} \text{ at } 300K,$$

which compares surprisingly well with the experimental value of 100 kJ mol⁻¹. For the smallest monovalent ion Li⁺ ($a = 0.068$ nm), this rises to about 50 $k_B T$ or 125 kJ mol⁻¹

(experimental value: 142 kJ mol^{-1}), while for the small divalent cations Mg^{2+} ($z = 2$, $a = 0.065 \text{ nm}$) and Be^{2+} ($z = 2$, $a = 0.03 \text{ nm}$), it will rise even further to about $100 k_B T$ and $150 k_B T$, respectively. The strongly attractive interaction between ions and water is responsible for promoting the "ionic" nucleation of rain drops in thunderclouds. In other types of clouds the nucleation of water occurs around uncharged particles, molecules or molecular groups that have a strong affinity for water.

1.6 IONS IN POLAR SOLVENTS

When ion-water interactions take place in bulk water the above energies will be reduced by a factor of about 80, the dielectric constant of water; but even then the strength of the interaction will exceed $k_B T$ for small divalent and multivalent ions, and it is by no means negligible for small monovalent ions. But before we proceed it is essential to understand what this interaction energy means. Within the continuum approach let us consider the ion water interaction in bulk water as given by Eq. 1, where we note that it contains an orientation term $\cos \theta$. At large separations the water molecules would be randomly oriented relative to the ion, and if they remained randomly oriented right up to the ion, the interaction energy would be zero since the spatial average of $\cos \theta$ is zero. For an ion in a polar solvent, Eq. 1 therefore gives us an estimate of the free energy change brought about by orienting the polar solvent molecules around the ion, that is, the reference state of zero energy is for randomly oriented dipoles. We have therefore established that the ion dipole energies calculated for ions in water are comparable to or greater than $k_B T$ and reflect the strong aligning effect that small ions must have on their surrounding water molecules.

For small or multivalent ions in highly polar solvents, the strong orientation dependence of their ion-dipole interaction will tend to orient the solvent molecules around them, favouring $\theta = 0$ near cations and $\theta = 180^\circ$ near anions. Thus, in water Li^+ , Be^{2+} , Mg^{2+} and Al^{3+} ions have a number of water molecules orientationally bound to them. Such ions are called solvated ions or hydrated ions, and the number of water molecules they bind — usually between 4 and 6 — is known as their hydration number. It should be noted, however, that these bound water molecules are not completely immobilized and that they do exchange with bulk water, albeit more slowly. The hydration number is more of a qualitative indicator of the degree to which ions bind water rather than an exact value. Closely related to the hydration number is the effective radius or hydrated radius of an ion in water, which is larger than its real radius. Because smaller ions are more hydrated they tend to have larger hydrated radii than larger ions. Hydration numbers and radii can be deduced from measurements of the viscosity, diffusion, compressibility, conductivity, solubility, and various thermodynamic and spectroscopic properties of electrolyte solutions, the results rarely agreeing with one another.

More insight into the nature of ion hydration can be gained by considering the average time that water molecules remain bound to ions. In the pure liquid at room temperature the water molecules tumble about with a mean reorientation time or rotational correlation

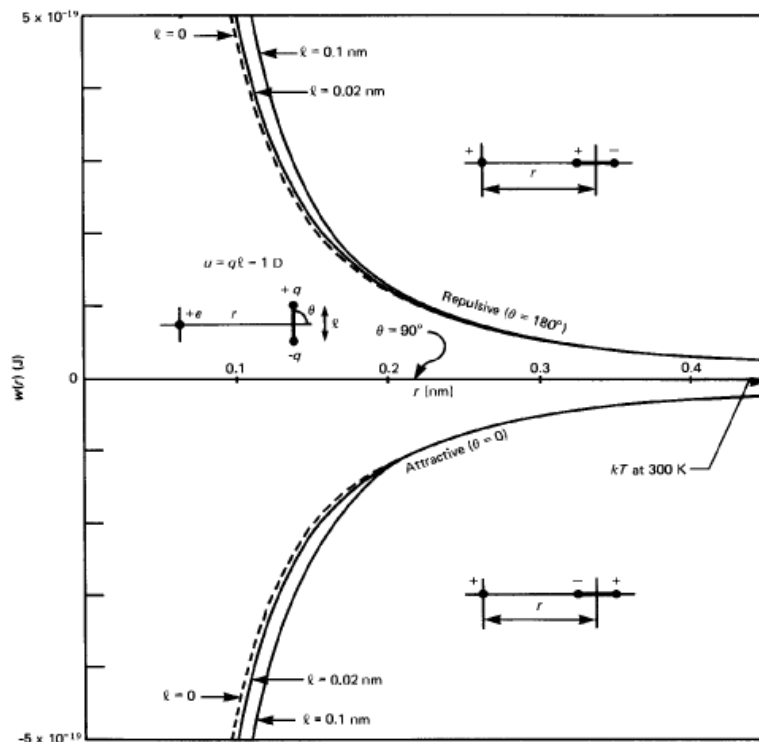


Fig. 4.2. Charge-dipole interaction energy in vacuum ($\epsilon = 1$) between a unit charge e and a dipole of moment $u = ql = 1$ D oriented at different angles θ to the charge. Solid lines are exact solutions, Eqs (4.3) and (4.4), for finite-sized dipoles with $l = 0.02$ nm and $l = 0.10$ nm; dashed lines are exact solutions for $l = 0$, which correspond to the approximate point-dipole formula, Eq. (4.5). Note that for typical interatomic spacings ($r \approx 0.3$ – 0.4 nm) the strength of the pair interaction greatly exceeds the thermal energy kT at 300 K.

