Chapter 4: molecule – a community of atoms

background reading

Atkins, P. (1994), *The Second Law*, Scientific American Library, W. H. Freeman, New York, paperback edition.

Atkins, P. (1995), *The Periodic Kingdom: a journey into the land of the chemical elements*, Weidenfeld and Nicolson, London.

Atkins, P. (2007), *Four Laws that Drive the Universe*, Oxford University Press.

Conway, E. (2023), *Material World: a substantial story of our past and our future*, W. H. Allen, London.

Czerski, H. (2017), *Storm in a Teacup: the physics of everyday life*, Black Swan, Transworld Publishers, London.

Cotterill, R. (2008), *The Material World*, Cambridge University Press.

Emsley, J. (2001), *Nature's Building Blocks: an A-Z guide to the elements*, Oxford University Press, Oxford.

Lucretius (1968), *On the Nature of the Universe*, translated by R. Latham, Penguin, London.

notes

Constructive comments are welcome.

The chapter header shows the molecule glycine, from Chemspider, CSID:730, http://www.chemspider.com/Chemical-Structure.730.html (accessed 07:32, Jun 28, 2023)

perceiving the atomic nature of the everyday world

"***a ring is worn thin***", Lucretius 1968:36.

4.1 molecular structures

4.1.1 bringing atoms together

Figure 4.1 is based on: (a) Emsley 2001:178; (b) Clugston 2000:69 and Keeler 2006:figure 5.3; (c) OrbiMol 3.1, at https://www.lct.jussieu.fr/pagesperso/orbimol/fr/index-fr.shtml; (d) Atkins 2002:figure 5.51, Clugston 2000:82, and Stephen Lower at http://www.chem1.com/acad/webtext/chembond/cb10.html. The orbital clouds of electron charge are around atoms and molecules, and may contain 1 or 2 electrons, but in this initial diagram they are all given the same shade of light grey. Later diagrams will discriminate different types of electron orbitals.

"**Consequently, helium forms no molecules**", Emsley 2001:178. Helium can be made to combine with other elements under extreme conditions, such as being ionised or put under high pressure, see https://en.wikipedia.org/wiki/Helium.

"***the power of an atom***", Pauling, quoted in Keeler 2008:271. Electronegativity is a powerful organising principle for understanding how the elements form compounds with each other, and is sometimes shown as a third dimension in the periodic table, for example, in Norman 1995:figure 2.4, and also Mark Winter's WebElements, at https://www.webelements.com/periodicity/eneg_pauling/.

"**In the fourth outcome**", I've chose sodium as the example metal because, along with chlorine, it illustrates 3 of the 4 major types of bonding, shown in figure 4.13.

"***made of nuclei and electrons***", Jensen 1998:821. Jensen says, logically, that we should talk of dinuclear and polynuclear molecules rather than diatomic or polyatomic molecules, but I will stay with the familiar terms, even if these are not strictly correct.

a continuum of sharing

the four types of bonding between atoms and molecules

"**The three main types of chemical bonding**", four basic types of bonding between atoms and molecules are recognised: van der Waals, covalent, ionic, and metallic and (Keeler 2008:chapter 1, Atkins 2002:chapters 2 and 5, Simon 2013:chapter 6, and also Mark Leach at http://www.meta-synthesis.com/webbook/38_laing/tetrahedra.html).

I'm putting all interactions between neutral atoms and molecules, which includes dispersion forces and dipole-dipole forces, under the collective name of van der Waals forces, following Atkins 2006:629, Keeler 2008:6, Jim Clark at http://www.chemguide.co.uk/atoms/bonding/vdw.html, and Stephen Lower at http://www.chem1.com/acad/webtext/states/interact.html (see the note to section 4.1.6 on van der Waals forces). Dipole-dipole forces only act on polar molecules, while dispersion forces are universal, and so I've put dispersion bonding in figure 4.1.

4.1.2 covalent bonds and molecular orbitals

This section is based on Keeler 2006:chapters 5 and 6, and 2008:chapters 3−5, Atkins 2002:chapters 2−3, Atkins 2006:chapter 11, Clugston 2000:sections 5.1−5.7, Stephen Lower at http://www.chem1.com/acad/webtext/chembond/cb08.html#SEC1, and Richard Spinney at https://undergrad-ed.chemistry.ohio-state.edu/mo/index.html.

There are two major quantum mechanical descriptions of molecules, valence-bond theory and molecular orbital theory (Atkins 2006:chapter 11). In valence-bond theory, the starting point is the concept of the shared electron pair, and it introduces *sigma* and *pi* bonds, and hybrid orbitals. In molecular orbital theory, electrons are not regarded as belonging to particular bonds, but are treated as spreading throughout the entire molecule. The concept of an atomic orbital is extended to a molecular orbital, which is a wavefunction that extends over all the atoms in a molecule. Molecular wavefunctions can be very complicated, and so approximate molecular orbitals are often built up by combining simpler atomic orbitals, and I've largely followed this approach in this chapter.

the hydrogen molecule

Figure 4.2 is based on Keeler 2006:figures 5.3−5.5. The relative directions of the axes follow Keeler 2008:chapter 3, and it is the convention for the two nuclei to lie on the *z*-axis.

This diagram introduces the conventions that will be used in future diagrams. Atomic and molecular orbitals do not have sharply defined boundaries, but I've marked them with different boundary lines so they can be seen more clearly, and also to indicate what type of orbital they are. Non-bonding atomic orbitals have dotted boundaries (····); bonding atomic orbitals have dashed boundaries (- - - -); and molecular orbitals have solid line boundaries (—). Orbitals are also shaded according to the number of electrons they hold: pale = 1, and darker = 2.

Figures 4.2−4.4 are intended to show simply how atomic orbitals combine to make molecular orbitals. So, they don't show the anti-bonding orbitals, but only the bonding orbitals, and show only electron spin (↑ or ↓), but not phase, or density of electron charge. The naming of molecular orbitals, such as the *sigma* (1*s*,1*s*) orbital, is taken from Atkins 2002:chapter 3.

For a clear diagrammatic presentation of molecular orbitals in diatomic molecules, see Keeler 2006:chapters 5−6 and 2008:chapters 3−4, and also the Chemogenesis Web book by Mark Leach at http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html.

The hydrogen molecule is only possible because the quantisation of energy results in a "*well-defined element called hydrogen with universal properties*", whose atoms can share their electron orbitals (Barrow 1992:197). See the note to section 3.7.3.

hydrogen fluoride

Figure 4.3 is based on Keeler 2006:figures 5.25−5.26. I've exaggerated the asymmetry of the *sigma (*$1s$,$2p_z$) orbital, so it does not obscure the other $2p$ orbitals.

the nitrogen molecule

Figure 4.4 is based on Keeler 2006, fig.5.12−5.18, 6.14 and 2008:figures 3.22−3.27.

sigma and pi molecular bonds

"**The two nitrogen atoms are bound**", Keeler 2006:72, 2008:121, Atkins 2002:148.

"**All single covalent bonds are sigma bonds**", Atkins 2002:130.

"**Both the the *sigma* and *pi* orbitals**", Keeler 2008:114. *Sigma* orbitals have a cylindrical symmetry about the inter-nuclear axis (Atkins 2006:365, Keeler 2008:152). Keeler 2008:99 explains how to distinguish *sigma*, *pi* and *delta* orbitals: (1) draw a circle around the inter-nuclear axis, and then (2) count the number of planar nodes that you encounter (n) when you follow this circular path round one circuit, (3) for *sigma* $n = 0$, for *pi* $n = 1$, and for *delta*, $n = 2$.

"**Consequently, a *sigma* covalent bond**", Keeler 2006:96 and 2008:114.

4.1.3 carbon and hybrid atomic orbitals

"**Now we'll see how different atomic orbitals**", Atkins 2002:131, Keeler 2006:83 and 2008:149 Atomic orbitals can combine to produce a variety of hybrid orbitals (Atkins 2002:133, Keeler 2008:149). Here we just look at sp^3 hybrid orbitals.

In polyatomic molecules the molecular orbitals can extend over all the atoms in the molecule, and these can be difficult to describe. For example, the lowest energy molecular orbital in methane encompasses all five atoms (Keeler 2008:figure 4.17). Hybrid atomic orbitals are a useful approximation to the full picture of a molecule, because they enable us to build up a description of bonding in terms of orbitals between pairs of atoms (Keeler 2006:93 and 2008:137 and 156).

"**Now the carbon atom**", Keeler 2008:151.

"**These four hybrid orbitals**", Keeler 2006:83 and 2008:151

"**The carbon atom in part (a-i)**", Atkins 2002:131,

"**The *sp*^{3} orbitals on two carbon atoms**", Keeler 2008:152, Atkins 2002:134.

"**Carbon chains form the backbones**", Keeler 2006:90, Atkins 2002:138. The sp^3 hybrid orbitals are highly directional in forming bonds with other atoms. The spherical $2s$ orbital has no preferred direction; the $2p$ orbitals point in two opposite directions; but the sp^3 orbital points unequivocally in one direction (Keeler 2006:84).

Figure 4.5(a) and (b) are based on Atkins 2002:131, Keeler 2006:figures 6.5−6.6 and 2008:figures 4.18−4.20, Stephen Lower at http://www.chem1.com/acad/webtext/chembond/cb06.html, and Jim Clark at http://www.chemguide.co.uk/basicorg/bonding/methane.html. Animations of hybrid orbitals are available from Ian Hunt at http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch02/ch2-3-1.html. The sp^3 hybrid orbitals have been "slimmed" down so they can all be seen more clearly.

Figure 4.5(c) is based on Keeler 2006:figure 6.15 and 2008:figure 4.22, and Atkins 2002:figures 3.16 and 3.20.

carbon's ability to form large molecules

"***intrinsic mediocrity***", "***aggressive shedder***", and "***avid receiver***", all from Atkins 1995:145.

"**Consequently, there are more compounds**", Atkins 2002:137.

"**Moreover, of all the elements**", McMurry 2000:3.

"**Combinations of single and double bonds**", the benzene molecule is usually portrayed as shown here, but in fact the molecular orbitals encompass all the atoms in the molecule (Atkins 2002:139 and 154, Keeler 2008:594).

"**Carbon-based rings**", the heme group, see Garret 2005:491 and Voet 1999:162.

"***aperiodic crystal***", Schrödinger 2007:5.

In **figure 4.6** the molecular structures of methane, ethylene (also known as ethene), n-octane, benzene, diazepam, guanine, and cytosine are from ChemEd DL, at http://chemdata.umr.umn.edu/resources/models360/models.php, kindly made available by Professor Xavier Prat-Resina.

The saccharine molecule is from https://chemapps.stolaf.edu/jmol/jmol.php?model=saccharin, kindly made available by Professor Robert Hanson.

The short length of the polymer PTFE is from https://pslc.ws/macrog/ptfe.htm, kindly made available by Dr, Lon Mathias. The PSLC site shows 3–D models of a wide variety of polymers, at https://pslc.ws/modelhtms/poly3D.htm.

The image of the heme group is from https://chemapps.stolaf.edu/jmol/jmol.php?model=, using the SMILES code "OC(=O)CC/c6c(\C)c3n7c6cc2c(/CCC(O)=O)c(/C)c1cc5n8c(cc4n([Fe]78n12)c(c=3)c(C=C)c4c)c(\C=C)c5\C", from https://en.wikipedia.org/wiki/Heme_B.

The image of the short length of DNA shown in part (j) has kindly been made available, by Professor Angel Herráez, of the University of Alcalá de Henares (Madrid), under CC BY-NC-SA 3.0 license, available at https://creativecommons.org/licenses/by-nc-sa/3.0/deed.en. The image has been modified to show the guanine-cytosine base pair outlined at the top. Compare this with Alberts 2008:figure 4-3, and McMurry 2000:figure 28.7. This view of the DNA molecule is also available at https://biomodel.uah.es/en/model3/adn.htm.

Many molecular structures are available at https://chemapps.stolaf.edu/jmol/jmol.php?model, just add "=molecule name", without the "", as shown in the specific examples given above. Wikipedia entries on molecules give links to their structures. Chemspider, at http://www.chemspider.com/, is a comprehensive database of molecular structures, each with its own Chemspider ID.

