

## 2.1 Introduction

Everything is made from atoms. That is the key hypothesis. The most important hypothesis in all of biology, for example, is that everything that animals do, atoms do. In other words, there is nothing that living things do that cannot be understood from the point of view that they are made of atoms acting according to the laws of physics

The Feynman lectures in physics, Vol. 1, 1963 (pp. 1–8).

Richard Feynman's hypothesis is the core of our goal as food chemists; we want to be able to relate all of the properties of foods to the atoms they contain. For some questions, this is fairly straightforward ("this fat is harder because it is more crystalline") while others are so complex we struggle to even frame them in terms of chemistry ("why does this sauce taste creamier than that one?"). However, in principle if we can properly understand how the atoms are behaving, we should be able to explain any behavior of food.

A common approach to many problems in science is to divide the subject up into a hierarchy of structures and focus only on the most relevant. For example, an engineer might notice that when a building collapses individual bricks are still intact in the rubble. From that observation, it would be sensible to study the cement holding the bricks together rather than the strength of the bricks themselves. By analogy, most of the physical changes in foods involve changes in the arrangements of molecules rather than the breaking and making of bonds within molecules. There-

fore, the atomic scale is far less important to most of our physical problems than the molecular scale and we can treat molecules as the building blocks of our food, reframing Feynman's hypothesis as:

*Everything that food does, molecules do.*

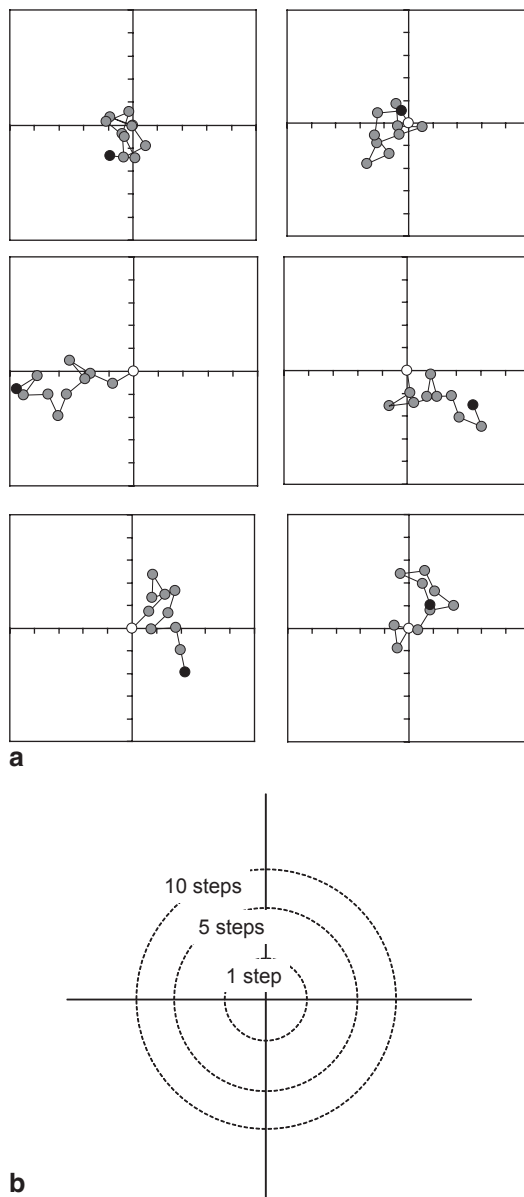
So what do molecules do? Their behavior is governed by the laws of thermodynamics described in the last chapter but to properly relate chemical behavior to chemical structure we need to understand the nature of kinetic and potential energy at the molecular level. Molecules have kinetic energy because of their masses and velocities while potential energy results from intra- and intermolecular bonding. In this chapter, we will start by considering molecular movement then look at bonding. We will finally return to Feynman's hypothesis and look at some ways that molecular properties can be related to bulk properties of a food.

## 2.2 Molecular Motion

Each molecule has a kinetic energy equal to  $\frac{1}{2} kT$  in each direction (x, y, and z) or  $\frac{3}{2} kT$  overall ( $\sim 2.75 \times 10^{-21}$  J). In a gas, this energy leads to very fast molecular motion, approaching the speed of sound for many molecules at room temperature, but in a liquid the molecules are very densely packed and their movement is limited by interactions with their neighbors. They will move away from their starting position, but only slowly as they collide frequently with other molecules exchanging momentum and changing

