24 Intermolecular Interactions

Atoms and molecules, even uncharged ones, are attracted to each other. They can form noncovalent as well as covalent bonds. We know this because they condense into liquids and solids at low temperatures. Noncovalent interactions between uncharged particles are relatively weak and short-ranged, but they are the fundamental driving forces for much of chemistry, physics, and biology. These intermolecular interactions can be understood through measurements of the pressures of nonideal gases. The laws of electrostatics explain the attractions between charged atoms, say Na^+ and Cl^-. But what forces cause neutral atoms to bond together noncovalently? To a first approximation, the bonding between neutral molecules can also be explained by electrostatic interactions. Even when the atoms have no net charge, they have *charge distributions* and *polarizabilities*, which lead to weak attractions.

Molecules Repel Each Other at Very Short Range and Attract at Longer Distances

A bond between two particles is described by a *pair potential $u(r)$*, the energy as a function of the separation r between the particles.

The force $f(r)$ between two particles is the derivative of the pair potential:
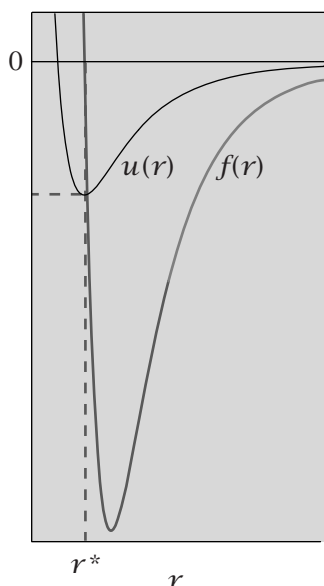
$$f(r) = -\frac{du(r)}{dr}.$$

(24.1)

Figure 24.1 The energy of interaction $u(r)$ between two particles as a function of their separation r, and the corresponding force $f = -du/dr$; r^* is the equilibrium bond length.
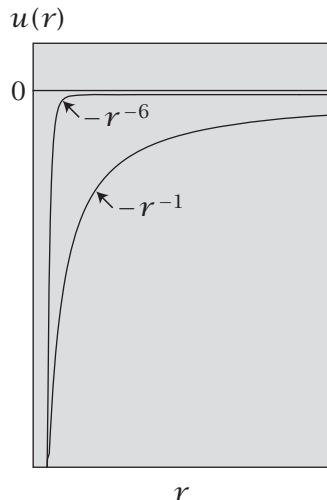

Figure 24.2 The range of an interaction. r^{-1} is long-ranged and r^{-6} is short-ranged.

Pair potentials have three main features (see Figure 24.1). First, particles do not interact if they are far apart ($u \to 0$ and $f \to 0$ as $r \to \infty$). Second, if two particles are close enough, they attract each other ($f < 0$ indicates that a positive force acts along the $-r$ direction to bring the particles together). Third, particles repel if they are too close together ($f > 0$ indicates that a positive force acts along the $+r$ direction to separate the particles).

At $r = r^*$, the attraction balances the repulsion, and the pair potential is at a minimum, so the force between two particles is zero. r^* represents the average length of an intermolecular 'bond.' Although the functional form for $u(r)$ is different for covalent bonds than for weaker interactions, all bonds have these main features: no interaction at very long range, attraction at short range, and repulsion at very short range, leading to an average equilibrium bond length where the net force is zero.

Intermolecular forces can be divided into two classes: those that are *long-ranged* and those that are *short-ranged*. The *range* is defined by the dependence of u on the separation r. Intermolecular interactions are commonly modeled as a power law:

$$u(r) = (\text{constant})r^{-p}, \tag{24.2}$$

where p is a positive integer. Interactions are called short-ranged if $p > 3$ and long-ranged if $p \le 3$. The Coulombic interaction $u(r) \propto \pm 1/r$ is long-ranged, while $u(r) \propto \pm 1/r^6$ is short-ranged, whether the interactions are attractive ($u(r)$ is negative) or repulsive ($u(r)$ is positive) (see Figure 24.2).

When two atoms are very close together in space, they repel, owing to the Pauli principle that electrons in the same state can't occupy the same space. Quantum mechanical calculations show that these very short-ranged repulsions can best be modeled as exponential functions or power laws, typically with $p = 9, 12$, or 14.