time of about 10^{-11} s. This also gives an estimate of the lifetime of the water-water bonds formed in liquid water (the hydrogen bonds). But when the water molecules are near ions various techniques, such as oxygen nuclear magnetic resonance, show that the mean lifetimes or exchange rates of water molecules in the first hydration shell can be much longer, varying from 10^{-11} s to many hours. For very weakly solvated ions (usually large quantities monovalent ions) such as $\text{N}(\text{CH}_3)_4^+$, Cl^- , Br^- and I^- , these lifetimes are not much different from that for two water molecules, and they can even be shorter (referred to as negative hydration). Cations are generally more solvated than anions of the same valency since they are smaller — having lost rather than gained an electron. Thus, for K^+ , Na^+ and Li^+ the residence times of water molecules in the primary hydration shells are about 10^{-9} s. Divalent cations are always more strongly solvated than monovalent cations, and for Ca^{2+} and Mg^{2+} , the bound water lifetimes are about 10^{-8} s and 10^{-6} s, respectively. Even longer lifetimes are observed for very small divalent cations such as Be^{2+} (10^{-3} s), while for trivalent cations such as Al^{3+} , La^{3+} , and Cr^{3+} these can be many seconds or hours. In such cases the binding is so strong that an ion-water complex is actually formed of fixed stoichiometry. In fact, these quasi-stable complexes begin to take on the appearance of (charged) molecules and are often designated as such, e.g. $[\text{Mg}(\text{H}_2\text{O})_6]^+$, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$. In particular, protons (H^+) always associate with one water molecule, which goes by the name of the hydronium ion (H_3O^+), while three water molecules are solvated around this ion to form $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$. Likewise, the hydroxyl ion (OH^-) is believed to be solvated by three water molecules forming $\text{OH}^-(\text{H}_2\text{O})_3$.

1.7 DIPOLE-DIPOLE INTERACTIONS - 4.7

When two polar molecules are near each other there is a dipole-dipole interaction between them that is analogous to that between two magnets. For two point dipoles of moments μ_1 and μ_2 at a distance r apart and oriented relative to each other as shown in Fig. 2.2, the interaction energy may be derived by a procedure similar to that used to obtain the energy for the charge-dipole interaction, and we find

$$w(\vec{\mu}_1, \vec{\mu}_2) = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r}_{12})(\vec{\mu}_2 \cdot \hat{r}_{12})}{4\pi\epsilon r^3}$$

or equivalently

$$w(r, \theta_1, \theta_2, \phi) = -\frac{\mu_1\mu_2}{4\pi\epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]$$

This equation shows that maximum attraction occurs when two dipoles are lying in line, when the energy is given by

$$w(r, 0, 0, \phi) = -\frac{\mu_1\mu_2}{4\pi\epsilon r^3}$$

while for two dipoles aligned parallel to each other the energy $w(r, 90^\circ, 90^\circ, 180^\circ)$ is half of this value at the same inter-dipole separation, r . The equation also shows that for two equal

dipoles of moment 1 D, their interaction energy in vacuum will equal $k_B T$ at $r = 0.36$ nm when the dipoles are in line and at $r = 0.29$ nm when parallel. Since these distances are of the order of molecular separations in solids and liquids, we see that at normal temperatures dipolar interactions (alone) are strong enough to bind only very polar molecules.

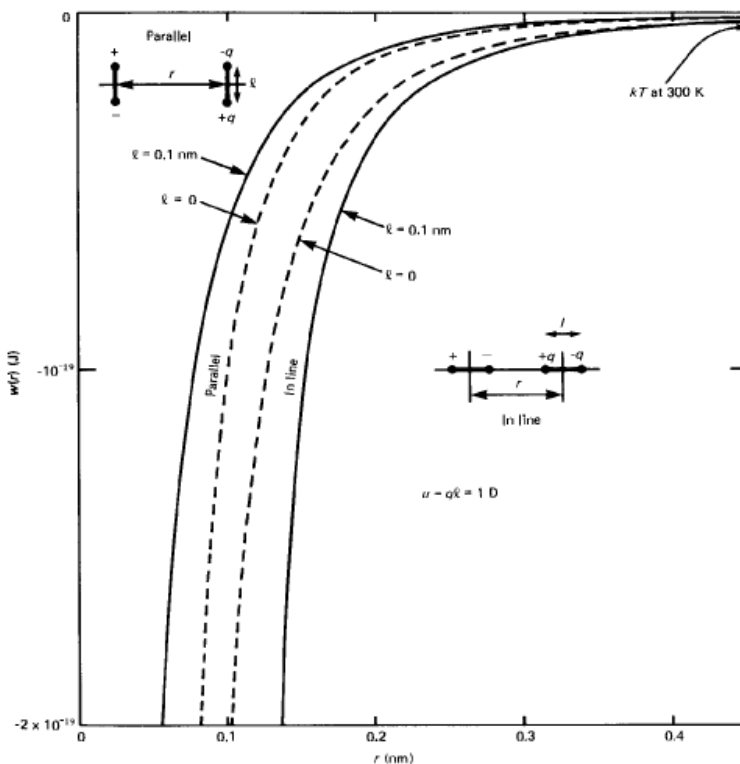


Fig. 4.3. Dipole-dipole interaction energy in vacuum between two dipoles each of moment 1 D. Note how much weaker this interaction is compared to the charge-dipole interaction (Fig. 4.2) and the large effect of finite dipole size.