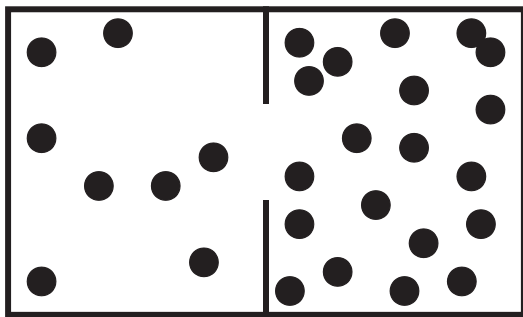
direction. The net effect of the multiple collisions is that the trajectory of a moving molecule is a random walk—a series of small steps where the direction of each is not affected by previous steps (Fig. 2.1a). Because each step is in a random direction, it is as likely to take a molecule up as it is down or left as it is right. Therefore the average net displacement is zero after a random walk of any length. However, the combination of steps is unlikely to take the molecule exactly back to its starting point and most random paths will end a certain distance from the starting position. In a random walk, the average displacement is proportional to the square root of the number of steps taken and hence the square root of time. Figure 2.1b shows the average displacement for a molecule after 1, 5, and 10 steps; the direction of movement is unknown but molecules will move slowly away from their starting positions.

Despite the random progression of an individual molecule, the net effect will be to move from regions of high concentration to those of low concentration. (As we saw in the previous chapter, activity rather than concentration is the real driving force for diffusion as it also incorporates molecular interactions that can hold molecules together or force them apart. However, for our treatment of molecular motion we will continue to discuss concentrations for the ideal case where there are no molecular interactions.) This effect is merely statistical—imagine a box containing two chambers separated by a window, any one of the molecules has a statistical possibility of moving through the window into the other chamber over a given time period and there will be a constant exchange of molecules between the chambers (Fig. 2.2). If there was, say, a 1% chance of the random walk of a given molecule taking it through the window in a given second and there were 100 molecules in the right-hand chamber and 1000 in the left then in a typical second 1 molecule would move right to left and 10 from left to right—a net movement of 9 molecules from left to right. A smaller concentration gradient would lead to a smaller rate of mass transfer, for example if there were 600 on one side and 500 on the other, the net rate of exchange would only be only 1. Each exchange reduces the



**Fig. 2.1** a Example 10-step molecular random walks. The starting position shown at the origin as an *open point*, the final position as a *filled point* and intervening steps as *shaded points*. The molecule moves in a straight line until it collides with another molecule (not shown) and moves off in another random direction. b The average distance away from the starting position increases with the square root of the number of steps taken but the average net displacement after the walk is zero as random movements in one direction are cancelled by random movement in the opposite direction

concentration gradient so the rate of exchange will decrease over time. The net movement of



**Fig. 2.2** A box of molecules separated into two chambers by a window. Each molecule is following a random walk so each has an equal chance of passing through the window in a given time period. The rate of diffusion through the window is proportional to the concentration difference between the chambers

molecules through a window of unit area per unit time is the flux ( $J$ ) and, as our thought experiment has shown, is proportional to the concentration gradient ( $dc/dx$ ) (i.e., Fick's first law):

$$J = -D \frac{dc}{dx} \quad (2.1)$$

(Note the negative sign because flow is from high to low concentration.) The proportionality constant,  $D$ , is the diffusion coefficient of the molecules. The diffusion coefficient can be measured experimentally, typically by measuring changes in local concentration over time or by gradient field nuclear magnetic resonance (NMR).

Albert Einstein related the macroscopic phenomenon of diffusion to the microscopic random walk:

$$D = \frac{kT}{6\pi\eta r} \quad (2.2)$$

where  $\eta$  is the viscosity of the material the molecule is diffusing through,  $r$  the effective molecular radius and  $kT$  the thermal energy of the system (i.e., the product of the Boltzmann constant and absolute temperature). A molecule diffuses more slowly through a viscous material and a larger molecule will feel more drag than a smaller one and diffuse more slowly. Equation 2.2 can be used to relate measurements of diffusion coefficient to molecular dimensions. For example, the self-diffusion coefficient of water (the capacity

of a water molecule to diffuse in other identical water molecules) is measured by NMR as about  $2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Taking the viscosity of water as  $9 \times 10^{-4} \text{ Pa s}$ , the diameter of a water molecule comes out as  $2 \text{ \AA}$ , which is reasonably close to the value of about  $3 \text{ \AA}$  from molecular modeling. However, care must be taken using Eq. 2.2 in this manner. Firstly, polymers and ions are frequently highly hydrated so several water molecules will be entrained with the diffusing molecule and move along with it. Consequently, the effective size measured for the diffusing polymer or ion will be that of the molecule of interest plus the hydration layer. Secondly, viscosity measured at the bulk scale with fluid flow measurements (see Chap. 7) may not correspond to the viscosity causing drag on the diffusion molecules at the microscopic level. For example, the diffusion coefficient of sucrose molecules decreases with sucrose concentrations due to the increasing solution viscosity. However, adding a small amount of xanthan gum causes no significant change in sucrose diffusion coefficient despite a large change in measured viscosity (Basaran et al. 1999). This discrepancy is probably because the xanthan polymer can spread out and make the bulk solution viscous (see Chap. 7), there are still large pores and the sucrose molecules are free to move through the gaps and are not affected by them.