Short-Ranged Attractions Can Be Explained as Electrostatic Interactions

Electrostatic interactions are long-ranged. The exponent in Equation (24.2) is $p = 1$ in Coulomb's law, $u(r) = \mathscr{C}/r$. Yet Coulomb's law can also explain weak intermolecular attractions, which are short-ranged. Even neutral atoms and molecules, which have no net charge, have *charge distributions*: some positive charge here and some negative charge there.

There are three different ways in which a shorter-ranged exponent ($p > 1$) can arise from Coulombic interactions between neutral molecules. (1) Atoms and molecules may be *multipoles*, such as *dipoles* or *quadrupoles*, in which the charge density varies throughout the molecule, even when there is no net charge. The interactions between multipoles are shorter-ranged than the interactions between monopoles. (2) When dipolar atoms or molecules are free to orient, orientational averaging reduces the range of interaction. (3) Molecules are *polarizable*. They can be induced to have charge distributions by the electric field from nearby atoms or molecules or other sources. The interactions between polarizable molecules are shorter-ranged than the interactions between molecules having fixed dipoles. Here are the details.
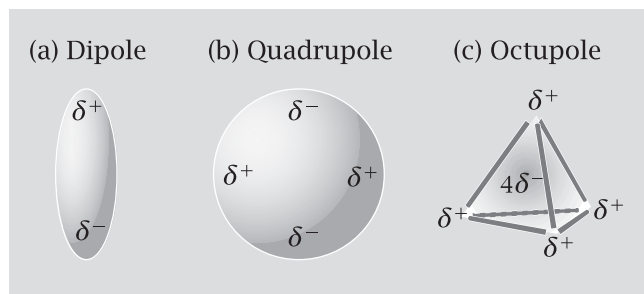
(a) Dipole (b) Quadrupole (c) Octupole

Figure 24.3 The moments of charge distributions are monopoles (not shown), (a) dipoles, (b) quadrupoles, (c) octupoles, etc.; δ^- and δ^+ indicate partial negative and positive charges.

A Charge Distribution Is Characterized by Its Multipole Expansion

Any spatial distribution of charge $\rho(x, y, z) = \rho(\mathbf{r})$ can be described by a *multipole expansion*, a series in which the first term is called the *monopole*, the second is the *dipole*, the third is the *quadrupole*, then the *octupole*, etc. The various terms are *moments* of the distribution in the same way that the mean and standard deviation are related to the first two moments of a probability distribution (see Chapter 1).

The zeroth moment, the monopole, is the total charge of the distribution, $\int \rho(\mathbf{r}) \, dV$. The first moment $\int \mathbf{r}\rho(\mathbf{r}) \, dV$, the dipole, describes a symmetric arrangement of equal amounts of positive and negative charge separated by a vector $\mathbf{r}$. The dipole is the lowest-order distribution for a molecule that has no net charge (see Figure 24.3). A quadrupole is the next lowest-order distribution for a molecule that has no net charge and no net dipole moment. An octupole has no net charge, or dipole, or quadrupole moment. There is no tripole or pentapole, etc., because these distributions can always be expressed more simply as linear combinations of some amount of net charge plus some amount of dipole moment, plus some amount of quadrupole moment, etc. In this way, any charge distribution can be described by a multipole expansion, a sum of moments. For example, a molecule having a dipole moment in addition to a net charge can be described by a sum of the first two terms in a multipole expansion.

Let's consider dipoles. There are two types: permanent and induced. A *permanent* dipole occurs when a charge separation is always present in a molecule, even in the absence of any external electric fields. An *induced dipole* is a charge separation that arises only in the presence of an applied electric field. Some molecules have both permanent and induced dipole moments.

A permanent dipole is characterized by its dipole moment $\boldsymbol{\mu} = q\boldsymbol{\ell}$ (see Equation (21.16)). Dipole moments are measured in units of debyes (D). One debye equals 1×10^{-18} esu cm $= 3.33564\times10^{-30}$ coulomb meter (C m). When one positive charge (such as a proton) is separated from one negative charge (such as an electron) by 1 Å, the magnitude of the dipole moment is $q\ell = (1.6022\times 10^{-19}\,\mathrm{C})\times(1\times10^{-10}\,\mathrm{m})\times[1/(3.33564\times10^{-30}\,\mathrm{C\,m})] = 4.8033\,\mathrm{D}$.