References for molecules: for heme, see Garrett 2005:138 and 491−499, Voet 1999:162; for PET, see McMurry 2000:1275; for diazepam see McMurry 2000:560; for saccharin see McMurry 2000:1064; for DNA and the bases guanine and cytosine, see Garrett 2005:chapter 10, Alberts 2008:197−199, McMurry 2000:1160. For the hierarchy of molecular structures found in living organisms, see Garrett 2005:figure 1.8.

4.1.4 unequal charge sharing and polar molecules

a continuum of bonding

“**We’ll see in chapter 5**”, Alberts 2008:50.

In **figure 4.7** the images of molecules are from the Orbimol database at http://www.lct.jussieu.fr/pagesperso/orbimol/fr/index-fr.shtml#., licensed under a CC BY-NC-ND 3.0 license. The Orbimol image of H_2 is in agreement with the one given by the PhET simulation “Molecule Polarity (1.02.02)”, at https://phet.colorado.edu/sims/cheerpj/molecule-polarity/latest/molecule-polarity.html?simulation=molecule-polarity. Orbimol shows a single bond in the CO molecule; it is in fact a triple bond (https://en.wikipedia.org/wiki/Carbon_monoxide).

I’ve used the well-established values of dipole moments to calculate the partial charges. When two partial charges, $+q$ and $-q$ Coulombs, are separated by a distance *d* metres, they produce an electric dipole with a dipole moment, $\mu = qd$ Cm. Dipole moments are usually given in Debye, D, where 1 D = 3.3×10^{-30} Cm (Atkins 2006:620).

The dipole moment of the NaCl molecule in the gas phase is 9 D (Nelson 1967:10), and the bond length is 236 pm (HyperPhysics at http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/NaCl.html#c1). From these figures we can calculate that the partial charge is $\sim 1.3 \times 10^{-19}$ C, or ~0.8*e*, where *e* is the electron charge. This tells us that about 0.8 of the electron charge is transferred from the sodium to the chlorine atom, so the Na–Cl bond is ~80% ionic. This agrees with Chemistry LibreTexts, example 12.4.2, at https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Map%3A_Physical_Chemistry_for_the_Biosciences_(Chang)/12%3A_The_Chemical_Bond/12.4%3A_Electronegativity_and_Dipole_Moment.

The carbon monoxide molecule has a dipole moment of 0.12 D and a bond length of 113 pm (https://en.wikipedia.org/wiki/Carbon_monoxide), giving a small partial charge of ~0.02*e*.

the water molecule

“**The ball-and-stick view**”, Alberts 2008:51.

“***shines through the thinned cloud***”, Atkins 2013:5.

All three views of the water molecule in **figure 4.**8 are from ChemEd DL, at http://chemdata.umr.umn.edu/resources/models360/models.php?. **Part (a)** is based on Alberts 2008:figure 2-12. The electrostatic potential surface, shown in **part (b)**, agrees with Atkins 2002:125, Keeler 2008:148 and Martin Chaplin, at https://water.lsbu.ac.uk/water/water_molecule.html. The partial charge values are those given by Chaplin.

We can take a simple view of the oxygen atom as having four hybrid atomic orbitals, which approximate to sp^3 hybrids, with two of these hybrids forming the two O – H bonds, and the other two hybrids then becoming non-bonding lone pairs (Keeler 2006:85 and 94, and 2008:146 and 160). This predicts the right bond angle, and a polar molecule, with a large partial negative charge at the oxygen end, balanced by partial positive charges at the hydrogen ends.

4.1.5 extended structures

silicates - network covalent crystals

“**analogue of methane**”, Atkins 2002:798.

“**But carbon and silicon**”, Norman 1995:53 and 65.

“**Silicon dioxide is a solid**”, Atkins 2002:784.

“**Moreover, silicate crystals**”, for silicate minerals, see Atkins 2002:794 and Cotterill 2008:165.

“**It’s estimated that over half the earth’s crust**”, Cotterill 2008:154.

“**Consequently, about 90% of the rocks**”, Clugston 2000:chapter 19.5, Cotterill 2008:165−168. For a review of minerals in the Earth’s crust, see Cotterill 2008:chapter 7.

In **figure 4.9(a) and (b)**, the views of the CH_4, SiH_4 and CO_2 molecules, and the silicate tetrahedron are from https://chemapps.stolaf.edu/jmol/jmol.php?model=silicate. The chain of silicate tetrahedra in **part (c)** is built up from two slightly different views of a single silicate tetrahedron.

The linked tetrahedra in **part (d)** are based on http://butane.chem.uiuc.edu/pshapley/Environmental/L27/1.html, and https://openpress.usask.ca/physicalgeology/chapter/5-4-silicate-minerals-2/, and these can also be seen in Cotterill 2008:166, and Clugston 2000:341.

The ionic crystal shown in **parts (e) and (f)** is based on on Atkins 2002:figures 2.4, 5.37 and 5.38, Durrant 2000:64, and Stephen Lower at http://www.chem1.com/acad/webtext/states/crystals-ionic.html.

The metal crystal shown in **part (g)** is based on Atkins 2002:figure 5.51, Clugston 2000:82, and Stephen Lower at http://www.chem1.com/acad/webtext/chembond/cb10.html.

The graph in **part (h)** is based on Mark Leach at http://www.meta-synthesis.com/webbook/38_laing/tetrahedra.htm.

ionic crystals – sodium chloride

“**Thus, Na^+ and Cl^- ions spontaneously**”, Atkins 2002:section 5.11.

the metallic state

“**The ions are attracted**”, Simon 2013:59.

a suite of metallic properties

“**The mobile population of electrons**”, Cotterill 2008:chapter 10, Atkins 2002:section 5.14 and Stephen Lower at http://www.chem1.com/acad/webtext/chembond/cb10.html.

“**Because the electrons in a metal**”, Cotterill 2008:239, Atkins 2002:257.

“***our own image on a smooth metallic surface***”, Atkins 1995:43.

“**The atoms of some elements**”, notably the *d*-block elements iron, cobalt and nickel, Cotterill 2008:241, Simon 2013:chapters 20−21.

“**It has been argued**”, Cotterill 2008:chapter 9.

metallic properties emerge as the cluster gets bigger

“**Metallic elements**”, Leach at http://www.meta-synthesis.com/webbook/38_laing/tetrahedra.htm, Roduner 2006, and Stace 1988 and at https://www.nottingham.ac.uk/chemistry/documents/iyc2011clusters.pdf. I have used Stace’s graph for the melting point of gold clusters, and his formula: number of atoms, $N = (R_{\text{cluster}}/R_{\text{atom}})^3$, where *R* stands for radius, and 0.144 nm as the gold atomic radius in the metallic state (Atkins 2002:appendix 2D). From Stace’s graph, a melting point of 800 K (527°C) correlates with a cluster size of ~2.5 nm diameter, which contains ~700 atoms. The melting point is getting close to the bulk value of 1,064°C for cluster sizes bigger than 20 nm diameter, which contain about 350,000 atoms.

comparing covalent and metallic bonds

"***to be metallic requires, in a sense, a looseness of electrons***", Atkins 1995:42.

"***universal pool of electrons***", Feynman 1964:30-3.

4.1.6 van der Waals bonding – attraction without sharing any electron charge

"**These attractions are generally called van der Waals forces**", Atkins 2002:sections 5.1–5.5, and Keeler 2008:6 for a simple overview, and Atkins 2006:section 18.4 for more detail. Van der Waals forces are sometimes called inter-molecular forces between molecules, to distinguish them from the intra-molecular forces within molecules, such as covalent bonds, that bind atoms into molecules (Atkins 2002:221, Laing 1993).

I'm putting all interactions between neutral atoms and molecules under the collective name of van der Waals forces, following Atkins 2006:629, Keeler 2008:6, Jim Clark at http://www.chemguide.co.uk/atoms/bonding/vdw.html, and Stephen Lower at http://www.chem1.com/acad/webtext/states/interact.html.

Within this broad grouping, particular interactions are sometimes given their own names: Keesom interactions (dipole-dipole), Debye interactions (permanent and induced dipole), and dispersion (sometimes called London) interactions (induced dipoles) – see, for example, Atkins 2002:227, Atkins 2006:section 18.4.

The van der Waals interaction is sometimes defined as an attractive force between molecules that varies as the inverse of the sixth power of the distance between them, so $F \propto 1/d^6$ (Atkins 2006:629, Mahan 2011:75). For some authors, only those forces arising from fluctuating dipoles are called van der Waals interactions (Cotterill 2008:68, Simon 2013:57).

The dispersion and dipole-dipole interactions are the weakest of the van der Waals interactions, and also fade away quickest with distance (Atkins 2002:table 5.1). While dispersion forces are individually weak, their net effect in a large aggregate of molecules can be considerable. Also, dispersion forces become stronger with bigger molecules that have more electrons, and which can acquire bigger fluctuating partial charges. The dispersion force is always attractive, and is the only force that can bind non-polar atoms and molecules together (Atkins 2002:228).

dispersion forces

"**Charge fluctuations**", Keeler 2008:7.

"**Dispersion forces are always attractive**", Atkins 2002:228. The attractive dispersion force can be seen as the electrical analogue to a bar magnet magnetising a paper clip, so that the clip is then attracted to the magnet – regardless of which pole of the magnet is brought up to the clip (Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/waal.html).

dispersion forces and everyday substances

"**We can use boiling points as a qualitative guide**", Jim Clark at http://www.chemguide.co.uk/atoms/bonding/vdwstrengths.html#top.

"**If these gases are simply cooled**", Atkins 2002:228 and self-test 5.2A.

"**Part (d) also gives the boiling points of a few straight-chain hydrocarbons**", these are the normal or n-alkanes, McMurry 2000:figure 3.4, Atkins 2002:229.

"**A molecular solid or liquid has two levels of binding**", Atkins 2002:221, Laing 1993.

"**So, benzene**", Atkins 2002:253.

"**However, a temperature of around 1,000°C**", Brioukov 1999.

"**Bitumen is a naturally occurring hydrocarbon**", http://www.petroleum.co.uk/bituemn [sic].

Figure 4.10, parts (a) and (b) are based on Atkins 2002:section 5.4, Atkins 2006:section 18.4, and Stephen Lower at http://www.chem1.com/acad/webtext/states/interact.html.

The molecular solid, in **part (c)**, is based on Atkins 2002:figures 5.4 and 5.6, and Jim Clark at http://www.chemguide.co.uk/atoms/bonding/vdw.html.

In **part (d)**, the data on the boiling points are from the respective Wikipedia pages, and from Atkins 2002:table 5.2 for inert gases. The boiling points of the straight-chain hydrocarbons are sensitive to the chain length, especially for short-chain molecules (McMurry 2000:figure 3.4).

dipole-dipole forces

Figure 4.11 is based on Atkins 2002:section 5.3, Atkins 2006:section 18.4, Jim Clark at http://www.chemguide.co.uk/atoms/bonding/vdw.html, and Stephen Lower at http://www.chem1.com/acad/webtext/states/interact.html.

In **parts (c) and (d)** The boiling points of butane and 1-fluorobutane are from https://www.chemguide.co.uk/atoms/bonding/vdwstrengths.html#top.

water and hydrogen bonding

"**A hydrogen bond is highly directional**", Atkins 2002:232.

"**At any moment**", Chaplin at https://water.lsbu.ac.uk/water/water_hydrogen_bonding.html.

"**These dynamic bonds**", Stephen Lower at http://www.chem1.com/acad/webtext/states/water.html#SEC2, and Garrett 2005:33.

"**The result is that there are no water molecules**", the directionality of hydrogen bonding leads to the formation of different clusters of water molecules, see Chaplin at https://water.lsbu.ac.uk/water/clusters_overview.html.

"**The hydrogen bond is a weak bond**", Chaplin at https://water.lsbu.ac.uk/water/water_hydrogen_bonding.html, and Atkins 2002:759.

"**Nonetheless, the properties of liquid water**", Jim Clark at http://www.chemguide.co.uk/atoms/bonding/vdwstrengths.html#top, and Stephen Lower at http://www.chem1.com/acad/webtext/states/interact.html.