As solution viscosity increases, the diffusion coefficient and hence the mobility of the molecules will decrease. Viscosity increases with increasing concentration and decreasing temperature. At a characteristic temperature and concentration, viscosity reaches a level that no molecular translational movement is possible at which point the liquid is said to have entered a glassy state. Glassy materials are hard and brittle because the molecules cannot flow past one another in response to applied force and instead just shatter. The rates of chemical reactions are very slow in the glassy state as for molecules to react they must first diffuse through the solution to come into contact with one another. We will return to the glass transition in the context of crystallization in Chap. 6.

## 2.3 Bonding and Molecular Structure

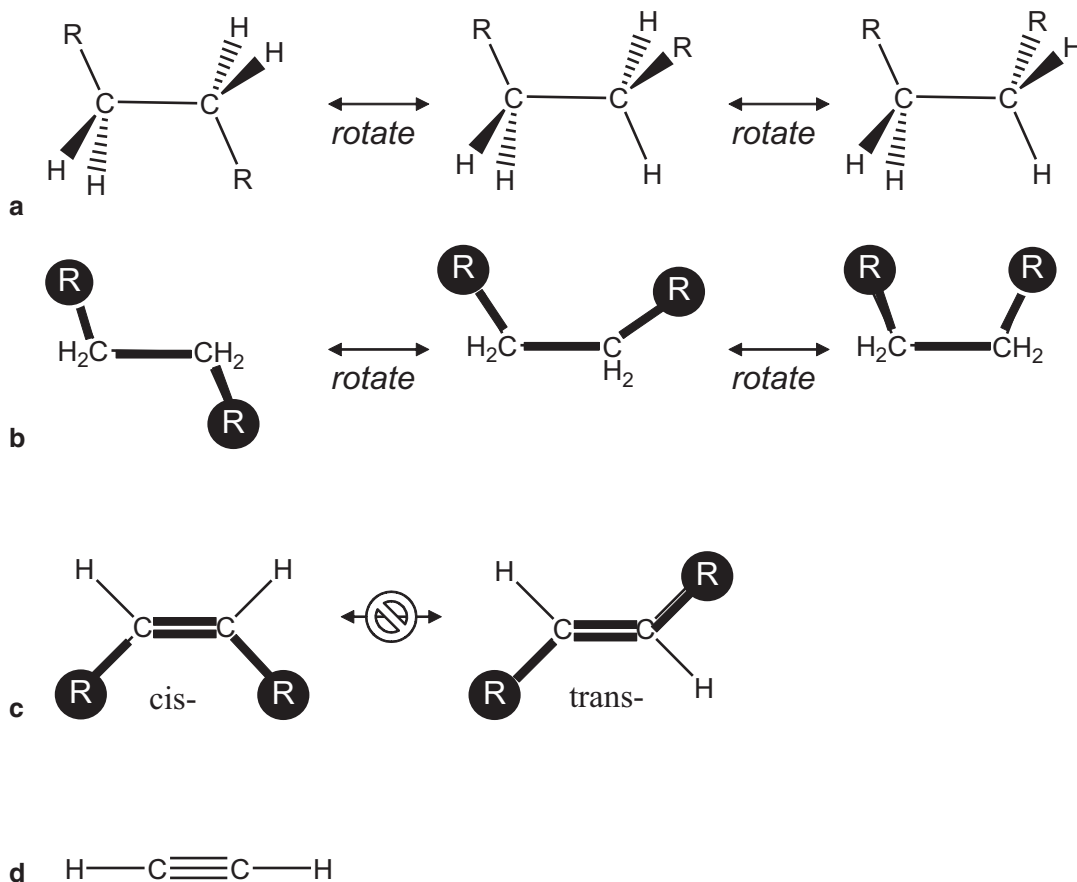
Molecular motion is random and will tend to increase entropy by evenly distributing molecules in space. Any structure we see must therefore arise from forces acting between atoms and holding them in a preferred arrangement. We used gravity as an example of a force in the first chapter but gravity, although very long range, depends on the masses of the objects involved. While it dictates the movement of heavy objects we see at the macroscopic level (e.g., throwing a ball), the tiny masses of atoms means the gravitational contribution to chemical bonding insignificant. However, gravity is just one of the four fundamental forces of the universe. In addition, the strong and weak nuclear forces act with great strength at very short ranges and are responsible for the properties of the atomic nucleus. However, as the atomic nuclei do not change in foods, nuclear forces are irrelevant and we are left with electrostatic forces, the mutual attraction of like charges and repulsion of unlike charges, as the sole remaining interaction responsible for all chemical bonding.