Table 24.1 gives some dipole moments. For example, water, which has no net charge, has a permanent dipole moment of 1.85 D, due to the partial negative charge on the oxygen and the partial positive charges on the two hydrogens. Figure 24.4 shows how dipole moments can arise from molecular asymmetry.
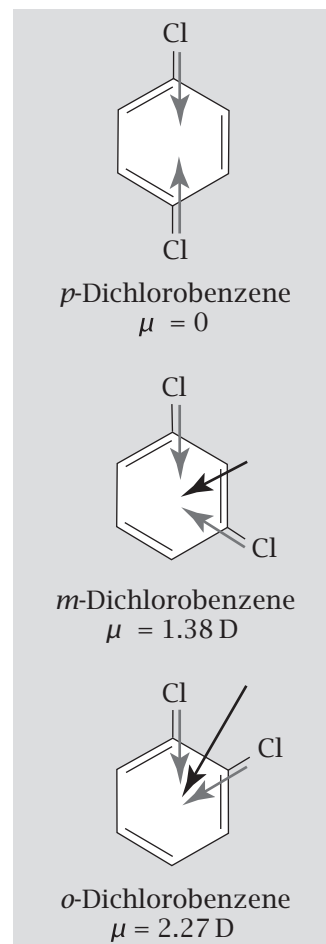

p-Dichlorobenzene
$\mu = 0$

m-Dichlorobenzene
$\mu = 1.38\,\mathrm{D}$

o-Dichlorobenzene
$\mu = 2.27\,\mathrm{D}$

Figure 24.4 Permanent dipole moments can depend on molecular symmetry. The dipole moment (←) is the vector sum of unit dipoles (←). Source: PW Atkins, *Physical Chemistry*, 6th edition, WH Freeman, New York, 1998.

Table 24.1 Dipole moments μ and polarizability volumes, $\alpha' = \alpha/4\pi\varepsilon_0 = \alpha\mathcal{C}$, where α is the polarizability.

Molecule	μ (10^{-30} C m)	μ (D)	α' (10^{-24} cm^3)
H_2	0	0	0.819
N_2	0	0	1.77
CO_2	0	0	2.63
CO	0.390	0.117	1.98
HF	6.37	1.91	0.51
HCl	3.60	1.08	2.63
HBr	2.67	0.80	3.61
HI	1.40	0.42	5.45
H_2O	6.17	1.85	1.48
NH_3	4.90	1.47	2.22
CCl_4	0	0	10.5
$CHCl_3$	3.37	1.01	8.50
CH_2Cl_2	5.24	1.57	6.80
CH_3Cl	6.24	1.87	4.53
CH_4	0	0	2.60
CH_3OH	5.70	1.71	3.23
CH_3CH_2OH	5.64	1.69	
C_6H_6	0	0	10.4
$C_6H_5CH_3$	1.20	0.36	
o-$C_6H_4(CH_3)_2$	2.07	0.62	
He	0	0	0.20
Ar	0	0	1.66

Source: PW Atkins, *Physical Chemistry*, 6th edition, WH Freeman, New York, 1998; *Handbook of Chemistry and Physics*, CJF Böttcher and P Bordewijk, *Theory of Electrical Polarization*, Elsevier, Amsterdam, 1978.

Neutral Molecules Attract Because of Charge Asymmetries

Table 24.2 Some covalent bond energies.

Bond	Energy (kcal mol^{-1})
C−C	80.6
C=C	145.2
C≡C	198.1
C−H	98.3
O=O (in O_2)	118.1
F−F (in F_2)	37.0

Source: RS Berry, SA Rice, and J Ross, *Physical Chemistry*, Wiley, New York, 1980.