Figure 4.3 shows the variation of the pair interaction energy with distance for two point dipoles of moments 1D approaching each other at different orientations; the solid curves are the exact solutions for finite-sized dipoles, here assumed to be of length $l = 0.1$ nm, while the dashed curves are based on Eq. (4.7) for two point dipoles. In general, we find that, even more than for the charge-dipole interaction, significant deviations from the ideal behaviour now occur for $r < 3l$, when Eq. (4.7) can no longer be used. At these smaller separations it is again necessary to analyse the interaction in terms of its individual charge-charge (Coulomb) contributions of which there will be four such terms for each pair of dipoles. The above calculations, and Fig. 4.3, appear to indicate that two dipoles always prefer to mutually orient themselves in line, but this is true only at the same value of r . Most dipolar molecules are also anisotropic in shape - being longer along the direction of the dipole, so that in practice the centres of two such cigar-shaped molecules can come

significantly closer together when they align in parallel, thereby making this interaction the more favourable one. The dipole-dipole interaction is not as strong as the previous two electrostatic interactions we considered, and for dipole moments of order 1D, it is already weaker than $k_B T$ at distances of about 0.35 nm in vacuum, while in a solvent medium this distance will be even smaller. This means that the dipole-dipole interaction, unlike the ion-dipole interaction, is usually not strong enough to lead to any strong mutual alignment of polar molecules in the liquid state. There are some exceptions, however, such as water whose small size and large dipole moment does lead to short range association in the liquid. The bond moments of OH^+ , NH^+ and FH^+ are unusually large. Since the electron-depleted H atom also has a particularly small size this means that other electronegative atoms such as -O, -N and -F can get quite close to these highly polar XH^+ groups and thus experience a very strong field. This results in a strong attractive force that can align neighbouring molecules possessing such groups (e.g., H_2O , NH_3 , HF , $\text{C}=\text{O}$, and many others) in both the liquid and crystalline state. Such liquids are called associated liquids, and the special type of interaction they experience is known as the hydrogen-bonding interaction. The hydrogen bonding interaction is no more than a particularly strong type of directional dipole-dipole interaction. Because of the small size of the $-\text{H}^+$ group it is far stronger than that predicted by the point dipole approximation. This interaction will be discussed further later on. For the moment, let us investigate the opposite situation: when the orientation dependence of dipole-dipole and ion-dipole interaction energies are much weaker than the thermal energy $k_B T$, and therefore unable to align molecules fully.

1.7.1 Mixing Energy and Entropy..... Average potential

At large separations or in a medium of high ϵ , when the angle dependence of the interaction energy falls below the thermal energy $k_B T$, dipoles can now rotate more or less freely. However, even though the values of $\cos \theta$, $\sin \theta$, etc. when averaged over all of space are zero, the angle-averaged potentials are not zero since there is always a Boltzmann weighting factor that gives more weight to those orientations that have a lower (more negative) energy.

We have learned from statistical mechanics that a description of the position and orientation of the dipole (assuming there is a fixed ion in the origin) can be calculated as

$$P(r, \theta) = \frac{e^{-\beta w(r, \theta)}}{Z}$$

where Z is the normalization

$$Z = \int r^2 dr \sin \theta d\theta d\phi e^{-\beta w(r, \theta)}$$

If we are interested only in the r dependence of the probability, we need to average over the angular variable

$$P(r) = \int P(r, \theta) \sin \theta d\theta d\phi$$

In this way, an angle-averaged potential $w(r)$ can be written as

$$P(r) = \frac{e^{-\beta w_{eff}(r)}}{Z'}$$

or

$$e^{-\beta w_{eff}(r)} = \frac{\int e^{-\beta w(r,\Omega)} d\Omega}{\int d\Omega} = \langle e^{-\beta w(r,\Omega)} \rangle_{\Omega}$$

where $d\Omega = \sin\theta d\theta d\phi$ corresponds to the polar and azimuthal angles θ and ϕ and the integration is over all of angular space.

You may be surprised that we are not calculating directly the angle-averaged potential. The reason is that in the averaging process we do not want to change the probability that the two interacting particles are found at distance r . Note that we have already significantly approximated the problem by assuming that the N -body problem can be reduced to a sum of independent two-body terms.