Electrostatic forces are responsible for all of the different types of chemical bonds. Whether they occur between atoms within a molecule (e.g., covalent bonds) or between different molecules (e.g., Van der Waals forces) are all just manifestations of this same underlying interaction. Having acknowledged the central mechanism for bonding, it is still helpful to divide bonds into different subcategories and then focus only on those most important to the problem in hand. With this in mind, we will divide the general phenomena of bonding into bonds holding atoms together as molecules and bonds between molecules (i.e., intramolecular and intermolecular bonds). We will briefly review the bonds holding a molecule together with a view to understanding the types of building blocks that will interact with one another via intermolecular forces to produce food structure.

Atoms consist of a tiny, massive, and positively charged nucleus associated with sufficient negatively charged electrons to neutralize the

overall charge. (An atom or molecule whose positive nucleus is not balanced with electrons is an ion). The position of the electrons cannot be stated precisely, but quantum mechanics can predict the atomic orbital—the region of space close to the nucleus where the electron is likely to occur. There is one first-level orbital ( $1s$ ), four second-level orbitals ( $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$ ), and four third-level orbitals ( $3s$ ,  $3p_x$ ,  $3p_y$ , and  $3p_z$ ) sometimes known as the first, second, and third electron shells. Each orbital can contain up to two electrons, and as the atom gets larger it will fill up the orbitals from lower to higher energy, for example, hydrogen has one electron which is typically in the  $1s$  orbital, helium has two electrons so both are in the  $1s$  orbital—filling it. Carbon has six electrons so the  $1s$  orbital is filled and the remaining four electrons half fill the second-level orbitals. A bond is when the orbitals from two atoms combine to form a molecular orbital with the pair of electrons distributed between the atoms. The properties of the bonding orbitals for simple molecules can, in principle, be calculated using quantum mechanics but here it will suffice to take a simple approach and merely note some of the important features of covalent bonds.

- **Fixed Valency.** Each type of atom tends to form a characteristic number of bonds (i.e., the valency) governed by the number of electrons needed to fill the outer electronic shell. Thus, hydrogen with one electron needs a second to fill its first-level orbital and achieves this by forming one bond, helium has two electrons so its first level orbital is already full and tends not to form bonds. Carbon has four electrons in its outer shell and must form four bonds to fill it. It is possible to form multiple bonds between two atoms when more than one pair of electrons is shared between them. For example, carbon can form one, two, or three bonds with another carbon atom to form the backbone of ethane, ethene, or ethyne (Fig. 2.3).
- **Polarization.** If the electron pair in the bonding orbital is evenly distributed between the two atoms, the bond is nonpolar, but if one atom has a greater affinity for electrons it will tend to draw them closer, leaving the

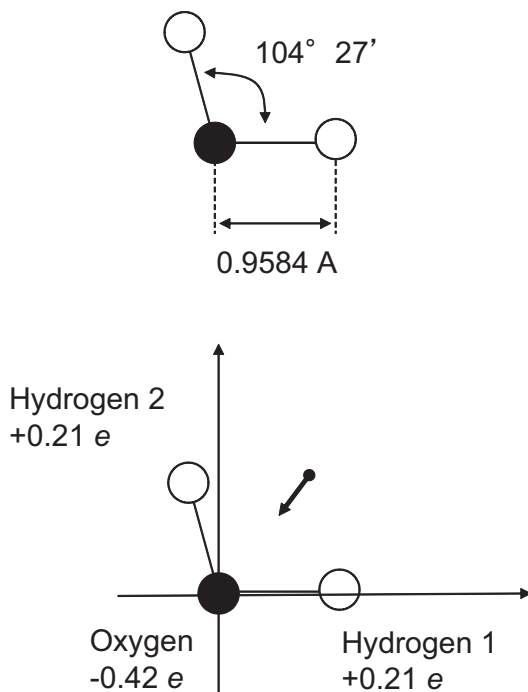


**Fig. 2.3** Single, double, and triple bonds structures as illustrated by **a** ethane, **b** ethene, and **c** ethyne. Some of the hydrogens are labeled as R-groups to illustrate the changes in conformation due to rotation about the carbon-car-

bon bond. The single bonds in ethane are free to rotate, profoundly changing the shape of the molecule (shown as a 2D projection in **b**). An energy barrier restricts rotation about double bonds

distribution skewed and the bond polarized. The atom with the greater share of the bonding electrons accumulates a fractional negative charge ( $\delta^-$ ) leaving the other atom with a slight positive charge ( $\delta^+$ ). The partial charges on the atoms in a molecule are readily calculated by most chemical drawing programs (e.g., the charges on water in Fig. 2.4 were calculated using MarvinSketch program from ChemAxon Kft., Hungary). The electron affinity of atoms can be expressed as electronegativity on the Pauling scale (Table 2.1); if a bond links two atoms, the electrons will tend to accumulate on the atom with the higher Pauling value and gain a partial negative charge. If the bond is very highly polarized,

the electrons will be effectively entirely associated with the more electronegative group which will gain a permanent negative charge (i.e., an anion) leaving the other group with fewer electrons than needed to provide charge neutrality (i.e., a cation). The degree of ionic character to a bond can be calculated as half the absolute value of the difference between the electronegativities of the atoms involved. For example, a carbon-hydrogen bond is  $|2.6 - 2.2|/2 = 20\%$  ionic while a carbon-oxygen bond is  $|3.5 - 2.6|/2 = 45\%$  ionic and a sodium-chloride bond is  $|0.9 - 3.15|/2 = 112.5\%$  ionic (note—values greater than 100% are taken as completely ionic bonds).