Interactions become shorter-ranged and weaker as higher multipole moments become involved. When a monopole interacts with a monopole, Coulomb's law says $u(r) \propto r^{-1}$. But when a monopole interacts with a distant dipole, Coulombic interactions lead to $u(r) \propto r^{-2}$ (see Equation (21.31)). Continuing up the multipole series, two permanent dipoles that are far apart interact as $u(r) \propto r^{-3}$. Such interactions can be either attractive or repulsive, depending on the orientations of the dipoles. Table 24.2 gives typical energies of some covalent bonds, and Table 24.3 compares covalent with noncovalent bond strengths.

Orientational Averaging Shortens the Range of Interactions

Compare two situations: (1) a charge interacts with a dipole that has a fixed orientation, and (2) a charge interacts with a dipole that orients freely over all possible angles (see Figure 24.5). The energy of a charge interacting with a rotating dipole is shorter-ranged than the energy of interacting with a fixed dipole. Here is the explanation.

Table 24.3 Various types of energy u (at 5 Å) and the dependence on distance r.

Type of Interaction	u (kcal mol^{-1})	Distance r Dependence
Ionic	66	$1/r$
Ion/dipole	4	$1/r^2$
Dipole/dipole	0.5	$1/r^3$
Dipole/induced dipole	0.012	$1/r^6$

Source: RS Berry, SA Rice, and J Ross, *Physical Chemistry*, Wiley, New York, 1980.

Equation (21.31) shows that when a charge Q is separated by a distance r from a dipole having a dipole moment of magnitude $\mu = q\ell$, constrained to a fixed angle θ, the pair energy is

$$u(r, \theta) = u_0 \cos \theta, \qquad \text{where} \qquad u_0 = \frac{\mathcal{C}Q\mu}{Dr^2}. \tag{24.3}$$

However, if a dipole is free to rotate over all angles θ, the *average* interaction energy is

$$\langle u(r) \rangle = \frac{\int_0^\pi u(r, \theta) e^{-u(r,\theta)/kT} \sin \theta \, d\theta}{\int_0^\pi e^{-u(r,\theta)/kT} \sin \theta \, d\theta}. \tag{24.4}$$

The factor of $\sin \theta$ accounts for the different numbers of dipoles that point in the different directions θ (see Example 1.26 and Figure 24.5). Relatively few dipole orientations point in the directions $\theta = 0°$ and $\theta = 180°$ where the area elements are small. More dipole orientations point toward $\theta = 90°$.

If the energy is small, $u/kT \ll 1$, you can use a Taylor series expansion for the exponential terms (see Equation (J.1) in Appendix J), $e^{-u/kT} \approx 1 - u/kT + \cdots$, and Equation (24.4) becomes

$$\langle u(r) \rangle \approx \frac{\int_0^\pi u_0 \cos \theta \left[1 - \left(\frac{u_0 \cos \theta}{kT} \right) \right] \sin \theta \, d\theta}{\int_0^\pi \left[1 - \left(\frac{u_0 \cos \theta}{kT} \right) \right] \sin \theta \, d\theta}. \tag{24.5}$$

Equation (24.5) has two terms in the numerator and two terms in the denominator. The first term in the denominator is

$$\int_0^\pi \sin \theta \, d\theta = -\cos \theta \Big|_0^\pi = 2.$$

To evaluate the other three terms, let $x = \cos \theta$. Then $dx = -\sin \theta \, d\theta$. The first term in the numerator of Equation (24.5) and the second term in the denominator are zero because

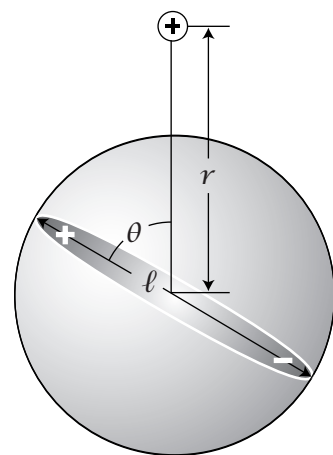$$\int_0^\pi \cos \theta \sin \theta \, d\theta = -\int_1^{-1} x \, dx = 0. \tag{24.6}$$

Figure 24.5 A charge is at a distance r from a dipole of length ℓ that is oriented at an angle θ from the axis between them.