Considering first the interaction between **a charge and a dipole**, for which

$$w(r, \Omega) = -\mu E \cos\theta \quad E = \frac{Q}{4\pi\epsilon_0 r}$$

$$e^{-\beta w_{eff}(r)} = \frac{1}{Z'} \int d\Omega e^{-\beta w(r,\Omega)}.$$

To find the missing constant, consider that for $r \rightarrow \infty$, $w(r) = 0$, $e^{-\beta w(r)} = e^{-\beta w(r,\Omega)} = 1$. Then the proportionality constant has to be $1/4\pi$

$$e^{-\beta w_{eff}(r)} = \frac{\int d\phi \int e^{-\beta w(r,\Omega)} \sin\theta d\theta}{4\pi}$$

We may note the spatially averaged values of some angles:

$$\langle \cos^2 \theta \rangle = \frac{1}{4\pi} \int_0^\pi \cos^2 \theta \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{1}{3}$$

$$\langle \sin^2 \theta \rangle = \frac{1}{4\pi} \int_0^\pi \sin^2 \theta \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{2}{3}$$

$$\langle \sin^2 \phi \rangle = \langle \cos^2 \phi \rangle = \frac{1}{2}$$

$$\langle \sin \theta \rangle = \langle \cos \theta \rangle = \langle \sin \theta \cos \theta \rangle = 0$$

$$\langle \sin \phi \rangle = \langle \cos \phi \rangle = \langle \sin \phi \cos \phi \rangle = 0$$

The charge-dipole potential $w(r, \Omega)$ is

$$w(r, \Omega) = -\vec{\mu} \cdot \mathbf{E} = -\mu E \cos \theta \quad E = \frac{Q}{4\pi\epsilon_0 r^2}$$

$$\begin{aligned} e^{-\beta w_{eff}(r)} &= \frac{2\pi}{4\pi} \int_{-1}^1 d \cos \theta e^{\beta E \mu \cos \theta} \\ &= \frac{1}{2} \int_{-1}^1 dt e^{\beta E \mu t} \end{aligned}$$

and calling $A = \beta E \mu$

$$= \frac{1}{2} \frac{1}{A} \int_{-A}^A dt e^{At} = \frac{1}{2} \frac{1}{A} (e^A - e^{-A})$$

if A is small

$$\begin{aligned} &\approx \frac{1}{2} \frac{1}{A} \left[1 + A + \frac{A^2}{2} + \frac{A^3}{3!} + \dots - (1 - A + \frac{A^2}{2} - \frac{A^3}{3!} + \dots) \right] = \\ &= \frac{1}{A} (2A + \frac{2}{3!} A^3) = 1 + \frac{A^2}{3!} \end{aligned}$$

or, expanding the exponential

$$1 - \beta w_{eff}(r) = 1 + \frac{(\beta E \mu)^2}{6}$$

The angle-averaged free energy for the charge-dipole interaction is therefore,

$$w_{eff}(r) \approx -\frac{1}{6} \left(\frac{Q\mu}{4\pi\epsilon} \right)^2 \frac{1}{k_B T r^4}$$

which is attractive and temperature dependent. The presence of a $k_B T$ in the average potential reflects the thermodynamic origin of the interaction, which now contains some entropic component, in addition to the energetic ones. We will see more and more in this course on this effect.

Thus, for a monovalent ion interacting with the polar solvent molecules of a medium of dielectric constant ϵ the interaction potential spherically averages will supersede the non-averaged one (charge-dipole) at distances larger than $r = \sqrt{Q\mu/4\pi\epsilon k_B T}$, which for a monovalent ion in water, setting $Q = e$, $\mu = 1.85D$, $\epsilon = 80$, becomes roughly 0.2 nm (i.e., about 0.1 nm out from an ion of radius 0.1 nm).

We can now see why only water molecules of the first shell around ions sometimes become strongly restricted in their motion, and we may anticipate that this should be the sort of range around an ion over which the properties of the solvent may be substantially

different from the bulk values. For the dipole dipole interaction, a similar Boltzmann averaging of the interaction energy, over all orientations $(\theta_1, \theta_2, \phi)$ leads to an angle-averaged interaction free energy of

$$w(r) = -\frac{\mu_1^2 \mu_2^2}{3(4\pi\epsilon)^2 k_B T} \frac{1}{r^6}$$

The Boltzmann-averaged interaction between two permanent dipoles is usually referred to as the orientation or **Keesom** interaction. It is one of three important interactions, each varying with the inverse sixth power of the distance, that together contribute to the total van der Waals interaction between atoms and molecules. The rotational averaged potentials show that beyond a certain distance the interaction energies fall faster than r^{-3} . In view of the previous analysis this confirms that neither ion-dipole nor dipole-dipole forces can produce long-range alignment effects in liquids.

1.8 Polarizability

1.8.1 Electronic contribution

We now enter the last category of electrostatic interactions we shall be considering those that involve molecular polarization, that is, the dipole moments induced in molecules by the electric fields emanating from nearby molecules. Actually, we have already been much involved with polarization effects: whenever the macroscopic dielectric constant of a medium entered into our consideration this was no more than a reflection of the way the molecules of the medium are polarized by the local electric field. Here we shall look at these effects in more detail, starting at the molecular level. All atoms and molecules are polarizable. Their (dipole) polarizability is defined according to the strength of the induced dipole moment μ_{ind} they acquire near an electric field E , viz.,

$$\mu_{ind} = \alpha E$$

For a non-polar molecule, the polarizability arises from the displacement of its negatively charged electron cloud relative to the positively charged nucleus under the influence of an external electric field. For polar molecules, there are other contributions to the polarizability, discussed in the next section. For the moment, we shall concentrate on the polarizabilities of non-polar molecules, which we shall denote by α_0 .