"**Molecules of glycerine and sugars**", Stephen Lower at http://www.chem1.com/acad/webtext/states/water.html#SEC2, and the simple sugars (monosaccharides) are described by Garrett 2005:section 7.2.

Figure 4.12 is based on Atkins 2002:section 5.5, Atkins 2006:section 18.4, Voet 1999:section 2.1, Stephen Lower at http://www.chem1.com/acad/webtext/states/water.html, and Martin Chaplin at https://water.lsbu.ac.uk/water/water_molecule.html and at https://water.lsbu.ac.uk/water/hydrogen_bonds.html.

water has unusual, biologically important properties

"**Typically, living organisms are aqueous systems**", Garrett 2005:31.

“**The properties of liquid water are dominated by hydrogen bonding**”, Atkins 2006:635, Garrett 2005:chapter 2, Voet 1999:chapter 2, Stephen Lower at http://www.chem1.com/acad/webtext/states/water.html#SEC2, and Martin Chaplin at https://water.lsbu.ac.uk/water/water_life.html.

“**It is estimated that, in the absence of hydrogen bonding**”, Chaplin at https://water.lsbu.ac.uk/water/phase_anomalies.html.

“**Second, water is an outstanding solvent**”, Voet 1999:23.

“**But water is a poor solvent**”, Garrett 2005:48.

“**It is considered**”, Voet 1999:24.

hydrogen bonding in biological structures

“**Cellulose is a polymer of the sugar glucose**”, Purves 1998:50, Garrett 2005:223, Cotterill 2008:439.

“**As the principal structural molecule**”, Purves 1998:49, Garrett 2005:223.

“**The mechanical strength of wood**”, Atkins 2002:233.

“**Hydrogen bonds give water a high cohesive strength**”, Purves 1998:33.

“**But a hydrogen bond is formed**”, Atkins 2002:232, Alberts 2008:54, and Berg 2012:8. A hydrogen bond has the general form A—H····B, where A and B are highly electronegative atoms, typically oxygen or nitrogen, but also possibly fluorine or chlorine. Hydrogen bonds, involving these atoms play a variety of rôles in biological structures (Stephen Lower at http://www.chem1.com/acad/webtext/states/water.html, Purves 1998:26, and Garrett 2005:15).

“**Hydrogen bonds play a vital rôle**”, Garrett 2005:154, Alberts 2008:126, Keeler 2008:9.

“**Figure 4.6 showed how the two strands of the DNA double helix**”, Purves 1998:248, and Alberts 2008:197. The polar molecules guanine and cytosine, can be viewed at http://www.lct.jussieu.fr/pagesperso/orbimol/fr/index-fr.shtml. Stephen Lower describes the main biological rôles of hydrogen bonding at http://www.chem1.com/acad/webtext/states/water.html.

4.1.7 the emergence of the materials of the everyday world

“**There are many atom combinations**”, Laing 1993.

“***transitions between these different regions is seamless***”, Keeler 2008:303.

Figure 4.13 is based on Jensen 1998, Laing 1993, Keeler 2008:figure 7.46, Mark Leach at https://www.meta-synthesis.com/webbook/38_laing/tetrahedra.php, and Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/bond.html#c1. Four basic types of bonding between atoms and molecules are recognised: covalent, ionic, metallic and van der Waals (Keeler 2008:chapter 1, and see also Mark Leach at http://www.meta-synthesis.com/webbook/38_laing/tetrahedra.html. Leach discusses several triangular systems of bonding, at http://www.meta-synthesis.com/webbook/37_ak/triangles.html. The triangular base of the tetrahedron corresponds to the Van Arkel diagram, linking metallic, covalent and ionic bonding. These are at the apexes of the triangle, and are the extremes of a seamless continuum of bond types (Keeler 2008:302). Figure 4.13 focusses only on the electron interactions that are the basis for the four types of bonding; others, such as Jensen and Leach have included the bulk materials they produce.

4.2 the three states of matter – solids, liquids and gases

This section is based on Simon 2013:chapters 7 and 12, Cotterill 2008:chapters 4 and 5, Tipler 1999:section 38-4, Atkins 1998:chapter 24, Atkins 2002:chapter 5, Atkins 2006:chapters 20 and 21, Bolton 1974:chapter 9, Bolton 2000:chapter 1, and Feynman 1998:chapter 1.

“**Our everyday world**”, Lucretius, writing in the 1st century BC, is an excellent example of interpreting the everyday macroscopic world in terms of the activities of minute atoms.

“**For example, the particles can be**”, Atkins 2002, sections 5.9−5.13.

thermal energy and molecular motion

“**At any temperature above absolute zero**”, the microscopic kinetic energy of atoms and molecules is often called thermal energy (Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/molke.html#c1).

“***although all the atoms are in motion***”, Lucretius:69., who uses the word “atom” for all fundamental particles.

4.2.1 the energy-distance curve

Figure 4.14(a) is based on Bolton 2000:figure 1.11, Atkins 2006:figures 1.13 and 18.10; **part (b)** is based on Cotterill 2008:104, Atkins 2002:figure 5.22, and Bolton 2000:figure 1.20; **part (c)** is based on Simon 2013:figure 7.3, Atkins 2002:figures 5.11, 5.12, and 5.15, and Bolton 2000:figure 1.19; **part (d)** is based on Atkins 2002:figure 4.24.

Part (b) has 25 particles in a regular 5x5 array; in part (c) these 25 particles have been arranged roughly within a circle, representing a spherical droplet. In part (d) the particles have been spaced roughly 9 diameters apart, as in ambient air, so where there were 25 particles in the solid and liquid states, we now see only 3.

Figure 4.14 is a simple depiction of the three familiar states of matter and it does not cover glasses, liquid crystals, quasicrystals, or plasmas. Real crystals are not perfect arrays of identical atoms, and can have defects, such as dislocations, which are local discontinuities in the crystal structure, foreign atoms of different sizes, and vacancies, where an atom is missing. All these defects enable diffusion to occur in crystals. In a typical metal close to its melting point about 1 in 1,000 atomic sites is a vacancy (Cotterill 2008:125). Only two liquids occur naturally in appreciable amounts on Earth – water and petroleum (Cotterill 2008:139).

An online simulation of diffusion in gases is available at https://phet.colorado.edu/sims/html/diffusion/latest/diffusion_en.html.

“**Consequently, the average separation**”, Bolton 2000:33, Tipler 1999:633.

“***all things are made of atoms***”, Feynman 1998:4.

“**So, there is a competition**”, Bolton 2000:20.

4.2.2 crystalline solids

“**Imagine an ensemble of particles**”, at sufficiently low temperatures even weak van der Waals forces will cause practically every substance to condense into a liquid and then into a solid (Tipler 1999:1219). If we keep decreasing the temperature, particle vibrations decrease until at absolute zero, 0 K, the particles have a minimum amount of vibration, but not zero. This minimum amount of motion is not enough to melt any substance, except for helium. Helium remains liquid, even at absolute zero, but it can be made to solidify if put under high pressure (Feynman 1998:10).

“**Our word “crystal”**”, Cotterill 2008:101.

“**The solid circles**”, if the particles in the top layer are directly above the particles two layers below, then this gives the hexagonal close-packed structure (hcp) (Cotterill 2008:105). If the particles in the top layer sit directly above the gaps between 3 particles 2 layers below, then this gives a different crystal structure, known as face-centred cubic (fcc). The difference can be shown in a 2−D figure (Atkins 2002:figures 5.22−26, Atkins 2006:figures 20.32−5), and can be explored with marbles or oranges, and seen in displays of fruit like apples and oranges. Of the common metals, zinc and titanium have the hcp structure, and copper, silver, gold and aluminium have the fcc structure (Atkins 2006:table 20.2). There is a third crystal structure that some metals take up, such as iron and chromium, and this is body-centred cubic (bcc), which is slightly less compact than hcp and fcc.

“**In this crystal arrangement**”, this is the coordination number, which is 12 for hcp and fcc, and 8 for bcc (Atkins 2002:section 5.9, Cotterill 2008:109). If solid spheres are arranged in the most compact hcp and fcc crystalline structures, the packing fraction, which is the volume of 3−D space filled by the spheres, is 0.74, so more than ¼ of the space inside these arrangements is empty (Atkins 2002:242, Atkins 2006:716). There is a limited range of possible crystal structures (Cotterill 2008:104−5).

“**Consequently, a crystalline structure**”, Feynman 1998:9.

“**So, all the particles in a crystal**”, Atkins 1994:180−181.

4.2.3 liquids

“**But as the temperature rises**”, Bolton 1974:229. A substance’s latent heat is a measure of the number of particle-particle bonds that must be broken to effect the change of state, solid to liquid, or liquid to gas. To vaporise a liquid requires breaking all the bonds in the liquid state so that the particles can move independently in the gas state. The inert gases, argon, neon, krypton and xenon, each have a latent heat of fusion that is ~1/5th of its latent heat of vaporisation (Bolton 1974:229). This suggests that the solid-liquid transition requires breaking about 1/5th as many bonds as the liquid-vapour transition. So, to melt a crystal one need only break around 2 out of 12 nearest-neighbour bonds, and to vaporise the liquid one must break the remaining 10 bonds – about five times as many.

A liquid’s short-range order is revealed by X-ray diffraction, from which one can derive its radial density function (see Bolton 2000:figures 1.16, 1.18 and 1.23 for gases, liquids and solids, and Atkins 2006:figure 17.14 for water at different temperatures).

“**The increased thermal energy**”, Atkins 1994:180−181.

“**A small water droplet**”, drops of water on a hydrophobic surface, such as aluminium foil rubbed with olive oil, will draw themselves into circular discs. Smaller drops, with a bigger surface area to volume ratio, will be more rounded, closer to a hemispherical shape.

4.2.4 gases

“***most of its time beyond the range of influence of others***”, Bolton 2000:21.

“***essentially on its own almost all the time***”, Cotterill 2008:101.

“**The word “gas” is derived**”, Bolton 2000:22.

“**But in fact**”, Bolton 2000:figure 1.12. If you plot the average kinetic energy at the boiling temperature against binding energy for a large number of elements, you find they roughly follow this 1:10 ratio.

moving molecules in still air

This section is based on Atkins 1998:sections 1.3 and 27.1, Atkins 2006:sections 1.3 and 21.1, and Tipler 1999:section 18-5.

“**Second, chemical reactions**”, Zewail 1999:figure 1.

Figure 4.15(a) is based on Atkins 2006:754, and Tipler 1999:554, and **part (b)** is based on Atkins 1998:figure 0.1, and Bolton 2000:figure 1.19, and uses the water molecules shown in figure 4.8.

Figure 4.15(a) is an attempt to give a rough idea of the relative size and spacings of molecules in ambient air, so the distribution is deliberately non-random, for the molecules are all roughly equally spaced. A truly random distribution has a large spread in the spacings, so that molecules are clustered in some regions and absent from others (Bolton 2000:figure 1.14). One method of estimating the mean free path in a gas is to “freeze” all the molecules but one, and I’ve used that idea in the figure, rather than trying to depict molecules moving with random speeds and directions (Tipler 1999:553).

The diatomic nitrogen molecule, N–N, is not spherical but we can take its effective diameter as about 0.38 nm (Tipler 1999:554), which is consistent with the value of 0.43 nm^2 for its collision cross-section (Atkins 2006:753).

the physics of gases

This section explains the basic physics of gases that underlies **figure 4.15(a).**

molecular spacings in air

The volume of 1 mole, that is, 6×10^{23} molecules (Avogadro’s number), under ambient conditions, at 1 atmosphere pressure and 25°C (~300 K), is 24.8 litres (Atkins 2006:11).

So, a 10 cm (1 dm) cube, with a volume of 1 litre, contains $6 \times 10^{23}/24.8 = 2.4 \times 10^{22}$ molecules.