**Fig. 2.4** Water (including dipole and bond angles). The partial charges on each atom are calculated by the structure drawing program (in this case Marvin from ChemAxon Kft., Hungary). Inset *arrow* is the equivalent dipole

**Table 2.1** Pauling scale values for electronegativities (Haynes et al. 2013).

Pauling number	
C	2.6
H	2.2
O	3.5
N	3.1
Na	0.9
Ca	1.0
Fe(II)	1.8
Fe(III)	1.9
Al	1.5
Cl	3.0

- **Fixed Geometry.** Covalent bonds are short (~1–2 Å) and very strong while multiple bonds tend to be shorter and stronger still (Table 2.2). The angles between bonds are fixed and depend on which orbitals are involved in bonding. We can again take a simplified approach and imagine the shapes result

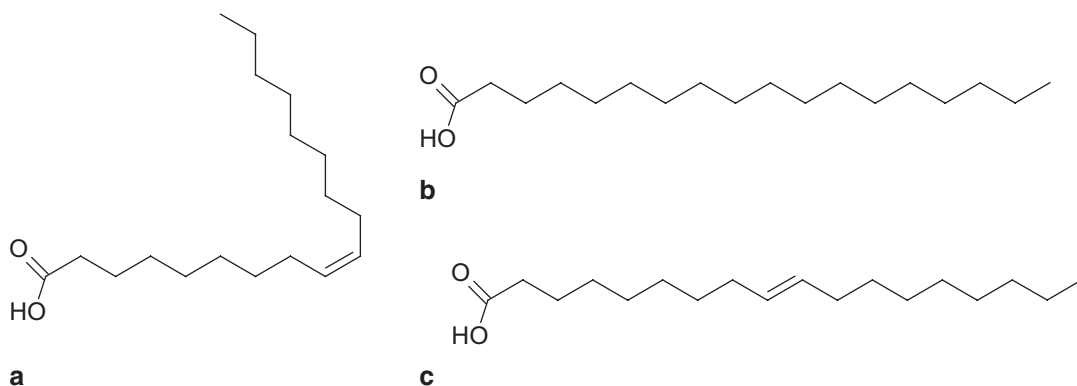
**Table 2.2** Covalent bond strengths and lengths (Haynes et al. 2013; Israelachvili 1991).

	Bond strength		Bond length (Å)
	(kJ mol <sup>-1</sup> )	(kT at 300 K)	
C–C	360	144	1.54
C=C	600	241	1.34
C=O	340	136	1.23
C–H	430	172	1.09
H <sub>2</sub> O H-bond	6–23	2.5–9	1.97

from the electrons in the bonds repelling one another. Thus, the carbon–hydrogen bond and the carbon–carbon triple bond in ethyne repel one another to give the bond angle of 180° (Fig. 2.3d). Similarly, the carbon–carbon double bond and the two carbon–hydrogen single bonds in ethene also repel one another resulting in a planar molecule with bond angles of 120° (Fig. 2.3c). Not all molecules are flat; the four bonds around each carbon in ethane repel one another to give a tetrahedral shape (bond angle 109.5°, Fig. 2.1a). Lone pairs of electrons (full outer shell orbitals not contributing to covalent bonds) also repel to one another as well as any bonding electrons so the bond angle in water (104.5°, Fig. 2.4) is closer to tetrahedral than to linear because oxygen has two lone pairs of electrons as well as two bonds.

We can get a sense of the strength of covalent bonds by comparing the bond energy to the thermal energy of the system. Bond energy means the amount of energy you need to put in to break the bond and thermal energy is the kinetic energy of molecules due to heat. As we saw in the previous chapter, thermal energy is given by  $kT$ , so at room temperature it is about  $4.1 \times 10^{-21}$  J ( $= 1.38 \times 10^{-23}$  JK<sup>-1</sup>  $\times$  300 K). The energy of a mole of carbon–carbon bonds is 360 kJ (Table 2.1) so the energy of each bond can be calculated by dividing through by Avagadro’s number:  $6 \times 10^{-19}$  J ( $= 360,000/6.02 \times 10^{23}$ ). The energy of the bond is 144 times that of the thermal energy at this temperature so we would expect thermal motion to have little effect; the probability of a bond breaking due to thermal energy using the Boltzmann distribution:





**Fig. 2.5** a Oleic acid, b Stearic acid, and c Elaidic acid

$$\frac{n_i}{n_0} = \exp\left(\frac{-\Delta E}{kT}\right) \quad (2.3)$$

where  $n_i$  is the number of molecules in the high energy state (e.g., nonbonded) and  $n_0$  the number in the low energy state (e.g., bonded). In this case  $n_i/n_0 = 1.86 \times 10^{-63}$ , a vanishingly small number, and we can be certain that unless the temperature is enormous, thermal energy alone will never break covalent bonds. Even as we heat a food and the molecular motions become faster, they are never likely to reach an intensity that the covalent bonds will spontaneously break and so, for our purposes, we can treat them as “fixed” linkages between atoms. Of course, making and breaking covalent bonds is important for many reactions in foods (e.g., the rancid aroma in oxidized fat results from the cleavage of carbon–carbon double bonds and the formation of carbon–oxygen bonds), and when we argue that bonds are fixed, we mean they will not break down by heat alone—there must be some sort of chemical mechanism proposed to allow the reaction to proceed. For the most part though, we will not deal with covalent bond reactions in this work and instead study the ways that intact molecules to build larger structures within food.

Although we can regard covalent bonds as permanent, we should not see them as rigid; they flex and vibrate elastically about their mean angles and lengths to a greater extent as they are heated. Importantly, single bonds are free to

rotate about their axis. Bond rotation can be responsible for dramatic changes in the shape of a molecule as illustrated in Fig. 2.3b which shows a 2D projection of the rotated forms of a substituted ethane compound (seen in Fig. 2.3a). The only significant restrictions to single bond rotation are interactions between substituent groups that may favor one configuration over another.

It is more difficult to rotate about a double bond as this would require breaking one of the bonds, rotating about the residual single bond, and then reforming the double bond in the opposite configuration. We can therefore treat the *cis*- (i.e., adjacent hydrogens on the same side of the molecule) and *trans*-isomers (i.e., adjacent hydrogens on the opposite side of the molecule) as different molecules with different properties. For example, most of the double bonds in natural vegetable oils are in the *cis*-configuration (e.g., oleic acid, Fig. 2.5a). To turn the liquid oils into solid fats for margarine, hydrogen is added across the double bonds to turn them into single bonds (i.e., hydrogenation, adding hydrogen to oleic acid converts it to stearic acid as shown in Fig. 2.5b). A by-product of this reaction is significant amounts of *trans*-fats (e.g., elaidic acid is the *trans* version of oleic acid, Fig. 2.5c). The original oleic acid has a kink in the chain due to the *cis* double bond while the saturated stearic acid and *trans* elaidic acid are straighter molecules. Although oleic and elaidic acids have the same chemical composition, the *cis* to *trans* isomerization raises the melting point from 4°C to 46.5°C.

Because of their strength and permanence, we can describe covalent bonds in terms of length, characteristic angles, and polarity and then treat the resulting molecules as more or less fixed building blocks from which we will assemble food structure. However, the bonds between molecules are usually much more tenuous and to understand them properly we will need a clear picture of how electrostatic forces acting at a distance give rise to a bond.

## 2.4 Intermolecular Forces

The closer you push the north poles of two magnets together, the more strongly they repel one another. Similarly, if you try to move the north pole of one magnet toward the south pole of a second, they will attract one another more and more strongly as they get closer. This is an everyday manifestation of the same electrostatic forces that are responsible for bonding. Rather than moving directly to a mathematical description of electrostatic forces, it is instructive to use an analogy to see how forces acting at a distance can give rise to bonds. Rather than pushing two magnets together, we will imagine pushing one ball across the sloping surface of a table toward a second, fixed ball. Various shapes of surface are shown in Fig. 2.6, the left hand figures show the height of the surface as a function of the separation between the two balls and the right-hand figures are the forces required to hold the moving ball at a given separation. If the table were flat (Fig. 2.6a), there would be no force needed to move the ball to any separation. If the surface sloped towards (Fig. 2.6b) or away from (Fig. 2.6c) the fixed ball, then the second ball would tend to roll away from it or towards it and would require a positive or negative force respectively to remain in a given position. The magnitude of the force required to hold the ball at a given position depends on the slope of the surface so in Fig. 2.6b and c the same force is needed to hold the moving ball at any separation from the fixed ball. Figure 2.6d shows a curved surface, the strength of the repulsive (positive) force increases as the separation