Polarizability can be calculated formally by quantum mechanics. You may have seen such a calculation for the hydrogen atom in a static electric field. From a classical point of view, to evaluate polarizability, one need to accept a reasonable simple model. Let us use the classical view of an atom as composed by a nuclear charge q and an homogeneous electronic density inside a sphere of radius R . The electron charge density is then

$$\rho_q = -\frac{q}{4\pi R^3/3}$$

Under the influence of an external field E the electron orbit is shifted by a distance d from the nucleus. Then the nucleus is subjected to two electric fields: the external field E and the field generated by the displaced charge density. Using Gauss theorem we can say that the electric field generated on the nucleus by the charge density is

$$4\pi d^2 E_q = \frac{\rho_q 4\pi d^3 / 3}{\epsilon_0} \quad \rightarrow \quad E_q = -\frac{qd}{4\pi R^3 \epsilon_0}$$

Then, by writing $E = E_q$,

$$\frac{qd}{4\pi R^3 \epsilon_0} = E \quad \rightarrow \quad \mu = 4\pi \epsilon_0 R^3 E$$

whence we obtain for the polarisability

$$\alpha_0 = 4\pi \epsilon_0 R^3$$

The unit of polarizability is therefore $4\pi \epsilon_0$ times a volume or $C^2 m^2 / J$. The polarizability of atoms and molecules that arises from such electron displacements is known as electronic polarizability. Its magnitude, apart from the $4\pi \epsilon_0$ term, is usually less than but of the order of the (radius)³ of the atom or molecule. For example, for water, $\alpha_0 / 4\pi \epsilon_0 = 1.48 \times 10^{-30} \text{ m}^3 = (0.114 \text{ nm})^3$, where 0.114 nm is about 15 % less than the radius of a water molecule (0.135 nm). Since the electronic polarizability is associated with displacements of electron clouds, it has long been recognized that the polarizability of a molecule can be obtained by simply summing the characteristic polarizabilities of its covalent bonds, since these are where the polarizable electrons are mostly localized.

1.8.2 Dipolar contribution

Up to now we have considered the polarizability arising solely from the electronic displacements in atoms and molecules. A freely rotating dipolar molecule (whose time-averaged dipole moment is zero) also has an orientational polarizability, arising from the effect of an external field on the Boltzmann-averaged orientations of the rotating dipole. Thus, in the presence of an electric field E these orientations will no longer time-average to zero but will be weighted along the field. If at any instant the permanent dipole μ is at an angle θ to the field E , its resolved dipole moment along the field is $\mu_z = \mu \cos \theta$, and its energy in the field is $-\mu E \cos \theta$, so that the angle-averaged induced dipole moment $\langle \mu_z \rangle$ is given by

$$\begin{aligned} \langle \mu_z \rangle = \mu_{ind} &= \frac{\int_{-1}^1 \mu \cos \theta e^{\beta \mu E \cos \theta} \sin \theta d\theta}{\int_{-1}^1 e^{\beta \mu E \cos \theta} \sin \theta d\theta} \\ &= \mu \frac{1}{\beta E \mu} \frac{\int_{\beta E \mu}^{\beta E \mu} x e^x dx}{\int_{\beta E \mu}^{\beta E \mu} e^x dx} \end{aligned}$$

Calling $A = \beta E \mu$

$$= \mu \frac{1}{A} \frac{\int_{-A}^A x e^x dx}{\int_{-A}^A e^x dx} = \mu \frac{1}{A} (A \coth(A) - 1)$$

From which

$$\frac{\langle \mu_z \rangle}{\mu} = \coth(\beta E \mu) - \frac{1}{\beta E \mu} \approx \frac{\beta E \mu}{3} - \frac{(\beta E \mu)^3}{45} + \frac{2(\beta E \mu)^5}{945}$$

At high T (or better at small $\beta E \mu$), we can stop at the first term in the expansion and write

$$\mu_{ind} = \langle \mu_z \rangle = \frac{\beta \mu^2 E}{3} \quad \mu E \ll k_B T$$

Since μ_{ind} is proportional to the field E , we see that the factor $\beta \mu^2/3$ provides an additional contribution to the molecular polarizability. This is known as the *orientational* polarizability:

$$\alpha_{orient} = \frac{\beta \mu^2}{3}$$

The total polarizability of a polar molecule is therefore

$$\alpha = \alpha_0 + \frac{\beta \mu^2}{3}$$

where μ is its permanent dipole moment. Thus, for example, a polar molecule of moment $\mu = 1D = 3.336 \times 10^{-30}$ C m at 300 K will have an orientational polarizability of

$$\alpha_{orient} = (4\pi\epsilon_0)8 \times 10^{-30} \text{m}^3$$

a value that is comparable to the electronic polarizabilities α_0 of molecules

In very high fields or at sufficiently low temperatures such that $\mu E \ll k_B T$, a dipolar molecule will become completely aligned along the field. When this happens (e.g., water near a small ion), the concept of a molecule's orientational polarizability breaks down, but the electronic polarizability still applies.