If we take the molecules as evenly distributed within this volume, this means there are $(2.4 \times 10^{22})^{1/3} \approx 3 \times 10^7$ molecules along each 10 cm (0.1 m) axis of the cube, so the average spacing between molecules is $0.1/3 \times 10^7 \approx 3.5 \times 10^{-9}$ m ≈ 3.5 nm (in agreement with Bolton 2000:21). So, the molecules are on average about 3.5/0.38 ≈ 9 molecular diameters apart.

average molecular speed due to thermal energy

The mean kinetic energy of a molecule, E_k, depends only on its temperature, regardless of what kind of molecule it is (Feynman 1963:39-10), and is given by the simple equation

$E_k = 3kT/2$

where k J/K is Boltzmann’s constant, and T K is the absolute temperature. Boltzmann’s constant has a very small value, 1.38×10^{-23} J/K, because it relates the energy of a single atom or molecule to its temperature.

So, a gas molecule’s mean kinetic energy at 300 K will be

$E_k = 3 \times 1.38 \times 10^{-23} \times 300/2 \approx 6.2 \times 10^{-21}$ J, which is $6.2 \times 10^{-21}/1.6 \times 10^{-19} \approx 0.04$ eV.

This energy is tiny compared to the dissociation energy for the triple bond in the nitrogen molecule, which is ~940 kJ/mole, equivalent to ~10 eV per molecule (Atkins 2006:table 11.3).

We know that an object’s kinetic energy is given by the well-known formula

$E_k = ½ mv^2$

where m kg is the object's mass, and v m/s is its velocity.

We can put together the two expressions for kinetic energy, and get

$E_k = 3kT/2 = ½ mv^2$

and rearrange this to find the velocity

$v = (3kT/m)^{1/2}$

A mole of nitrogen (N_2) molecules, that is 6 x 10^{23} molecules, has a mass of 28 x 10^{-3} kg, so a single molecule has a mass of ~4.7 x 10^{-26} kg. From this, we can easily calculate a nitrogen molecule's average speed in ambient air at 300 K (about 27 °C), as:

$v_{av} = (3 \times 1.38 \times 10^{-23} \times 300/4.7 \times 10^{-26})^{1/2} \approx 515$ m/s.

Oxygen makes up about 21% of the air around us and has a molar mass of 32 x 10^{-3} kg, which is slightly more than nitrogen, and so their average speed is slightly slower, around 480 m/s (Atkins 2002:figure 4.27).

A molecule's total energy is the sum of its energies in different modes of motion, which include translation (moving from one place to another), rotation and vibration, so:

$E_{total} = E_{translation} + E_{rotation} + E_{vibration}$

and these modes can be regarded as fairly independent.

Each mode of motion has a number of degrees of freedom. There are three degrees of freedom of translation, corresponding to the x-, y- and z-axes of space. The number of degrees of freedom in rotation and vibration depend on the shape of the molecule, and the number of atoms in it. A linear molecule like N_2 has 2 degrees of freedom in rotation, and one in vibration. A non-linear molecule like H_2O has 3 degrees of freedom in rotation, and 3 in vibration. Each degree of freedom of a molecule's motion is assigned an energy of $kT/2$, following the theorem of the equipartition of energy (Atkins 2006:sections 2.2 and 17.2, Tipler 1999:552, and Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/eqpar.html#c1).

In the explanation above, I've considered only a molecule's energy of translation, given by its kinetic energy. This is highly simplified, but it gives us a way to calculate the average speeds of molecules in randomly interacting ensembles, such as gases and liquids. For a fuller explanation, see Atkins 2002:chapter 4, Tipler 1999:sections 18-4 and 18-5, Atkins 2006:sections 2.2, 17.3 and 21.1, Feynman 1963:chapter 39, and Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/ktcon.html#c1.

In the calm warm air around us the molecules are moving around and hitting our skin at surprisingly high speeds, about half a kilometre per second. We don't notice these impacts because individual molecules are so light, and because collectively they are hitting us from all directions, so we experience only a steady pressure, and no net force from any one direction. We're very conscious of the collective impacts of air molecules in a gale force wind, because the wind is blowing from one direction, even though the air speed may only about 20 m/s. To experience the force of air moving in one direction at 500 m/s, which is about 1½ times the speed of sound, one would have to be in the path of the blast wave from a substantial explosion (Dewey 1964).

Maxwell-Boltzmann velocity distribution in gases

Because of their random collisions, molecules in a gas are moving at a range of speeds, and this is given by the Maxwell-Boltzmann distribution (Atkins 2006:figure 21.3, Tipler 1999:figure 18-14). The distribution function in terms of single molecules is:

$f(v) = 4\pi(m/2\pi kT)^{3/2}v^2\exp(-mv^2/2kT)$

where m is the molecular mass in kg, k is Boltzmann's constant (1.38 x 10^{-23} J/K), T is the temperature in K, and v is the speed in m/s (Tipler 1999:equation 18-37).

The distribution function for a macroscopic volume of gas is the same, but with the molar mass, M, in place of molecular mass, m, and the gas constant, R = 8.314 J/K/mol, in place of Boltzmann's constant (Atkins 2006:equation 21.4, and Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/kintem.html#c3).

This distribution function can be plotted in Excel for nitrogen gas, for which the molecular mass is 28 amu, or 28 x 1.66 x 10^{-27} ≈ 4.7 x 10^{-26} kg, for low (200 K), medium (300 K) and high (400 K) temperatures, and one gets the standard set of curves commonly shown in texts, such as Atkins 2006:figure 21.3, and Tipler 1999:figure 18-14.

The usual measure of the "average" molecular speed is the root mean square speed, which is is the average speed calculated from the average thermal energy, and is the square root of the mean of the squares of the speeds, and is $c = (3kT/m)^{1/2}$ (Atkins 2006:figure 21.6). For nitrogen in ambient air, with T = 300 K, this speed is ~515 m/s. We need only a rough figure for average speed, and I've gone for the round figure of 500 m/s, following Atkins 2006:754.

mean free path and collision rate

Under ambient conditions the mean free path of a nitrogen molecule between successive collisions is ~70 nm (Atkins 2006:754, Tipler 1999:554), somewhat less than 200 times its own diameter. With a mean speed of ~500 m/s, this means that the average time between collisions is ~0.14 nanoseconds, so a nitrogen molecule has on average ~7 x 10^9, or 7 billion collisions each second.

molecular spacings in liquid water

Figure 4.15(b) attempts to give a rough idea of the relative size and spacings of molecules in water.

Pure water has a molar mass of 18 g and a density of 1,000 g/dm^3, so its molarity is 1,000/18 ≈ 56 M. This means that there are 56 x 6 x 10^{23} x 10^3 = 3.4 x 10^{28} water molecules in 1 m^3, and so there are 3.3 x $10^{28}/(10^9)^3$ ≈ 34 molecules in a volume of 1 nm^3. We can visualise this as a 1 nm cube with 3.2 water molecules along each side, since $34^{1/3}$ ≈ 3.2. The figure is a 2–D representation of this, with about 9 molecules in a 1 nm square.

4.2.5 the thermal energy of water molecules

"**Like nitrogen molecules in air**", a mole of water (H_2O) molecules, that is 6 x 10^{23} molecules, has a mass of 18 x 10^{-3} kg, so a single molecule has a mass of ~3.0 x 10^{-26} kg.

A water molecule's average speed in water at 300 K (about 27 °C) is:

$v_{av} = (3kT/m)^{1/2} \approx 640$ m/s.

An online molecular speed calculator is available at http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/eqpar.html#c1.

"**With water molecules moving this fast**", Feynman gives a figure of 10^{14}/second for the collision rate (Feynman 1963:41-8); Zewail puts collision rates in liquids at around 10^{13}–10^{14}/second (Zewail 1999:figure 1), and Hoffmann gives a collision rate from water molecules of 10^{13}/second (Hoffmann 2012:145).

This motion of molecules is known by the rather bland term "thermal motion", but Peter Hoffmann observes that "*If we were reduced to the size of a molecule, we would be bombarded by a **molecular storm** – a storm so fierce, it would make a hurricane look like a breeze*" (Hoffmann 2012:72). However, the difference between a hurricane and a molecular storm is that a molecular storm has no preferred direction, so every collision from a water molecule comes from a random direction (Hoffmann 2012: 145).

"**For example, 1 litre of tepid water**", a water molecule's thermal energy at 300 K (about 27 °C) is the same as for nitrogen in air, that is, 6.2 x 10^{-21} J, or ~0.04 eV.

Pure water contains about 56 moles/litre, so 1 litre will hold about 56 x 6 x 10^{23} ≈ 3.3 x 10^{25} molecules.

Each of these molecules has an average thermal energy of ~6.2 x 10^{-21} J, and so 1 litre of water molecules has a total thermal energy of ~200,000 J, or 200 kJ. This is equal to the kinetic energy of a 1,000 kg car travelling at about 20 m/s (about 70 km/h, or 45 miles/h).

The explosive energy yield of TNT is ~4.2 kJ/g, and its density is 1.65 g/cm^3, so an energy of 200 kJ would require 200/4.2 ≈ 48 g of TNT, with a volume of 48/1.65 ≈ 29 cm^3, which is roughly the volume of a 3 cm cube (https://en.wikipedia.org/wiki/TNT).

4.2.6 the diffusion of water molecules

"***the random migration of molecules***", Berg 1993:5.

"***the gradual dispersal of one substance***" (Atkins 2002:196). Diffusion is also described as "*the migration of matter down a concentration gradient*" (Atkins 2006:747). And so we tend to think of diffusion in terms of concentration gradients of solute molecules in a solvent, where inhomogeneities are smoothed out (Atkins 2006:772). But it's not just solute particles that are moving about, because all the particles in the liquid are diffusing. If we drop a coloured sweet in a glass of water, and leave it undisturbed, then after a while we see that the colour is slowly dispersing, spreading sideways and upwards. It's natural to think of only the coloured "sweet" molecules moving, but they can only move because all the water molecules are moving around as well.

Diffusion does occur in metal crystals, but it is minor and very largely enabled by the existence of empty sites known as vacancies (Cotterill 2008:124).

"**Diffusion never stops**", Morris 2013:5−8.

liquids – the social state of matter

4.3 thermodynamics and molecular interactions

"**In the rest of this chapter**", The universe is a vast ensemble of energetic particles, which are all randomly moving and interacting with each other, and its life and evolution is enacted in a series of discrete particle events. This is an attempt to understand how the universe's evolution is driven and directed by the changing distribution of its energy. Accordingly, I describe things in terms of molecular, or statistical, thermodynamics, and focus on the 1st and 2nd laws, entropy, and the Gibbs free energy. These explain why things change the way they do, and how organised structures can be generated, and this lays the foundations for the emergence of biological life in Level 5.

The only reference to classical thermodynamics is the definition of entropy change. Although "*entropy is a thermodynamic concept, in the sense that it is a property of bulk samples of matter, it has a very straightforward molecular interpretation*" (Atkins 2002:341). Frank Lambert has written that "*the energy in the motion of molecules is essential to understand entropy*" (Lambert 2006:15).

A fully rigorous exposition of molecular and classical thermodynamics requires advanced mathematics, and this is what you find in academic texts. However, I think it's possible to give a simple, qualitative explanation of the statistical behaviour of large ensembles of molecules, and thereby explain everyday events, and that's what I've tried to do here. Peter Atkins has given a non-mathematical account of the 2nd law in Atkins 1994.

I've drawn on the writings of Peter Atkins, who has probably thought as much as anyone about the 2nd law and entropy, and also on the the work of Frank Lambert, who clarified the concept of entropy.

a universe full of energy and change

"**We've seen that the atoms and molecules**", I'm leaving out the three other modes of a molecule's energy, which are in its rotation, in the vibration of its atoms, and in its electrons being excited to higher energy orbitals (Keeler 2008:27). If we think of the "springy" bonds between the atoms in the molecules shown in figure 4.6, then we can imagine these molecules "ringing" with a variety of discordant frequencies when struck, perhaps like the sound a piano makes when you bang random keys at the same time. However, for our simple purposes, we can ignore these and think of a molecule's energy in terms of its movement through space; this is its energy of translation.

"**In our everyday world**", Atkins 1994:9.

4.3.1 a simple (5,5) system of molecules and energy units

"**We start with a very simple**", this follows the approach used by Keeler 2008:sections 1.10 and 6.3.1, Atkins 2002:section 7.5, Atkins 2010:section15.1, Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html, and Stephen Lower at http://www.chem1.com/acad/webtut/thermo/entropy.html.

"**The molecules in this system**", Keeler 2008:26, Atkins 2010:7.