The second term in the numerator of Equation (24.5) becomes

$$-\frac{u_0^2}{kT}\int_0^\pi \cos^2\theta \sin\theta\, d\theta = \frac{u_0^2}{kT}\int_0^\pi \cos^2\theta\, d\cos\theta = \frac{u_0^2}{kT}\int_1^{-1} x^2\, dx$$

$$= \left(\frac{u_0^2}{kT}\right)\frac{x^3}{3}\bigg|_1^{-1} = -\frac{2}{3}\frac{u_0^2}{kT}.$$

Combining all the terms in Equation (24.5) gives

$$\langle u(r)\rangle = -\frac{u_0^2}{3kT}$$

$$= -\frac{1}{3kT}\left(\frac{\mathcal{C}Q\mu}{D}\right)^2\frac{1}{r^4}. \tag{24.7}$$

Compare Equations (24.7) and (24.3). If the dipole angle is fixed, $u(r) \propto (-1/r^2)$. If the dipole rotates, the orientational average gives $\langle u(r)\rangle \propto (-1/r^4)$. The range of interaction is shorter when the dipole tumbles freely. This argument readily generalizes: because the energy of interaction of two permanent dipoles with fixed orientations is $u(r) \propto -1/r^3$, the interaction between two tumbling permanent dipoles is $u(r) \propto -(1/r^6)$. The interaction energy between two permanent dipoles that are free to rotate, that have moments μ_A and μ_B, and that have a center-to-center separation of r is

$$\langle u(r)\rangle = -\frac{2}{3kT}\left(\frac{\mu_A\mu_B}{4\pi\varepsilon_0 D}\right)^2\frac{1}{r^6}, \tag{24.8}$$

when averaged over all the possible angles of each dipole. Example 24.1 computes the magnitude of a dipole–dipole interaction.

EXAMPLE 24.1   The dipole–dipole interaction of ethanol molecules.   If two ethanol molecules are $r = 10\,\text{Å}$ apart in the gas phase, what is their average interaction energy $\langle u(r)\rangle$? Table 24.1 gives the dipole moment of ethanol as $\mu = 5.70\times10^{-30}\,\text{C m}$ per molecule. Equation (24.8) gives

$$\langle u(r)\rangle = -\frac{2}{3kT}\left(\frac{\mu^2}{4\pi\varepsilon_0}\right)^2\frac{1}{r^6}$$

$$= -\frac{2}{3(1.38\times10^{-23}\,\text{J K}^{-1}\text{ per molecule})(300\,\text{K})}$$

$$\times\left(\frac{(5.70\times10^{-30}\,\text{C m per molecule})^2}{4\pi\times8.85\times10^{-12}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1}}\right)^2\left(\frac{1}{10^{-9}\,\text{m}}\right)^6$$

$$\times 6.02\times10^{23}\text{ molecules mol}^{-1}$$

$$= -8.27\,\text{J mol}^{-1}.$$

At $r = 10\,\text{Å}$, this attraction is very weak owing to the r^{-6} distance dependence. At $r = 5\,\text{Å}$, the interaction is $2^6 = 64$ times stronger, $-529\,\text{J mol}^{-1}$.

London Dispersion Forces Are Due to the Polarizabilities of Atoms

Attractive interactions are universal. Molecules need not have net charge, or internal charge asymmetry, or even an ability to orient, to experience attractions. Even spherical uncharged inert gas atoms condense into liquids at very low temperatures. Such attractions were first described in 1937 by F London (1900–1957), an American physicist. They are called *London forces*, or *dispersion forces*. Two molecules can induce an attraction in each other because they are polarizable.

A *polarizable* atom or medium is one that responds to an applied electric field by redistributing its internal charge. In the simplest case, when an electrostatic field is applied to a polarizable atom, charge inside the atom redistributes to form a dipole pointing in the direction opposite to the applied field (see Figure 24.6). The dipole moment $\boldsymbol{\mu}_{\text{ind}}$ that is induced by the field $\mathbf{E}$ is often found to be proportional to the applied field, if the field is sufficiently small:

$$\boldsymbol{\mu}_{\text{ind}} = \alpha \mathbf{E}, \tag{24.9}$$

where α is called the *polarizability* of the atom or medium. (If the field is large, the dipole moment will not be linear in E but may depend on higher powers, $\mu = \alpha E + \alpha_2 E^2 + \alpha_3 E^3, \ldots$.) The polarizability is the induced dipole moment per unit of applied electric field. Table 24.1 lists some polarizabilities. Polarizabilities have units of volume, and they are typically about the size of a molecular volume, a few cubic ångströms.
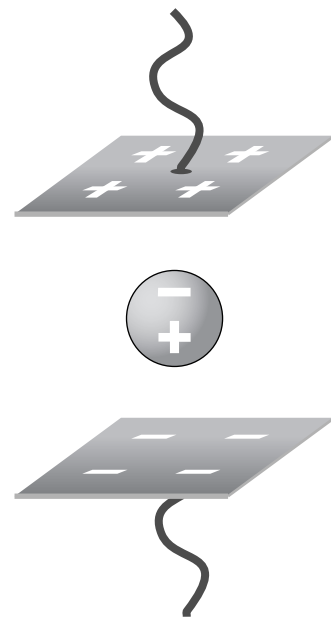

Figure 24.6 An applied field can induce a dipolar charge distribution in a neutral atom.

A Charge Will Polarize a Neutral Atom and Attract It

A neutral atom will be attracted to an electrostatic charge. How? The neutral atom becomes polarized by proximity to the electrical charge, causing the neutral atom to act like a dipole, which orients and is then attracted to the charge. Here's a simple model. Suppose a charge Q is at a distance r from the center of a neutral atom, as shown in Figure 24.7. The electric field from Q causes a redistribution of the charge inside the neutral atom, into amounts q and $-q$ that are separated by a distance Δr, giving an induced dipole moment $\mu_{\text{ind}} = q \, \Delta r$. Induction of the dipole results in an attractive force because Q is closer to the partial charge of opposite sign ($-q$ in this case), which it attracts, than to the partial charge of the same sign ($+q$), which it repels. The net force on the neutral atom is $f = (\text{charge}) \times E$ (see Equation (20.13)). It is the sum of the force
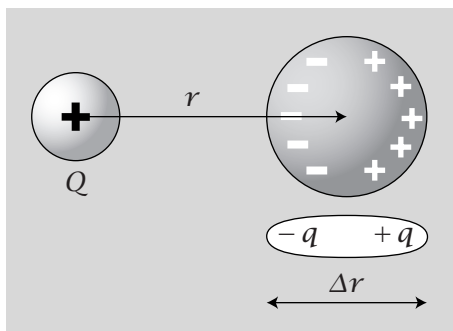

Figure 24.7 When a neutral atom (on the right) is in the electrostatic field of a charge Q, a charge separation is induced in the atom, modeled as a dipole. This attracts the neutral atom to the charge.

$(-q)E[r-(\Delta r/2)]$ of Q on the nearby charge $-q$, plus the force $qE[r+(\Delta r/2)]$ of Q on the more distant charge q:

$$f = -q\left[E\left(r-\frac{\Delta r}{2}\right)-E\left(r+\frac{\Delta r}{2}\right)\right] \approx q\,\Delta r\,\frac{dE}{dr} = \mu_{\text{ind}}\frac{dE}{dr}$$

$$= \alpha E\frac{dE}{dr}. \tag{24.10}$$

At a distance r from a charge Q, the field is $E = \mathcal{C}Q/Dr^2$ (see Equation (20.14)). Substituting $E = \mathcal{C}Q/Dr^2$ into Equation (24.10) and taking the derivative gives

$$f = -2\alpha\left(\frac{\mathcal{C}Q}{D}\right)^2\frac{1}{r^5}. \tag{24.11}$$

Integrating to express Equation (24.11) instead as an intermolecular potential yields

$$u(r) = -\int f(r)\,dr = -\frac{\alpha}{2}\left(\frac{\mathcal{C}Q}{D}\right)^2\frac{1}{r^4}. \tag{24.12}$$

The minus signs in Equations (24.11) and (24.12) show that the interaction of a charge with a neutral atom is attractive, irrespective of the sign of Q. Equations (24.11) and (24.12) show that the interaction is short-ranged ($p > 3$) and that the attraction increases with the polarizability of the neutral atom.