1.8.3 DIPOLE-INDUCED DIPOLE INTERACTIONS

The interaction between a polar molecule and a non-polar molecule is analogous to the ion-induced dipole interaction just discussed except that the polarizing field comes from a permanent dipole rather than a charge. For a fixed dipole μ oriented at an angle θ to the line joining it to a polarizable molecule, it may be shown that the magnitude of the electric field of the dipole acting on the molecule is

$$E = \frac{\mu(1 + 3 \cos^2 \theta)^{1/2}}{4\pi\epsilon_0 r^3}$$

TABLE 5.1 Electronic polarizabilities α_0 of atoms, molecules, bonds, and molecular groups^a

Atoms and molecules					
He	0.20	NH ₃	2.3	CH ₂ =CH ₂	4.3
H ₂	0.81	CH ₄	2.6	C ₂ H ₆	4.5
H ₂ O	1.48	HCl	2.6	Cl ₂	4.6
O ₂	1.60	CO ₂	2.6	CHCl ₃	8.2
Ar	1.63	CH ₃ OH	3.2	C ₆ H ₆	10.3
CO	1.95	Xe	4.0	CCl ₄	10.5
Bond polarizabilities					
Aliphatic	C—C	0.48	C—O	0.60	
Aromatic	C [≡] C	1.07	C=O	1.36	
	C=C	1.65	N—H	0.74	
Aliphatic	C—H	0.65	C—Cl	2.60	
	O—H	0.73	C—Br	3.75	
Molecular groups					
	C—O—H	1.28	CH ₂	1.84	
	C—O—C	1.13	Si—O—Si	1.39	
	C—NH ₂	2.03	Si—OH	1.60	

^a Polarizabilities α_0 are given in units of $(4\pi\epsilon_0)\text{\AA}^3 = (4\pi\epsilon_0)10^{-30} \text{ m}^3 = 1.11 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$. Note that when molecules are dissolved in a solvent medium their polarizability can change by up to 10%. Data compiled from Denbigh (1940), Hirschfelder et al. (1954) and Smyth (1955).

the interaction energy is therefore

$$w(r, \theta) = -\frac{1}{2}\alpha_0 E^2 = -\frac{1}{2} \frac{\mu^2 \alpha_0 (1 + 3 \cos^2 \theta)}{(4\pi\epsilon_0)^2 r^6}$$

(the factor 1/2 comes from the fact that it is necessary to account also the work requested to create the dipole $dW = \mathbf{E} \cdot qds = \mathbf{E} \cdot d\vec{\mu} = \alpha \mathbf{E} \cdot d\mathbf{E} = d(\alpha E^2/2)$)

For typical values of μ and α_0 , the strength of this interaction is small compared to $k_B T$. Hence one can expand the Boltzmann factor

$$e^{-\beta w_{eff}(r)} = \frac{1}{4\pi} \int e^{-\beta w(r, \Omega)} d\Omega \rightarrow 1 - \beta w_{eff}(r) = \frac{1}{4\pi} \int (1 - \beta w(r, \Omega)) d\Omega$$

or

$$w_{eff}(r) = -\frac{1}{2} \frac{\mu^2 \alpha_0 (1 + 3 \langle \cos^2 \theta \rangle)}{(4\pi\epsilon_0)^2 r^6} = -\frac{\mu^2 \alpha_0}{(4\pi\epsilon_0)^2 r^6} \quad (2)$$

since the angle average of $\cos^2 \theta$ is 1/3.

This is often referred to as the **Debye** interaction or the induction interaction. It constitutes the second of three inverse sixth power contributions to the total van der Waals interaction energy between molecules. The first we have already encountered in the angle-averaged dipole-dipole or Keesom interaction, which incidentally may also be

obtained from the previous expression by replacing α_0 by $\alpha_{orient} = \mu^2/3k_B T$ so that for two dipoles μ_1 and μ_2 it gives the Keesom free energy:

$$w_{eff}(r) = -\frac{\mu_1^2 \mu_2^2}{3k_B T (4\pi\epsilon_0)^2 r^6}$$

1.9 In a solvent....

The interaction between molecules or small particles in a solvent medium can be very different from that of isolated molecules in free space or in a gas. The presence of a suspending medium does more than simply reduce the interaction energy or force by a factor ϵ/ϵ_0 , as might appear from equations derived earlier. First, the intrinsic dipole moment and polarizability of an isolated gas molecule may be different in the liquid state or when dissolved in a medium. This depends in a complicated way on its interactions with the surrounding solvent and can usually only be found by experiment. Second a dissolved molecule can move only by displacing an equal volume of solvent from its path; hence, the polarizability in a medium must represent the excess polarizability of a molecule or particle over that of the solvent and must vanish when a dissolved particle has the same properties as the solvent. Qualitatively, we may say that if no electric field is reflected by a particle, it is 'invisible' in the solvent medium and consequently does not experience a force. The problem of knowing the excess or effective polarizability can be approached by treating a dissolved molecule or a small particle as a separate dielectric medium of a given size and shape. This continuum approach has an obvious advantage since the dielectric constant of a medium is usually known. Accordingly, a molecule i may be modelled as a dielectric sphere of radius a_i and dielectric constant ϵ_i . Now in a medium of dielectric constant ϵ , such a dielectric sphere will be polarized by a field E and acquire an excess dipole moment given by (Landau and Lifshitz, 1963, p. 44)