The simple molecular system in **figure 4.16** is based on Keeler 2008:figure 6.3 (10 units of energy, 14 molecules), Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html (9 energy units, 6 molecules), and Lower at http://www.chem1.com/acad/webtut/thermo/entropy.html (3 units, 3 molecules). In this simple model the molecules are individually distinguishable. This is a simplification of real bulk matter (Maczek 1998:chapters 1 and 5, Atkins 2006:579), but will still give us useful results.

The term kT is a measure of a molecule's thermal energy, where k is Boltzmann's constant, with a value of about 1.4 x 10^{-23} J/K and T is the temperature in Kelvin. A useful "rule of thumb" is that most molecules can access energy levels up to an energy about equal to the value of kT (Keeler 2008:28). A comfortably warm temperature is about 300 K (27 °C), and at this temperature the average motional energy of a molecule is roughly 4 x 10^{-21} J, or around 0.03 eV.

A molecule can possess energy in three independent modes: as movement (translation), rotation and vibration (Keeler 2008:28 , Atkins 1998:5, and 2007:43). These different modes have distinctly different energy level spacings. Typical spacings are: translation, ~10^{-22} eV; rotation, ~0.0001 eV; and vibration, ~0.01 eV (Keeler 2008:28, Atkins 2010:7). So we can roughly estimate that a "warm" molecule can access a huge number of translation energy levels (0.03/10^{-22} ≈ 10^{20}), hundreds of rotation energy levels (0.03/0.0001 ≈ 300), and maybe only the first few vibrational energy levels (0.03/0.01 ≈ 3). The electronic energy levels are more widely spaced (~6 eV) than the vibration energy levels, so atoms and molecules are usually in the lowest, ground state (Keeler 2008:27). So, molecules in everyday objects like teaspoons, which comprise around 10^{23} molecules, have a roughly similar number of accessible energy levels.

For the simple (5,5) system in **figure 4.16** and the further examples in **Table 4.1** I have used systems in which the numbers of energy units and molecules are equal, and the particles are all individually distinguishable. This is simplistic, but still gives meaningful results (Keeler 2008:207). Some writers refer to the energy units as energy quanta.

In this simple model the system at absolute zero will have zero energy, and have only one accessible microstate – perfect order. However, real molecular systems, with vast numbers of molecules, of the order of 10^{23}, and at temperatures above ~1 K, low enough to be at a "*practical zero of entropy*" are estimated to have about $10^{26,000,000,000,000,000,000}$ microstates (Kozliak 2005, Lambert 2006).

For **equation 4.1**, see Keeler 2008:208, Maczek 1998:3, Atkins 2010:566, and HyperPhysics at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html.

W is sometimes called the statistical weight of a configuration (Maczek 1998:3, Atkins 2010:566).

For **equation 4.2** see HyperPhysics at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html.

energy dispersal and the probability of a configuration

"**So, at any moment**", Leff 2012:274.

"**The randomly interacting system**", a given configuration can be reached in a number of different ways, and the number is known as the statistical weight of that configuration. "*It represents the probability that this configuration can be reached, from among all other configurations, by totally random means*" (Maczek 1998:3). Equation 4.1 gives the statistical weight of a configuration, and is the same as Maczek's equation 1.5.

"**However, the seven configurations**", Maczek 1998:4.

an isolated system spontaneously moves towards the highest probability configuration

"**In a sense, energy "rides" the molecules**", Lambert graphically describes how molecular collisions move the system from one microstate to the next (Lambert 2002b and 2005a).

a system in equilibrium spends most of its time in the most probable configuration"

"**So, the system's progress**", Peter Atkins notes that the chance of "*significant abnormalities*" occurring in in a model universe of 1,600 atoms is quite large (Atkins 1994:73).

"***a purposeful tendency***", Atkins 1994:58.

4.3.2 the Boltzmann distribution – the most probable molecular distribution across energy levels

"**This is the Boltzmann distribution**", Keeler 2008:27 and 209, Atkins 2007:13, Atkins 2010:8 and 567, Maczek 1998:chapter1.

The Boltzmann distribution tells us how molecules randomly exchanging energy units, in an isolated system with a fixed number of molecules and a fixed amount of total energy, are distributed across the different energy levels.

The principle is fairly simple (Atkins 2007:13, Maczek 1998:7). Molecules are distributed over a number of energy levels, with the numbers of molecules decreasing exponentially at successively higher levels (Atkins 2007:19, and 2010:8). This can be written mathematically as,

$N_{n+1}/N_n = \exp(-\Delta E/kT)$

where *N* is the number of molecules at energy level *n*, ΔE is the energy difference between successive levels, *k* is Boltzmann's constant (strictly, it is k_B), and *T* is the temperature in K. Instead of writing e^2, meaning "*e* to the power 2", we can write exp(2), and I have used this format in the equation. The term *kT* is a measure of the average energy of a molecule at temperature *T*. The temperature is "*the parameter that tells us the most probable distribution of populations of molecules over the available states of a system at equilibrium*" (Atkins 2007:14).

So, if the energy difference, ΔE, is equal to *kT*, the equation becomes:

$N_{n+1}/N_n = \exp(-1) = e^{-1} \approx 0.37$

so the number of molecules at each level is about 0.37 of the number in the level below.

However, the derivation of the Boltzmann distribution function "*is a formidable mathematical problem which uses the calculus of variations to derive the most probable distribution under the constraints of constant energy and constant number of particles*" (Rod Nave at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html, and for an example of the mathematical challenge, see Atkins 2010:585).

We need to know how many molecules in an isolated system of *N* molecules are at each level, and this is given by:

$N_n = N \exp(-E_n/kT) / \Sigma\exp(-E_n/kT)$

where there are N_n molecules at level *n*, each with an energy of E_n (Atkins 2010:568, equation 15.6a).

The term, "$\Sigma\exp(-E_n/kT)$", the denominator in the fraction, is just the sum of all the terms $\exp(-E_n/kT)$, for all the energy levels that molecules can access, and is called the molecular partition function (Atkins 2010:568). This tells us how many energy states are accessible to a molecule at the temperature of the system, and how molecules are distributed across these accessible states.

For molecular systems in the real world, with temperatures measured in Kelvin, Boltzmann's constant has the value ~1.38×10^{-23} J/K (Atkins 2007:14). A temperature of 0°C is about 273 K, so a normal, humanly warm temperature is about 300K.

For the simple model system shown in **figure 4.16**, we can set $k = 1$, and assume equally spaced energy levels separated by a fixed energy gap, ΔE. So, the lowest, zeroth energy level has an energy $E_0 = 0$, and the n^{th} level has an energy $E_n = n\Delta E$.

As the system's temperature is raised, the molecules have more energy, and the value of *kT* increases.

For warm systems, we can set *kT* to be equal to one energy level, so $kT = \Delta E$; then we can set *kT* at half an energy level for cold systems, so $kT = 0.5\Delta E$, and we can set $kT = 2\Delta E$ for hot systems.

To give the (5,5) system in figure 4.16 a total of 5 units of energy you need to set $kT = 1.45\Delta E$.

So, for the (5,5) system at a warm-to-hot temperature, where $E_n = n\Delta E$ and $kT = 1.45\Delta E$, the equation for the Boltzmann distribution becomes:

$N_n = N \exp(-n/1.45)/ \Sigma \exp(-n/1.45)$

The term, "$\Sigma\exp(-n/1.45)$" is the sum of all the terms $\exp(-n/1.45)$ for all the energy levels in the system, from 0 to 5, and is:

$e^0 + e^{-1/1.45} + e^{-2/1.45} + e^{-3/1.45} + e^{-4/1.45} + e^{-5/1.45}$, which is … $1 + 0.50 + 0.25 + 0.13 + 0.06 + 0.03 = 1.97$.

We can now calculate the number of molecules at the lowest, $n = 0$, level in the (5,5) system, as follows:

$N_0 = 5 \times e^{-0}/1.97 = 5 \times 1 / 1.97 \approx 2.5$

This tells us that about 2.5 molecules, half the total, will be at the zeroth energy level.

The numbers of molecules at the other levels come out as follows:

level	0	1	2	3	4	5		
number of molecules	2.49	1.25	0.63	0.31	0.16	0.08	total	~ 4.9 molecules

The curve in part (b) plots these population values.

These calculations can be done on a simple scientific calculator, but they are much easier with a spreadsheet. Once the basic calculations are set up, you can change the numbers of molecules and temperature very easily, and see how the Boltzmann distribution changes with temperature.

In **figure 4.17(a)** the calculation of average molecular occupancies is based on HyperPhysics, at http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html, which gives a nice description of the statistical behaviour of a system of 6 molecules sharing 9 energy units.

Part (b) gives the Boltzmann distribution curve for a system at a temperature where $kT = 1.45\Delta E$, giving the system a total energy of 5 units. In a system with many molecules the actual molecular distribution would follow this closely, but in a 5-molecule system, where a single molecule is 20% of the total, there are distinct deviations from the average distribution. Nonetheless, even a very simple (5,5) system shows the emerging outline of the Boltzmann distribution.

"***dynamic, living beast***", Atkins 2018:74.

4.3.3 bigger molecule-energy systems

"**But everyday objects**", Atkins 2002:F47, Atkins 2010:5. We can think simply of an amount of substance equal to its atomic or molecular weight in grams as containing 1 mole of particles. The number of particles in 1 mole is Avogadro's constant, which is about 6×10^{23}, and I've rounded this up to 10^{24}.

"**The number of stars**", Atkins 1994:46.

bigger systems have more microstates

"**Finally, the (140,140) system** ", Lambert 2005a puts the number of atoms in the universe as $\sim 10^{80}$.

The larger systems in **Table 4.1** have equal numbers of energy units and molecules, as explained in the note to figure 4.16.

All calculations were done for warm systems, with $kT = 1.45\Delta E$, as this set the system's total number of energy units equal to the number of molecules.

W_{system} is the total number of ways that Q energy units can be shared among N molecules, which is the total number of available microstates, and is calculated using equation 4.2.

The number of molecules at each energy level were calculated from the Boltzmann distribution, already given.

W_{probable} is the statistical weight of the most probable configuration, that is, the number of microstates in that configuration, and is calculated using equation 4.1, which is the same as Maczek 1998:equation 1.5 and Keeler 2008:208.

All calculations were done using EXCEL, which was invaluable in doing the repetitive calculations involved in drawing up table 4.1.

For the (140,140) system the sizes of factorials were too large for Excel, and factorials were found using the on-line facility https://www.calculatorsoup.com/calculators/discretemathematics/factorials.php.

For the (140,140) system, the number of accessible microstates is

$W(Q,N) = (Q+N-1)!/(Q! \times (N-1)!) = 279!/(140! \times 139!) = 6.0 \times 10^{562} / (1.35 \times 10^{241} \times 9.62 \times 10^{238}) \approx 5 \times 10^{82}$ accessible states.

Stephen Lower notes that if 1,000 molecules share 1,000 units of energy (quanta) there will be around 10^{600} accessible microstates, and this can be confirmed using equation 4.2. For a sample of gas large enough to be observable, only the most probable configuration need be considered, other configurations are so improbable that they can be ignored (http://www.chem1.com/acad/webtut/thermo/entropy.html).

big molecular systems are always in the most probable configuration

4.3.4 from randomness to stability

"**A tablespoon of water**", numbers of microstates in water are from Lambert 2005a and Lambert 2008.

Molecules in the air we breathe typically undergo about 1 billion collisions each second (Tipler 1999:554, Atkins 1998:30). A party balloon contains about 10^{23} molecules, so in one second there will be around $10^{23} \times 10^{9} = 10^{32}$ collisions. Even at this rate, in the lifetime of the universe this system will occupy only the tiniest fraction of the microstates in the most probable configuration.

"***all practical intents and purposes***", Keeler 2008:209.

"**For example, for a system of 10^{23} molecules**", Maczek 1998:5.

4.3.5 towards the most probable configuration

4.3.6 the First and Second Laws of Thermodynamics

the First Law and energy

"***the internal energy of an isolated system is constant***", Atkins 2007:29 and 2010:48.