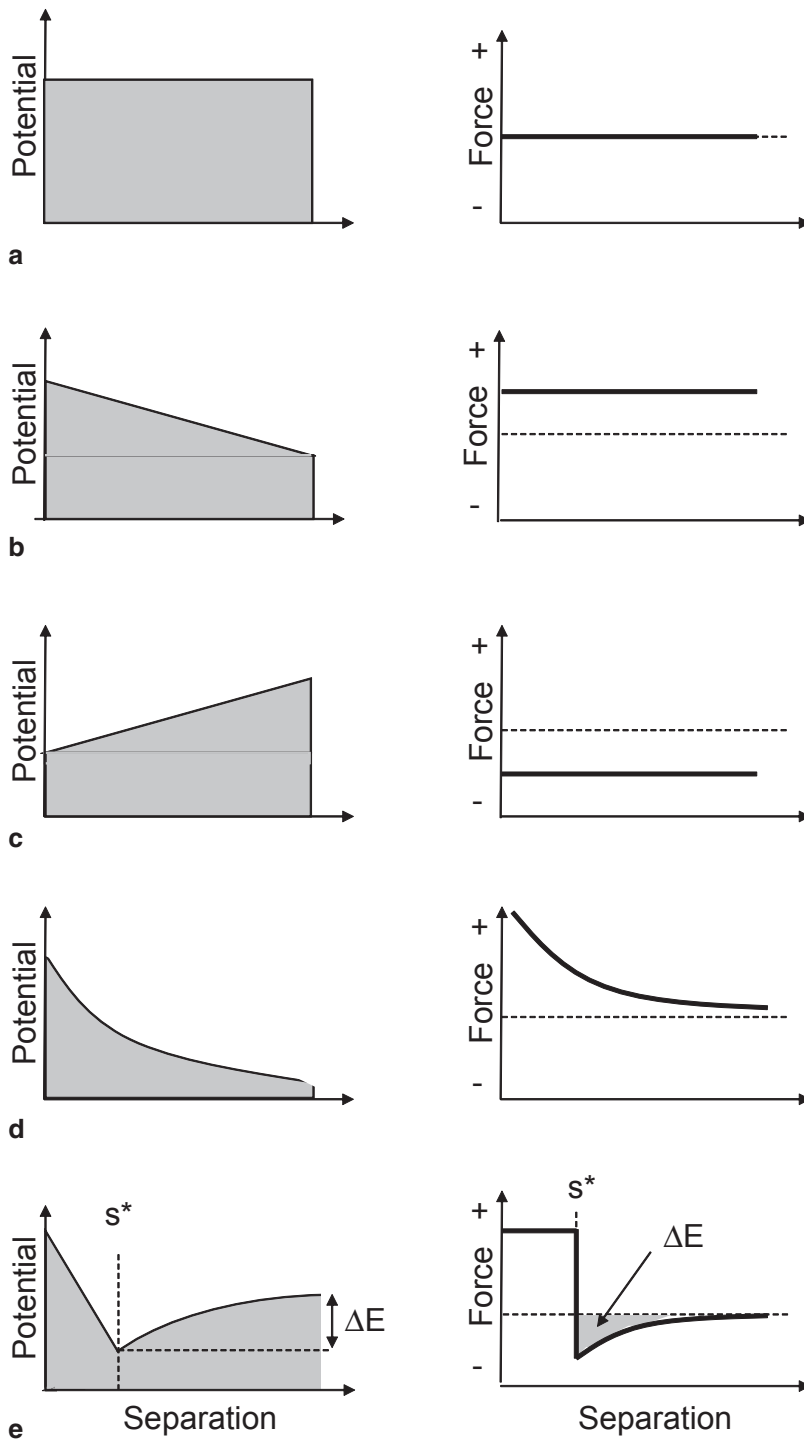
decreases. Figure 2.6e shows a complex surface, with an attractive force at long separations and a repulsive one at short separations. At an intermediate separation, the energy minimum, there is no net force acting on the moving ball and that position represents the equilibrium separation of the two balls. The moving ball will tend to roll into the energy minimum and stay there.

These trivial examples show how heavy balls will move according to a gravitational potential but we can reimagine the left hand figures as the electrostatic potential between two molecules as a function of separation. The right hand figures show the force acting on the moving molecule as it approaches the fixed molecule; if the force were negative at any point, it would tend to pull the molecules closer and if it was positive, the molecules would tend to repel one another. Figure 2.6a shows the potential for noninteracting particles (i.e., an ideal gas). Figure 2.6d shows a potential that gets steeper at shorter range. At long separations, there would be no forces between the molecules but, as separation decreases, the repulsive force gets stronger. This example corresponds to two similarly charged ions. Figure 2.6e represents a bonding potential. At long separations, there are no interactions between the molecules and they are free to move uninfluenced by one another. However, as they approach one another, the potential starts to curve downwards toward an energy minimum that tends to trap the molecules at a fixed separation from one another. The bond length is given by the separation at the energy minimum, that is, the separation when the slope of the potential, and thus the forces acting is zero (shown as  $s^*$  in Fig. 2.6e). The strength of the bond (shown as  $\Delta E$  in Fig. 2.6e) is the energy needed to pull the molecule out from the energy minimum and drag it to a range at which it no longer interacts with the fixed molecule. The bond energy at any separation can be expressed as either the depth of the energy minimum or the area under the force distance curve as shown in Fig. 2.6e.