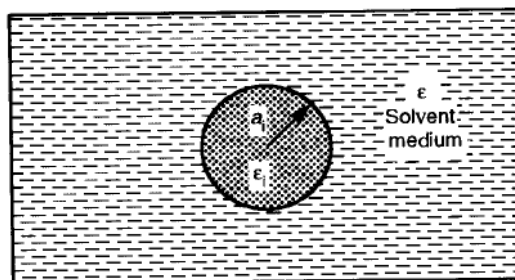
$$\mu_{ind} = 4\pi\epsilon_0\epsilon_r \left(\frac{\epsilon_i - \epsilon}{\epsilon_i + 2\epsilon} \right) a_i^3 E$$

so that its effective or excess polarizability in the medium is

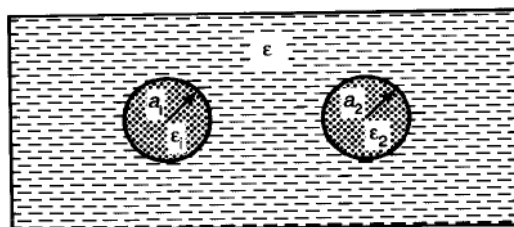
$$\alpha_i = 4\pi\epsilon_0\epsilon_r \left(\frac{\epsilon_i - \epsilon}{\epsilon_i + 2\epsilon} \right) a_i^3 = 3\epsilon_0\epsilon \left(\frac{\epsilon_i - \epsilon}{\epsilon_i + 2\epsilon} \right) v_i$$

where v_i is the volume of the molecule or sphere. This equation shows that for a dielectric sphere of high ϵ_i , in free space (where $\epsilon = 1$) its polarizability is roughly $\alpha_i \approx 4\pi\epsilon_0 a^3$, as previously found for a simple one-electron atom. Further, if $\epsilon > \epsilon_i$, the polarizability is negative, implying that the direction of the induced dipole is opposite to that in free space.

If we now consider two uncharged dielectric particles immersed in a medium, we obtain for the spherically averaged interaction potential



(a)



(b)

Fig. 5.3. A dissolved molecule or small solute particle can be modelled as a sphere of radius a_1 and dielectric constant ϵ_1 . Its total polarizability in a medium of dielectric constant ϵ is $\alpha_1 = 4\pi\epsilon_0\epsilon a_1^3(\epsilon_1 - \epsilon)/(\epsilon_1 + 2\epsilon)$.

$$w_{eff}(r) = -\frac{3k_B T}{r^6} \left(\frac{\epsilon_1 - \epsilon}{\epsilon_1 + 2\epsilon} \right) a_1^3 \left(\frac{\epsilon_2 - \epsilon}{\epsilon_2 + 2\epsilon} \right) a_2^3$$

which allows us to conclude that:

- (i) The net force between dissolved molecules or small particles in a medium can be zero, attractive, or repulsive, depending on the relative magnitudes of ϵ_1 , ϵ_2 and ϵ
- (ii) The interaction between any two identical uncharged molecules ($\epsilon_1 = \epsilon_2$) is always attractive regardless of the nature of the suspending medium. Interestingly, two microscopic air bubbles also attract each other in a liquid.

In addition we can expect that ions will be attracted to dissolved molecules of high dielectric constant (highly polar molecules where $\epsilon_2 > \epsilon$) but repelled from molecules of low dielectric constant (non-polar molecules where $\epsilon_2 < \epsilon$).

This approach will generally predict the right qualitative trends, but it is quantitatively somewhat model-dependent in that it treats solute molecules as if they were a uniform medium having bulk dielectric properties. It is essentially a continuum treatment where the molecular properties only appear in determining the molecular radius or volume. This may be valid for larger molecules, macromolecules, and small particles in solution but may fail for small molecules, especially when close together.

1.10 Dispersion Forces

The various types of physical forces so far described are fairly easy to understand since they arise from straightforward electrostatic interactions involving charged or dipolar molecules. But there is a further type of force, which like the gravitational force acts between all atoms and molecules, even totally neutral ones such as helium, carbon dioxide and hydrocarbons. These forces have been variously known as dispersion forces, London forces, charge-fluctuation forces, electrodynamic forces, and induced-dipole- induced-dipole forces. We shall refer to them as dispersion forces since it is by this name that they are most widely known. The origin of this name has to do with their relation to the dispersion of light in the visible and UV regions of the spectrum, as we shall see. The literature on this subject is quite voluminous, and the reader is referred to books and reviews. Dispersion forces make up the third and perhaps most important contribution to the total van der Waals force between atoms and molecules, and because they are always present (in contrast to the other types of forces that may or may not be present depending on the properties of the molecules) they play a role in a host of important phenomena such as adhesion, surface tension, physical adsorption, wetting, the properties of gases, liquids and thin films, the strengths of solids, the flocculation of particles in liquids, and the structures of condensed macromolecules such as proteins and polymers. Their main features may be summarized as follows:

1. They are long-range forces and, depending on the situation, can be effective from large distances (greater than 10 nm) down to interatomic spacings (about 0.2 nm).
2. These forces may be repulsive or attractive, and in general the dispersion force between two molecules or large particles does not follow a simple power law.
3. Dispersion forces not only bring molecules together but also tend to mutually align or orient them, though this orienting effect is usually weak.
4. The dispersion interaction of two bodies is affected by the presence of other bodies nearby. This is known as the non-additivity of an interaction.