"**the energy of the universe is constant**", this is as stated by Clausius in 1867, and Atkins 2007:62.

the Second Law and entropy

entropy is a measure of the dispersal of energy within a molecular system

"**We use the term "entropy"**", Atkins 2010:96 and 99. The word "entropy" comes from the Greek for "turning towards" (Atkins 2018:80).

Here I have followed the approaches of Lambert, and of Keeler and Wothers. Keeler 2008:206 says that there are "*a number of ways of defining entropy, but to start with by far the easiest approach is to take a microscopic view and think about how the behaviour of the individual molecules and atoms in a sample affects its entropy*". They also emphasise the connection between entropy and "*the distribution of molecules amongst the energy levels*" (Keeler 2008:212). Lambert 2006:15 emphasises that "*energy in the motion of molecules is essential to understand entropy in chemistry*".

In several publications, Lambert (2002b, 2006, 2012 and 2013) has proposed the view that entropy measures "*the dispersal of energy in a process in our material world*" so that "*entropy change measures the dispersal of energy: how much energy is spread out in a particular process, or how widely spread out it becomes (at a specific temperature)*" (both quotes are from Lambert 2013, and Lambert 2006 says something very similar).

A common metaphor for entropy is "disorder" (see, for example, Atkins 2002:351, Alberts 2008:66, Gribbin 1998). This is a simple and familiar metaphor, and one that at first seems helpful, but is fundamentally misleading (Keeler 2008:206, Lambert 2002a, 2005b, 2006). The term "disorder" is "*a contrived support for visualization rather than a fundamental physical or theoretical cause for a higher entropy value*". Disorder is a familiar word, and has become "*a code word for the "scientific" interpretation of everything disorderly from drunken parties to dysfunctional personal relationships, and even the decline of society*". But, "*entropy is not disorder. Entropy is not a measure of disorder or chaos. Entropy is not a driving force. Energy's diffusion, dissipation, or dispersion in a final state compared to an initial state is the driving force in chemistry. Entropy is the index of that dispersal within a system and between the system and its surroundings*" (all quotes from Lambert 2002a).

Peter Hoffmann writes, "*Equating entropy with disorder is convenient, but it is not a precise definition by any means. … Instead, entropy measures the degree to which energy is spread out*" (Hoffmann 2012:79).

The universe is a system of molecules, and all events within it are the results of molecular interactions. Accordingly, I've followed the molecular thermodynamics description of things, and defined entropy in molecular terms. The term "entropy" is widely used, and understood in many different ways, some of which are misleading, and these are well established in people's thinking. So, while I will try to explain and define entropy, I will use the term sparingly, to avoid evoking these prior associations. I'll use the term "entropy", and also the phrase "dispersal of matter and energy", referring to the dispersal of molecules in space, and energy across molecules and energy levels. This is undoubtedly clumsier, but it focusses on molecular systems and interactions.

"**This is Ludwig Boltzmann's equation**", Atkins 2007:68 and 2010:99. Everyday systems comprise very many molecules, and are always in their most probable configuration, so sometimes W is given as W_{max}, which is the number of microstates in the most probable configuration (Keeler 2008:209).

To bring the statistical value of entropy into line with entropies calculated using energy in Joules (J), and temperatures in Kelvin (K), the value of k_B is 1.38 x 10^{-23} J/K (Atkins 2007:14). It is usual to quote the entropy of one mole of a substance, so the units of entropy, S, are J/Kmol, or $\text{JK}^{-1}\text{mol}^{-1}$. For the very simple molecular systems that I describe here, I will give k_B a value of 1, effectively omitting it from the equation, following Atkins' model universe (1994:65). The term W is sometimes called the statistical weight of the configuration (Atkins 2006:575, Maczek 1998:3).

The classical thermodynamic definition of entropy change is $\Delta S = Q_{\text{rev}}/T$, which gives the entropy change, ΔS, of a system when Q J of energy are reversibly transferred at a temperature T K (Atkins 2010:97).

So, for a process that involves a change in entropy:

$\Delta S = k_B \ln W_{\text{final}} - k_B \ln W_{\text{initial}} = k_B \ln (W_{\text{final}} / W_{\text{initial}}) = Q/T$

and we can link the classical and molecular viewpoints. The two approaches are not quite the same, for the statistical approach defines an absolute entropy, while the classical approach defines a change in entropy (Atkins 2007:103).

The statistical and classical expressions for entropy change say the same thing in different ways. The classical expression for ΔS states that the transfer of a fixed amount of energy to a system will increase its entropy more when the system is cold than when it is hot. A cold molecular system will have molecules distributed over only a few energy levels, and so the transfer of energy will significantly increase the number of accessible energy levels. In contrast, a hot system will have molecules distributed over many energy levels, and the energy will only slightly add to this. So, the entropy change will be inversely proportional to the temperature, which is consistent with the classical statement (Atkins 2006:81, Keeler 2008:210).

"***one of the most important equations***", Baumann:30. Baumann puts Boltzmann's equation on a par with Newton's 2nd law ($F = ma$) and Einstein's equivalence of mass and energy ($E = mc^2$), and Keeler 2008:209 takes a similar view.

"***a more 'disorderly' distribution***", Atkins 2006:81 and 2010:99.

"**So we arrive at the Second Law of thermodynamics**", the Second Law is expressed in a great variety of ways: in its broadest universal terms by Tipler 1999:625, Atkins 2007:62; in terms of molecular thermodynamics by Atkins 2007:66, Maczek 1998:11, Keeler 2008:205; in terms of classical thermodynamics by Purves 1998:121, Atkins 2010:96; and in terms of devices like heat engines and refrigerators by Tipler 1999:625.

Two statements of the Second Law that are helpful for us here are "*Energy of all types changes from being localized to becoming dispersed or spread out, if it is not hindered from doing so. The overall process is measured by the increase in thermodynamic entropy*" (Lambert 2006), and also "*In a spontaneous process, the entropy of the Universe increases*" (Keeler 2008:205). I have chosen a statement of the Second Law that we can see operating in the (5,5) system, and that will be useful when we reach Level 5 and biological organisms.

"***the entropy of an isolated system***", Atkins 2010:96.

the Second Law is a probabilistic law of emergent behaviour

"***it is much more likely***", Baumann:27.

Molecular gases are examples of systems in which "*the sheer number of collisions produces an overall situation that defies exact description. Each collision is individually chaotic; yet, because each is effectively independent of the others, a stable statistical pattern of molecular velocities arises. These systems are classic examples of microscopic chaos creating a stable large-scale order. The larger the number of molecules in the system, the smaller will be the occasional fluctuations away from the stable average behaviour*" (Barrow 1992:130).

We're familiar with the pressure of air trapped inside a balloon or a tyre, which is produced by the impacts of the gas molecules on the walls of their container. Victor Stenger points out that if you have a gas with only 100 particles, then its instantaneous pressure will not be at all steady, but will vary by ~10% about its long-term average. For a typical macroscopic system, like a balloon, containing ~10^{24} particles, the pressure fluctuation is about 1 part in a trillion (Stenger 2006:115). Also see the note to figure 4.20(b).

"**The Second Law has no meaning**", Peter Hoffmann points out that the Second Law is a statistical law, and that systems tend towards their most probable state most of the time. So, if you are prepared to wait long enough, "*strange things can happen by chance. … Your cold coffee could spontaneously boil*" (Hoffmann 2012:130). How long you have to wait depends on the size of the system. "*In a large system, one visible with an optical microscope or larger, a violation of the second law will, for all practical purposes, never happen. However, a really small system (a single molecule, for example) can seemingly violate the second law relatively often*" (Hoffmann 2012:130).

Thus, we've seen that the (5,5) system can occasionally violate the Second Law, as it cycles randomly through its tiny number of microstates (see the end of section 4.3.1 and 4.3.2).

the universe is the ultimate system

"***however much energy there was***", Atkins 2007:23.

"***the energy of the universe is constant***", Clausius 1867:365.

“**The universe’s entropy must inexorably increase**”, here we need to distinguish between microscopic and macroscopic events (Zee 2007:276).

For example, imagine pouring some hot water into some cold water, to cool it down. On the microscopic scale, the molecules in each water sample are moving at a range of speeds, but the hot water molecules have a high average speed, while the cold molecules have a low average speed. The hot and cold water molecules randomly collide, and eventually settle at a middling average speed, which we register as lukewarm.

The physics of molecular collisions is time reversal invariant, and any individual collision will run backwards just as easily as forwards. Thus, a fast-moving “hot” molecule may collide with a slow “cold” one, and both recoil at a middling “lukewarm” speed. But, such a collision can occur in reverse, so that “*two molecules, both moving at a stately pace, could collide in such a way that one of them goes zipping off while the other moves slowly*” (Zee 2007:276).

If this happened on the macroscopic scale, then we would see a region of hot water in one place and a cold region in another place. For this to happen would require billions of individual collisions like the one described above. The probability of this happening is extremely small, but not exactly zero. “*If we could watch a glass of lukewarm water long enough, far longer than the present age of the universe, we would see the water separating for just a moment into ice and hissing steam*” (Zee 2007:276).

Individual molecular collisions can run forwards or backwards, so if we’re shown “before” and “after” pictures we can’t say which comes first, because there is no indication of past or future. However, if we’re shown one picture of a mixture of hot and cold water and another of lukewarm water, we know for sure that the mixture comes first. We now can distinguish the future from the past – we have an “arrow of time” (Gribbin 1998:20).

The consensus appears to be that the arrow of time in the macroscopic phenomena of our everyday world is generated by the collective behaviours of the vast numbers of particles involved (Zee 2007:276). Thus, the Second Law of thermodynamics sets the direction of our everyday sense of time.

“***the entropy of the universe tends to a maximum***”, quote from Clausius 1867:365, and see also Tipler 1999:625, Keeler 2008:205, and Atkins 2007:62. Peter Atkins suggests that the initial entropy of the universe was zero (Atkins 2018:93).

“**These two laws**”, Atkins 2007:65.

4.4 the thermodynamics of everyday events

4.4.1 temperature and entropy

“**So, the change in a system’s entropy**”, Keeler 2008:210, Atkins 2010:99.

“**The effect of a temperature increase**”, Lambert 2002b. At 0°C the number of microstates in 1 mole of water molecules is $\sim 10^{2,000,000,000,000,000,000,000,000}$, and at 1°C, it is $\sim 10^{2,010,000,000,000,000,000,000,000}$, and the ratio $10^{2,010,000,000,000,000,000,000,000}/10^{2,000,000,000,000,000,000,000,000} = 10^{22}$.

In classical thermodynamics the entropy change (ΔS J/K) of a system due to the transfer of energy (q J) at a temperature (T K) is given by

$\Delta S = q/T$

This fundamental relationship in classical thermodynamics (see for example, Keeler 2008:section 6.5, Atkins 2006:section 3.2, Atkins 2007:chapter 3) has its basis in the statistical behaviour of molecular systems, as shown in figure 4.18.

Figure 4.18 is based on Keeler 2008:figures 1.26 and 6.5, and see also Atkins 2010:figure 15.6, and Atkins 2007:figure 4.

As a molecular system gets hotter, kT increases, and the term ($-E_n/kT$) in the Boltzmann equation is a smaller negative number, so the molecular population shrinks less quickly as you ascend to higher energy levels. The result is that the molecular distribution shifts to higher energy levels. A useful “rule of thumb” is that the most of the molecules are on energy levels up to the value of kT (Keeler 2008:28).

The Boltzmann distributions for each temperature were calculated using these values of $kT/\Delta E$; cold, 0.75; warm, 1.15; hot, 1.55; very hot, 2.15. So, for cold systems, where $kT = 0.75\Delta E$, very few molecules are above the first energy level. For the warm system, where $kT \approx \Delta E$, a few molecules are above the first level, and for the very hot system, where $kT \approx 2\Delta E$, there are now a few molecules above the second level. To get the molecular distributions shown here the Boltzmann distribution has been rounded to the nearest whole molecule.

4.4.2 a cup of tea cools and an ice cube melts

“**The combined system**”, Atkins 2018:72.

This simple example ignores the enthalpy (formerly known as the latent heat) of melting ice (Atkins 2002:304). The example of a cup of tea cooling in **figure 4.19(a)** is similar to the example in Atkins 1994:53.