To understand the interactions between molecules we must calculate the shape of the electromagnetic potential. In the next few sections,



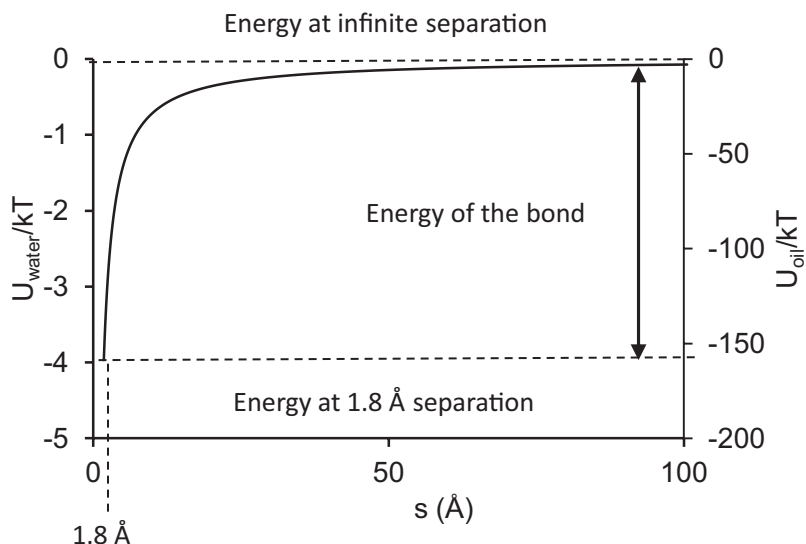
**Fig. 2.6** Energy potentials (*left*) and corresponding force–distance plots (*right*) between a fixed particle at separation zero and a second moving particle. **a** A flat potential—no forces acting. A potential with a constant **b** positive or **c** negative slope results in a repulsive (positive) or attractive (negative) force respectively. **d** Curved potential means force (negative slope) also changes with distance. **e** A complex potential with negative and positive forces as a function of distance. The minimum energy/zero force is the equilibrium separation ( $s^*$ ) of the particles and  $\Delta E$  is the energy required to move them from this separation out to a range where they no longer interact



we will look at various types of intermolecular interaction that might contribute to the overall interactions (i.e., types of bond). We will then sum

the individual interactions to get the full electromagnetic potential function and calculate the bond strength and length.

**Fig. 2.7** Interaction potential between a sodium and chloride ion in water ( $\epsilon_r=78$ , left axis) and oil ( $\epsilon_r=2$ , right axis)



## 2.5 Ion–Ion Interactions

The interaction energy between two charges a distance  $s$  apart is given by Coulomb’s law:

$$U_{ii}(s) = \frac{q_1 q_2}{4\pi \epsilon_0 \epsilon_r s} \quad (2.4)$$

where  $q_1$  and  $q_2$  are the magnitudes of the charge in coulombs (the charge on an electron is  $1.602 \times 10^{-19}$  C) and  $\epsilon_0$  and  $\epsilon_r$  are the dielectric permittivity of a vacuum ( $=8.85 \times 10^{-12}$  C<sup>2</sup> N<sup>-1</sup> m<sup>-2</sup>) and the relative dielectric constant of the medium separating the charges, respectively. The importance of equations such as this is to concisely and precisely state what we know about the interaction. For example, the common observation “like charges repel one another” is contained within Coulomb’s law: If the sign of  $q_1$  and  $q_2$  are similar then  $U(s)$  is positive and there would be an energy cost to bring the charges together. Coulomb’s law helps explain why sodium and chloride ions can sit alongside one another in a salt crystal but sodium and potassium ions cannot. Another common observation “salt dissolves in water but not in oil” can be quantitatively understood in terms of Coulomb’s law as the relative dielectric permittivity of oil is much less than that of water (approximately 2 and 78, respectively). The interaction potential between two dissimilar charges as a function of separation distance in oil

and water are shown in Fig. 2.7. The potential is negative in both cases and the ions attract one another, but the magnitude of the potential is much greater at a given separation in oil than in water. For example, taking the radius of a sodium ion as 1 Å and a chloride ion as 1.8 Å, their minimum separation should be 1.8 Å; if we wanted to dissolve them in a solvent, we would have to move the point charges from this separation out to an infinite distance. If we move the ions apart in water, the energy cost would be about 15 kT, a large energy barrier but not insurmountable. If we tried to move the ions apart in an oil solvent, the energy cost would be a prohibitive 600 kT. (A word of caution: In all of these calculations, we are assuming that the solvent can be described as a continuum with a dielectric permittivity equal to its bulk measured value. This probably reasonable at wide separations where there are many solvent molecules between the charges and their many different conformations tend to cancel each other out. However, when the separation between the ions is small, the exact arrangement of the few atoms and local charges on the solvent molecules will make a huge difference to the effective permittivity and the results from Eq. 2.4 will become unreliable as the essential graininess of matter becomes important.)

The range of the interaction is given by the functional dependence of the potential on separation distance. In this case, the potential is pro-

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