Similarly, when two neutral atoms interact, they induce dipoles in each other, with a pair interaction $u(r) \propto (-1/r^6)$ that is also proportional to the polarizabilities α of the two dipoles.

All the short-ranged attractions we have described, involving multipoles, induced polarization, and orientational averaging, lead to power laws with $p \geq 3$, and are collectively called *van der Waals* forces.

The fact that dipoles interact with a distance dependence r^{-6} gives a physical basis for the form of the attractive interaction in a widely used energy function called the **Lennard–Jones potential**,

$$u(r) = \frac{a}{r^{12}} - \frac{b}{r^6},$$

where a and b are parameters that depend on the types of interacting atoms [1, 2]. The positive sign in the first term implies a repulsion, and the minus sign in the second term implies an attraction. The repulsive part of this potential, a/r^{12}, was originally chosen because it can be calculated rapidly by computers using the square of r^{-6}. The virtue of this model is that it captures the universal features of a short-ranged attraction and even shorter-ranged repulsion, and the two parameters a and b give enough flexibility for the model to predict experimental data fairly accurately.

Hydrogen Bonds

Hydrogen bonds are weak interactions (typically a few kcal mol^{-1}) that occur when a hydrogen is situated between two other atoms. For example, a hydrogen bond can form between an amide and carbonyl group, $N-H\cdots O=C$. In this case, the $N-H$ group is called the *hydrogen bond donor* and the $C=O$ group is called the *hydrogen bond acceptor*. To a first approximation, a hydrogen bond

can be described as an electrostatic interaction between the N−H dipole and the O=C dipole. Hydrogen bonds act to align the N−H and O=C bonds, and to stretch the N−H bonds. To describe hydrogen bonds more accurately requires a quantum mechanical treatment of the charge distribution.

Empirical Energy Functions

A popular approach to modeling the interactions and conformations of large molecules, particularly in solution, is to assume an energy U that is a sum of terms: (1) Coulombic interactions between charged atoms, (2) spring forces that stretch and bend bonds, (3) periodic potentials for torsional rotations around bonds, and (4) a Lennard–Jones potential for nonbonded interactions [3–5]. For example,

$$U = \sum_{\text{bond lengths } b} \frac{K_b}{2}(b-b_0)^2 + \sum_{\text{bond angles } \theta} \frac{K_\theta}{2}(\theta-\theta_0)^2$$

$$+ \sum_{\text{dihedral angles } \phi} K_\phi[1+\cos(n\phi-\delta)]$$

$$+ \sum_{\text{nonbonded pairs } i<j} \left(\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^6} + \frac{Cq_iq_j}{Dr_{ij}} \right), \qquad (24.13)$$

where K_b is the spring constant for stretching bonds, b_0 is the equilibrium bond length, K_θ is the spring constant for bending bonds, and θ_0 is the equilibrium bond angle. K_ϕ and δ are torsional constants, and a_{ij} and b_{ij} are Lennard–Jones constants for atoms i and j separated by a distance r_{ij}. The summation over the index $i < j$ is a convenient way to count every interaction only once. Summing the pair interaction energies u_{ij} over all indices, $\sum_{\text{all } i} \sum_{\text{all } j} u_{ij}$, would count every interaction exactly twice. For example, the interaction of particle 2 with particle 3, u_{23}, is equal to u_{32}. Thus,

$$\sum_{i<j} u_{ij} = \frac{1}{2} \sum_{\text{all } i} \sum_{\text{all } j} u_{ij}. \qquad (24.14)$$

Much of what is known about intermolecular interactions comes from measuring the pressures of nonideal gases. The simplest model that relates intermolecular interactions to the pressures of gases is the van der Waals model.

The van der Waals Gas Model Accounts for Intermolecular Interactions

Real gases are more complex than ideal gases. The ideal gas model predicts that the pressure depends only on the temperature and the gas density ($\rho = N/V = p/kT$). The pressure of an ideal gas does not depend on the types or atomic structures of the gas molecules. But ideal behavior applies only at low densities where molecules don't interact much with each other. For denser gases, intermolecular interactions affect the pressures, and gases differ from each other