4.4.3 why does one end of a teaspoon not spontaneously heat up?

4.4.4 air leaks out of a tyre

Figure 4.20 is based on Keeler 2008:figure 6.6, Atkins 2002:figure 7.8, Atkins 2007:figure 12, and Lower at http://www.chem1.com/acad/webtut/thermo/entropy.html. The Boltzmann distributions have been calculated using $kT/\Delta E = 1.25$ for the confined gas in (a) and $kT/\Delta E = 2.5$ for the expanded gas in (b), and this matches Keeler 2008:figure 6.6.

“**If we apply quantum mechanics**”, the spacing of levels depends inversely on the volume of the container (Atkins 2007:66, Keeler 2008:211, Atkins 2010:584). Quantum mechanics computes the wavelengths of the standing waves that can fit between the walls of the box, and then interprets the wavelengths as energies. A box twice as big, allows standing waves with twice the wavelength, whose energy is halved (Atkins 2007:66).

The example in figure 4.20 is not easy to explain by classical thermodynamics, because it involves no energy transfer to the system, and Frank Lambert has written that it “*made me despair of ever understanding entropy when I was a student of 18*” (Lambert 2006). However, the explanation in terms of energy levels and molecular thermodynamics is quite straightforward .

“**But consider the reverse process**”, this can be modelled with tossing coins (H = left side, and T = right side) tossing a small number can give you all H or all T, but as you increase the number of coins, say to 1,000, the chance of even a significant deviation from 50:50 becomes vanishingly small (Lower, at http://www.chem1.com/acad/webtut/thermo/entropy.html).

“**For the system shown in part (b)**”, this example is based on Tipler 1999:625.

4.4.5 a puddle freezes

“**We’ll now look at the familiar example**”, the freezing of water is described by Keeler 2008:218. Atkins 2007:figure 16 shows the variation of Gibbs energy with temperature for the gas, liquid and solid states of water.

“**We would expect**”, Keeler 2008:211.

Figure 4.21 is based on Keeler 2008:figure 6.12.

counting microstates

“**In the liquid state at 273 K**”, numbers of microstates are from Lambert 2008. The value of W can be calculated from experimentally determined standard values of entropy, S^0, using the Boltzmann equation, $S = k_B \ln W$. The value of S^0 for ice at 273K is 41.34 J/K mol, and for water at 273K it is 63.34 J/K mol. From these we can calculate the values of $\log W_{\text{water}}$ as 2×10^{24}, and $\log W_{\text{ice}}$ as 1.3×10^{24}. A standard value of entropy, S^0, is a measure of the motional energy dispersed in a substance as it is heated from 0 K to the standard temperature, and that “*the substance must have to exist stably*” at the standard temperature (Lambert 2006, Atkins 2002:357).

“**Freezing is an exothermic process**”, the thermal energy transferred is known as the enthalpy of fusion, formerly known as the latent heat (Atkins 2002:304).

“**The surroundings are very large**”, while the temperature of the surroundings is “*for all practical purposes unchanged*”, yet “*energy has been accommodated and a tiny redistribution of populations has occurred*” (Atkins 2018:73). In classical thermodynamics the surroundings are regarded as the rest of the universe, and so the temperature of this enormous molecular ensemble is considered to remain unchanged, and the increase in entropy of the surroundings is given by the equation $\Delta S = Q/T$, where Q J is the energy transferred to the surroundings from the water as it freezes at temperature T K.

the balance of entropy changes sets the freezing point

“**Water has a fixed freezing point**”, I want to show how the molecular configurations in water and ice determine the temperature at which water freezes. The following calculations bring together the molecular and classical approaches to entropy, but this does use a circular argument. The number of microstates in water and ice at 273 K, given in the previous section, have been calculated from their known entropy values. I wanted to start with the molecular systems, and so I have done the reverse calculation, and worked from microstates to entropy. The calculation broadly follows Keeler 2008:218.

We can use the values of W_{puddle} and $W_{\text{surroundings}}$ to calculate the freezing point of water.

Recall **equation 4.3**, which said:

$S = k_B \ln W$

For a system transformation that changes the number of microstates from W_1 to W_2, the entropy change is

$$\begin{aligned}\Delta S_{\text{system}} &= k_B \ln W_2 - k_B \ln W_1 \\ &= k_B (\ln W_2 - \ln W_1)\end{aligned}$$

so for water freezing from liquid to solid ice

$$\Delta S_{\text{water}} = k_B (\ln W_{\text{ice}} - \ln W_{\text{water}})$$

We know that $W_{\text{ice}} = 10^{1.3 \text{ million billion billion}}$, so $\log W_{\text{ice}} = 1.3 \times 10^{24}$. We need to use natural logs (ln) in Boltzmann’s equation, and not base 10 logs (log). We convert a base 10 log to a natural log by multiplying it by ln10, which is very close to 2.3.

So $\ln W_{\text{ice}} = 2.3 \times \log W_{\text{ice}} = 2.3 \times 1.3 \times 10^{24} = 3.0 \times 10^{24}$, and $\ln W_{\text{water}} = 2.3 \times \log W_{\text{water}} = 2.3 \times 2.0 \times 10^{24} = 4.6 \times 10^{24}$.

Thus we can say that for 1 mole of water molecules freezing, the entropy change is

$$\begin{aligned}\Delta S_{\text{water}} &= k_B (\ln W_{\text{ice}} - \ln W_{\text{water}}) \\ &= 1.38 \times 10^{-23} \times (3.0 \times 10^{24} - 4.6 \times 10^{24}) \\ &= -22.0 \text{ J/K}\end{aligned}$$

The motional energy that the water molecules possessed in the liquid state, but not in the solid state, is transferred to the surrounding molecules, enabling them to access higher energy levels, and thereby increasing their entropy. In the case of water, 1 mole of water molecules transfers 6,000 J to its surroundings in the course of freezing (Keeler 2008:218).

The entropy increase of the surrounding molecules is given by the classical thermodynamic definition of entropy change:

$\Delta S_{\text{surroundings}} = Q/T_{\text{surroundings}}$

where Q J is the energy transferred at the temperature T K.

For the water to freeze spontaneously, there must be a net increase in entropy, so:

$Q/T_{\text{surroundings}} > \Delta S_{\text{water}}$

so $\quad Q/\Delta S_{\text{water}} > T_{\text{surroundings}}$

so $\quad 6{,}000/22.0 \approx 273 > T_{\text{surroundings}}$

So, water can only spontaneously freeze to ice if the temperature is below 273 K. In the act of freezing, the entropy of one mole of water molecules decreases by a fixed value, and consequently a fixed quantity of thermal energy is transferred to the surroundings. The entropy increase of the surroundings depends on the temperature at which the thermal energy is transferred. The lower the temperature, the bigger the entropy increase. At temperatures below 273K the entropy increase in the surroundings exceeds the entropy loss of the water molecules, and water freezing produces a net increase in entropy, and so water can spontaneously freeze. So, the balance of entropy changes sets the temperature at which water can freeze.

4.5 chemical reactions and rearranging atoms

“**They don’t break up**”, a temperature of several thousand degrees is needed to break up an individual water molecule: https://en.wikipedia.org/wiki/Water_splitting.

chemical reactions rearrange atoms into new molecular communities

“***In some reactions***”, Atkins 1992:27.

“***no more than elaborate forms of cooling***”, Atkins 1994:107.

4.5.1 the dissociation of N_2O_4 into $2NO_2$

“**Nitrogen dioxide**”, Atkins 2002:816, Emsley 2001:292.

“**Two nitrogen dioxide, NO_2, molecules**”, Peter Atkins explains the entropy changes in this reaction (Atkins 1994:114).

Figure 4.22 is based on Keeler 2006:figures 2.3, 2.4, and 2.15, and Atkins 2002:figure 7.27.

The 3–D molecular structures of N_2O_4 and NO_2 are from ChemEd DL, at http://www.chemeddl.org/resources/models360/models.php.

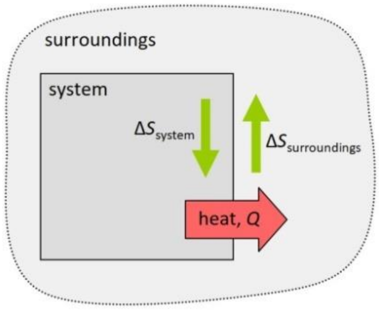
“**So, low temperatures favour**“, we usually think of chemical reactions as going to completion, where all the reacting molecules are consumed in the reaction. But in general, chemical reactions go to an intermediate equilibrium position, in which there are appreciable amounts of both reactants and products, and the position of the equilibrium depends on external conditions like temperature or pressure (Keeler 2008:203). The reversible $N_2O_4 \leftrightarrow 2NO_2$ reaction is an example.

4.5.2 Gibbs free energy and spontaneous chemical reactions

"**The Gibbs free energy**", see Lambert 2002b, 2005b, Keeler 2006:16 and 2008:220, Atkins 2002:370, 2007:89, and 2010:113. The Gibbs energy is of the greatest importance in chemistry and in the field of bioenergetics, the study of energy utilisation in biology (Atkins 2007:91).

Gibbs free energy

the basic concept of free energy



Peter Atkins gives a simple explanation of the concept of free energy (Atkins 1994:168, and see the inset figure). Imagine a local system of molecules within their surroundings, and together these comprise a small, self-contained universe. The system can potentially undergo a chemical reaction that reduces its entropy, but this is not possible because it would reduce the total entropy of the universe. But if the reaction transferred energy to the surroundings as heat, then this would increase their entropy. If the entropy increase in the surroundings exceeded the entropy decrease in the system, that is, $\Delta S_{surroundings} > \Delta S_{system}$, then the reaction would proceed spontaneously.

This raises the question – what is the minimum amount of energy that must be transferred to the surroundings for the reaction to be spontaneous?

The entropy increase in the surroundings is given by the expression Q/T, where Q is the amount of energy transferred at the temperature T. For the reaction to be just spontaneous, $\Delta S_{surroundings} = \Delta S_{system} = Q_{min}/T$, where Q_{min} is the minimum energy transfer needed just to produce a net increase in entropy. If we rearrange this, we get $Q_{min} = T \times \Delta S_{system}$.

However, if the system transfers an amount of energy, Q_{total}, which is greater than Q_{min}, then there is an excess of energy, which we can call Q_{free}. So, $Q_{free} = Q_{total} - Q_{min} = Q_{total} - T \times \Delta S_{system}$.

This is called free energy because it is not committed to increasing the entropy of the universe, and is freely available for other activities, such as doing external work, or assembling molecules.

the derivation of the Gibbs free energy

Lambert 2002b, 2005b, Keeler 2006:section 2.7 and 2008:sections 6.6 and 6.7, and Atkins 2002:370 give derivations of the Gibbs free energy. The following is based on their explanations.

Imagine a self-contained universe of particles in which a local system of particles are rearranging themselves into a more tightly bound configuration, and transferring the released binding energy to their surroundings.

The entropy (S_{system}) of the system of particles changes as a result of their rearrangement, and the entropy of the surroundings ($S_{surroundings}$) changes due to the energy transferred from the system. The entropy of the universe ($S_{universe}$) changes as a result, and the change ($\Delta S_{universe}$) is the sum of these two changes, so …

$\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$ equation 4.4

We know that any spontaneous change must increase the entropy of the universe, so $\Delta S_{universe} > 0$.

We have a problem with this equation because it refers to the system, the surroundings, and also the whole universe, and we can only make measurements on the system. The following argument develops the formula for the Gibbs free energy, in which every term is referenced to the system.

We've seen that we can express an entropy change in a system of particles as the energy transferred to or from the system divided by the temperature, so in general we can write …

$\Delta S = \Delta Q/T$

where ΔQ is the energy transferred at a temperature T.