Dispersion forces are quantum mechanical in origin and amenable to a host of theoretical treatments of varying complexity, the most rigorous of which would take us into the world of quantum electrodynamics. Their origin may be understood intuitively as follows: for a non-polar atom such as helium, the time average of its dipole moment is zero, yet at any instant there exists a finite dipole moment given by the instantaneous positions of the electrons about the nuclear protons. This instantaneous dipole generates an electric field that polarizes any nearby neutral atom, inducing a dipole moment in it. The resulting interaction between the two dipoles gives rise to an instantaneous attractive force between the two atoms, and the time average of this force is finite. For a simple semiquantitative understanding of how these forces arise, let us consider the following model, based on the interaction between two Bohr atoms. In the Bohr atom an electron is pictured as orbiting around a proton. The smallest distance between the electron and proton is known as the first Bohr radius a_0

The Bohr atom has no permanent dipole moment. However, at any instant there exists an instantaneous dipole of moment

$$\mu = a_0 e$$

whose field will polarize a nearby neutral atom giving rise to an attractive interaction that is entirely analogous to the dipole-induced dipole interaction discussed previously. The energy of this interaction in vacuum will therefore be given as (see the interaction energy of a dipole with a polarizable molecule, Eq. 2)

$$w(r) = -\frac{\mu^2 \alpha_0}{(4\pi\epsilon_0)^2} \frac{1}{r^6} = -\frac{e^2 a_0^2 \alpha_0}{(4\pi\epsilon_0)^2} \frac{1}{r^6}$$

where α_0 is the electronic polarizability of the second Bohr atom, which is approximately $4\pi\epsilon_0 a_0^3$.

To estimate the radius a_0 of the Bohr atom, we remember that a_0 is the radius at which the Coulomb energy $e^2/4\pi\epsilon_0 a_0$ is equal to $2I$, that is,

$$a_0 = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2I} = 0.053nm,$$

where I is the first ionization energy. Indeed, in the Bohr atom, under the hypothesis that the electron orbit is circular, one can write an equivalence between the Coulomb force and the centripetal force

$$\frac{e^2}{4\pi\epsilon_0 a_0^2} = \frac{mv^2}{a_0}$$

and simplifying a_0 one obtain a relation for the potential and kinetic energy

$$\frac{e^2}{4\pi\epsilon_0 a_0} = mv^2 \quad \rightarrow \quad V = -2K$$

such that the energy satisfies

$$E = V + K = \frac{V}{2} = -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{1}{2}$$

The ionization energy $I = -E$ is for the Bohr model $I = 2.2 \times 10^{-18}$ J.

Using this expression for α_0 and the previously calculated expression for a_0 , we immediately find that the above interaction energy can be written as

$$w(r) = -\frac{2\alpha_0^2 I}{(4\pi\epsilon_0)^2} \frac{1}{r^6} =$$

Except for a numerical factor, it is the same as that derived by London in 1930 using quantum mechanical perturbation theory. London's famous expression for the dispersion interaction energy between two identical atoms or molecules is (London, 1937)

$$w(r) = \frac{-C_{disp}}{r^6} = -\frac{3}{4} \frac{\alpha_0^2 I}{(4\pi\epsilon_0)^2} \frac{1}{r^6}$$

London's equation has since been superseded by more exact, though more complicated expressions, but it can be relied upon to give fairly accurate values, though these are usually lower than more rigorously determined ones. From the above simple model we see that while dispersion forces are quantum mechanical (in determining the instantaneous, but fluctuating, dipole moments of neutral atoms), the ensuing interaction is still essentially electrostatic—a sort of quantum mechanical polarization force. And we may further note that the r^{-6} distance dependence is the same as that for the other two polarization interactions (the Keesom and Debye forces) that contribute to the net van der Waals force, discussed in Section 5.6. But before we consider these three interactions collectively let us first investigate the nature of dispersion forces.

To estimate the strength of the dispersion energy, we may consider two atoms or small molecules with $\alpha_0/4\pi\epsilon_0 = 1.5 \times 10^{-30}$ m and $I \approx 2 \times 10^{-18}$ J (a typical ionization potential in the UV). We thus find that for two atoms in contact at $r = \sigma \approx 0.3$ nm, $w(\sigma) = -4.6 \times 10^{-21}$ J $\approx k_B T$. This is very respectable energy, considering that the interaction appears at first

sight to spring up from nowhere, But when we recall that the inducing (instantaneous) dipole moment of even a small hydrogen (Bohr) atom is of order $a_0e \approx 2.4D$, we can appreciate why the dispersion interaction is by no means negligible. Thus, while very small non-polar atoms and molecules such as argon and methane are gaseous at room temperature and pressure, larger molecules such as hexane and higher molecular weight hydrocarbons are liquids or solids, held together solely by dispersion forces. The solids are referred to as van der Waals solids, and they are characterized by having weak undirected 'bonds', and therefore low melting points and low latent heats of melting. For spherically symmetrical inert molecules such as neon, argon and methane, the van der Waals solids they form at low temperatures are dose-packed structures with 12 nearest neighbours per atom. Their lattice energy (12 shared 'bonds' or six full 'bonds' per molecule) is therefore approximately $6w(\sigma)$ per molecule, though if the attractions of more distant neighbours are also included the factor of six rises to 7.22. The expected molar lattice energy or cohesive energy of a van der Waals solid is therefore

$$U \approx 7.22N_0 \left[\frac{2\alpha_0^2 I}{4(4\pi\epsilon_0)^2 \sigma^6} \right]$$

where σ is now the equilibrium interatomic distance in the solid. Thus, for argon, since $\alpha_0/(4\pi\epsilon_0) = 1.63 \times 10^{-30} \text{ m}^3$, $I = h\nu = 2.52 \times 10^{-18} \text{ J}$, and $\sigma = 0.376 \text{ nm}$, we obtain $U = 7.7 \text{ kJ/mol}$.