First we deal with the surroundings. The entropy of the surroundings changes as a result of the energy transferred from the system. Because $\Delta S = \Delta Q/T$, we can say that $\Delta S_{surroundings} = -(\Delta H/T)_{system}$, where ΔH is the energy transferred from the system to the surroundings at the temperature of the reaction – hence the minus sign, because the system loses the heat energy. So, we can write …

$\Delta S_{universe} = -(\Delta H/T)_{system} + \Delta S_{system}$ equation 4.5

Now we deal with the universe. We can express the change in the entropy of the universe in terms of an energy divided by a temperature, so we assign a value to the energy that the system can disperse freely to the universe, which we call the Gibbs free energy, with the symbol, G. Now we can express the change in entropy of the universe in terms of the Gibbs free energy, and say …

$\Delta S_{universe} = -(\Delta G/T)_{system}$ equation 4.6

We put these last two equations together and we get …

$-(\Delta G/T)_{system} = -(\Delta H/T)_{system} + \Delta S_{system}$

All three terms are entropies, but two of them are expressed as energy/temperature, and all are in terms of the system, and so we can now omit the suffix "system". The first term, $-\Delta G/T$, is the entropy change of the universe, and is negative because the free energy, $-\Delta G$, is the net "*dispersible energy*" that comes from the system. The second term, $-\Delta H/T$, is the entropy change in the surroundings due to energy transferred from the system. The last term, ΔS, is the entropy change in the system, due to the rearrangment of the local ensemble of particles.

For the reaction to be spontaneous, the entropy of the universe must increase, so $\Delta S_{universe} > 0$, and so the first term must be positive. This means that ΔG must be negative, and so for a spontaneous reaction the Gibbs energy, G, must decrease.

Finally, we multiply each term by $-T$, so we get …

$\Delta G = \Delta H - T\Delta S$ equation 4.7

in which each term is now an energy, and this is the standard expression of the Gibbs free energy.

The change in free energy, ΔG, represents the "*the quantity of energy that can be dispersed to the universe*" by a chemical reaction (Lambert 2002b).

Peter Hoffmann describes free energy as "*the difference between the* ***total*** *energy of the system and* ***unusable*** *thermal energy, leaving the* ***usable****, free part of the energy*" (Hoffmann 2012:101).

Although it has the units of energy, Δ*G* is not a true energy, and is not conserved, and is more closely related to entropy than to energy because it represents the entropy change of the universe associated with a reaction in one local system within that universe. The value of Δ*G* tells us whether a reaction can spontaneously proceed or not. A reaction with a negative value of Δ*G* will increase the entropy of the universe and can spontaneously occur.

The reaction might be thermodynamically favourable, but there are other factors that decide whether it actually proceeds, as is explained in section 4.5.4.

"***the energy that can be dispersed to the universe***" and "***dispersible energy***" are both from Lambert 2002b.

"***just a disguised form***", Atkins 1994:171.

"**This will be a dynamic equilibrium**", Atkins 2007:97.

4.5.3 the ball and the slope – a model of a chemical reaction

"**The original stored potential energy**", Atkins 1994:60 gives a molecular picture of a collision.

Figure 4.24(a) is based on Lambert 2012:figure 1, Atkins 1994:60, and Alberts 2008:figure 2-56; **part (b)** is based on Purves 1998:figure 6.5, and **part (c)** is based on Alberts 2008:figure 2-56 and Atkins 1994:160, 2002:figure 7.28, and 2007:figure 17.

"**The ball rolling downhill**", Purves 1998:124, Campbell 2008:147.

4.5.4 the combustion of methane

cooking on gas

"**I will finish this chapter**", Peter Atkins gives a graphic description of the combustion of a methane molecule (Atkins 2013:30). He describes the reaction in terms of radicals, which are groups of atoms produced by the break-up of a molecule. I've simplified things to show all the molecules breaking up more or less simultaneously, and their atoms rearranging themselves into new molecules.

"**For the CH_4 and O_2 molecules to react**", the methane and oxygen molecules are moving around freely and colliding in the gas state, at an average speed of around 500 m/s. But the energies in these collisions are only a small fraction of 1 eV, which is quite insufficient to break any bonds, and so an external activation energy must be provided. If there were no activation energy for methane combustion then methane would spontaneously catch fire immediately on contact with oxygen. All common chemical reactions have sizeable activation energy barriers that prevent them instantly obeying the Second Law and reacting. So the Second Law tells us which reactions can proceed spontaneously, but it is the size of the activation energy barrier that decides if this reaction proceeds or not.

"**There is no strict sequence of events**", Atkins 2013:30.

"***chemical reaction is like a weight***", Atkins 1994:171.

Figure 4.25 is based on Atkins 2002:F76, 309, 313, and Jim Clark at https://www.chemguide.co.uk/physical/energetics/bondenthalpies.html. The 3−D molecular structures are from http://www.chemeddl.org/resources/models360/models.php.

For simplicity, figure 4.25 shows the combustion of the methane molecule occurring in a single step, like an atomic "free-for-all", but the reaction actually takes place in a number of steps, typified by this three-step mechanism (Peters 1987)…

1) $CH_4 + O_2 \rightarrow CO + H_2 + H_2O$

2) $CO + H_2O \leftrightarrow CO_2 + H_2$

3) $O_2 + 2H_2 \rightarrow 2H_2O$

If we add up these partial reactions, and eliminate the molecules that appear on both sides, then we get the full combustion reaction …

4) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

The standard enthalpy of combustion of methane is the energy released by the combustion of 1 mole of methane, with all reactants and products in their standard states at 298 K and 1 atmosphere (Atkins 2002:314). If the water produced is in the vapour state the enthalpy, Δ*H* = −802 kJ/mol, and if the water is in the standard, liquid state, then Δ*H* = −890 kJ/mol. The difference is due to the latent heat released by the water when it condenses, which is 44 kJ/mol. So 2 moles of water will release 88 kJ, which accounts for the difference between the two enthalpy values (Atkins 2002:313). I've used the combustion where the water is in the vapour state, in order to avoid the complication of the condensation step.

Bond enthalpy values are from Keeler 2008:table 6.1, Atkins 2002:tables 6.7 and 6.8, and Jim Clark at https://www.chemguide.co.uk/physical/energetics/bondenthalpies.html.

A bond enthalpy is the energy stored in a chemical bond, and its value is given in kJ for a mole of molecules, that is 6×10^{23} molecules. A bond enthalpy of 1 kJ/mol is equivalent to 0.010 eV/molecule, where $1\ J = 6.25 \times 10^{18}$ eV. I use the older and more familiar term "bond energy", rather than the current term "bond enthalpy".

The average molecular energy is given by the value of $3kT/2$, which at 300 K is about 0.04 eV. So not even the most energetic molecules have enough energy to break a bond in any methane or oxygen molecules, and so these molecules will co-exist without reacting.

4.6 the universe – the biggest system of all

the universe is a molecular continuum

"***an island entire of itself***", from the 17th Meditation by John Donne (https://en.wikipedia.org/wiki/Devotions_upon_Emergent_Occasions), and Peter Atkins wrote, "*John Donne was unknowingly expressing a version of the second law when he wrote … that no man is an island*" (Atkins 2007:78).

In this chapter, I've tried to understand everyday events from the perspective of the wider universe, and so I've avoided any words that might potentially be emotive. Consequently I've not used terms like "chaos", "decay", and "corruption" (Atkins 1992, 1994), or "disorder", which is commonly used, but is now recognised as misleading (Keeler 2008:206, Lambert 2002a, 2005b, 2006).

Energy can be graded by its quality (Dyson 1971, Atkins 1992, 1994, and 2018), and this leads to a concise statement of the 1st and 2nd laws: "*although the quantity of energy in the universe remains constant, its quality tends to degrade*. … *Here is thermodynamics in a nutshell: the quantity of energy survives; its quality declines*" (Atkins 2018:82).

However, to think of energy in terms of its quality tends to lead one to view the universe as a decaying system: "*the deep structure of change is decay. What decays is not the quantity but the quality of energy*. … *Energy's quality, but not its quantity, decays as it spreads in chaos*" (Atkins 1992:21). However, energy does not simply "*spread in chaos*", because the generation of local regions of low entropy is a natural outcome of the process of energy's dispersal.

The quality of energy is relevant, because "*High quality, useful energy, is localized energy. Low quality, wasted energy is chaotically diffuse energy*" (Atkins 1992:23). However, it's potentially misleading to describe low quality energy as "*wasted*", because it may have generated high quality energy in the process of being dispersed.

A deep consideration of the 2nd law led Peter Atkins to conclude that "*we are the children of chaos, and the deep structure of change is decay. At root, there is only corruption, and the unstemmable tide of chaos. This is the bleakness we have to accept as we peer deeply and dispassionately into the heart of the universe*" (Atkins 1994:200). But perhaps this is the human perspective, all too aware of a precarious and transient existence at the top of the universal hierarchy. Instead, if we follow the universe's evolution, and work upwards from the level of fundamental particles, we see how the lowest matter ultimately becomes conscious of itself and of others.

the universe's energy must be ever more widely dispersed …

"**Like the (5,5) system**", the universe is a system free from all external influences (Atkins 1994:30). Peter Atkins extrapolates from a model universe of 1,600 atoms to the universe that we inhabit (Atkins 1994:74).

"**As its matter and energy become ever more widely dispersed**", John Barrow observes that "*the Universe appears to be far more orderly than we have any right to expect. It has a tiny entropy level compared with the largest value that we could conceive of it possessing if we were to reorganize the observed matter into other configurations. This implies that the entropy level at the beginning of the expansion of the Universe must have been staggeringly small, which implies that the initial conditions were very special indeed*" (Barrow 1992:159). He is, however, cautious about drawing any conclusions about the entropy of the whole universe.

Victor Stenger imagines the universe at earliest time that can be measured, which is the Planck time, about 5 x 10^{-44} seconds (Stenger 2006:38 and 135). At this time, the universe was indistinguishable from a black hole, which implies that its entropy was a maximum. He concludes that our universe began in "*total chaos, with no order or organization*" (Stenger 2006:136). As the universe expanded, its entropy increased, but not as fast as the maximum allowable entropy, and this enabled the creation of order. Thus, "*the universe could have begun in maximum disorder and yet produced order without the violation of the second law or any other principle of physics*" (Stenger 2006:136, and see also p. 296).

… but its distribution can vary

"**However, there are no curbs**", Atkins 2007:62.

"***Thus, whenever a local molecular system***", Atkins 2007:82, and see also Atkins 2018:85.

the emergence of structure

"**A gas has no coherent structure**", Atkins 1994:180.

"**In contrast, a crystalline solid**", so "*we shall regard structure and coherence as synonymous*" (Atkins 1994:181).

all events are spontaneous

"**In the grand scheme of things**", Atkins 1994:157 and 172.

"***a crystal forms***", Atkins 2007:82.

the universe is committed to evolving

"***return to a less probable one***", Atkins 1994:74.

"***trapped in the future***", Atkins 1994:74.

"**There is no externally imposed motive**", a theme in Atkins 1992 and 1994. For example, "*everything is driven by motiveless, purposeless decay*" (Atkins 1992:23).

"**… the outcomes of probabilities**", Atkins 1994:74.

the universe is long-lived enough for life to evolve

"**The universe's vast size**", Paul Davies has observed that "*The universe has not reached thermodynamic equilibrium yet because it has only been disordering itself for eighteen billion years or so, and that is nowhere long enough to complete the process*" (Davies 1984:20, written before the currently accepted age of about 14 billion years).

4.7 review of levels 3 and 4

4.7.1 ceaseless activity is wrapped up

"**This force can't even "reach"**", Weinberg 1993:134.

"***"fluttering" pions***", Smith 2003:150.

4.7.2 similarities and differences between levels

"**There is a fundamental similarity**", Close 2007a:105.

"**Every nucleon is attracted**", for the water-drop model of the nuclide, see Williams 2001:section 4.3.

"**Because the binding energies**", it takes about 6−8 MeV to remove a nucleon from a nuclide, and only a few eV to remove an electron from an atom (Weinberg 1993:61 and 105).

"***atoms can be dislodged***", Atkins 1992:11.

4.7.3 the inanimate universe is complete

"***At the level of atoms***", Han 1999:122. Excerpt from "Quarks and Gluons: a century of particle charges", by M. Y. Han, © 1999, World Scientific Publishing Co. Pte. Ltd.

a self-assembling universe

4.7.4 exploring all possible outcomes

"***the opportunity to exlore at random***", Atkins 1992:25.

"***just as an infinite literature***", Atkins 1995:137.

4.7.5 the next level

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