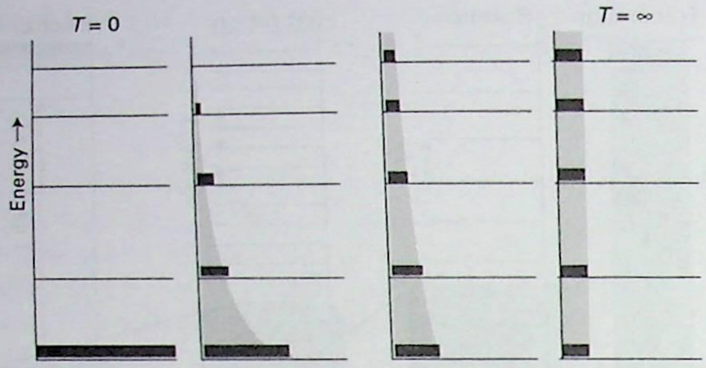

Figure B.4 The Boltzmann distribution of populations for a system of five energy levels as the temperature is raised from zero to infinity.

constant. When both the numerator and denominator in the exponential are multiplied by N_A, eqn B.25a becomes

$$\frac{N_i}{N_j}=\mathrm{e}^{-(E_i-E_j)/RT} \qquad \textit{Alternative form} \qquad \text{Boltzmann distribution} \qquad \text{(B.25b)}$$

where $R=N_Ak$. We see that k is often disguised in 'molar' form as the gas constant. The Boltzmann distribution provides the crucial link for expressing the macroscopic properties of matter in terms of microscopic behaviour.

Brief illustration B.7 Relative populations

Methyl cyclohexane molecules may exist in one of two conformations, with the methyl group in either an equatorial or axial position. The equatorial form is lower in energy with the axial form being 6.0 kJ mol⁻¹ higher in energy. At a temperature of 300 K, this difference in energy implies that the relative populations of molecules in the axial and equatorial states is

$$\frac{N_a}{N_e}=\mathrm{e}^{-(E_a-E_e)/RT}=\mathrm{e}^{-(6.0\times10^3\,\mathrm{J\,mol^{-1}})/(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times300\,\mathrm{K})}=0.090$$

where E_a and E_e are molar energies. The number of molecules in an axial conformation is therefore just 9 per cent of those in the equatorial conformation.

Self-test B.7 Determine the temperature at which the relative proportion of molecules in axial and equatorial conformations in a sample of methyl cyclohexane is 0.30 or 30 per cent.

Answer: 600 K

The important features of the Boltzmann distribution to bear in mind are:

- The distribution of populations is an exponential function of energy and temperature.
- At a high temperature more energy levels are occupied than at a low temperature.
- More levels are significantly populated if they are close together in comparison with kT (like rotational and translational states), than if they are far apart (like vibrational and electronic states).

Physical interpretation

Figure B.5 summarizes the form of the Boltzmann distribution for some typical sets of energy levels. The peculiar shape of the population of rotational levels stems from the fact that eqn B.25 applies to *individual states*, and for molecular rotation quantum theory shows that the number of rotational states corresponding to a given energy level—broadly speaking, the number of planes of rotation—increases with energy; therefore although the population of each *state* decreases with energy, the population of the *levels* goes through a maximum.

One of the simplest examples of the relation between microscopic and bulk properties is provided by **kinetic molecular theory**, a model of a perfect gas. In this model, it is assumed that the molecules, imagined as particles of negligible size, are in ceaseless, random motion and do not interact except during their brief collisions. Different speeds correspond to different energies, so the Boltzmann formula can be used to predict the proportions of molecules having a specific speed at a particular temperature. The expression giving the fraction of molecules that have a particular speed is called the **Maxwell–Boltzmann distribution** and has the features summarized in Fig. B.6. The Maxwell–Boltzmann distribution can be used to show that the average speed, v_{mean}, of the molecules depends on the temperature and their molar mass as

$$v_{\text{mean}}=\left(\frac{8RT}{\pi M}\right)^{1/2} \qquad \textit{Perfect gas} \qquad \text{Average speed of molecules} \qquad \text{(B.26)}$$

Thus, the average speed is high for light molecules at high temperatures. The distribution itself gives more information. For instance, the tail towards high speeds is longer at high temperatures than at low, which indicates that at high temperatures more molecules in a sample have speeds much higher than average.

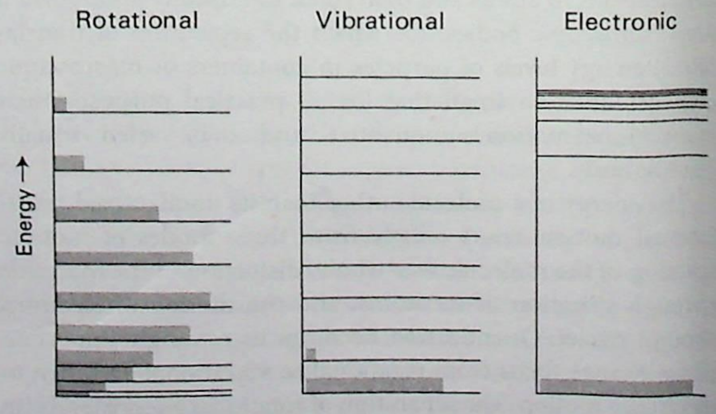

Figure B.5 The Boltzmann distribution of populations for rotational, vibrational, and electronic energy levels at room temperature.

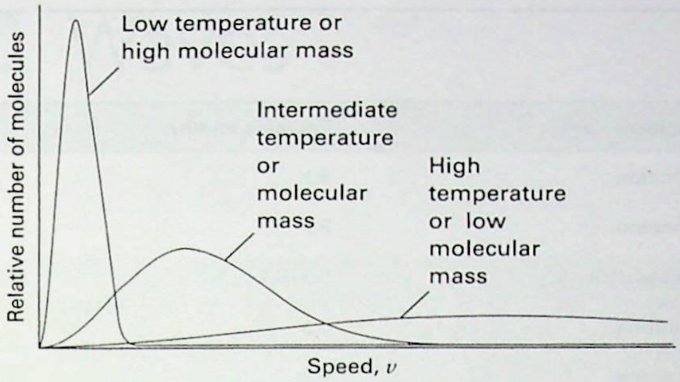

Figure B.6 The (Maxwell–Boltzmann) distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

(b) Equipartition

Although the Boltzmann distribution can be used to calculate the average energy associated with each mode of motion of an atom or molecule in a sample at a given temperature, there is a much simpler shortcut. When the temperature is so high that many energy levels are occupied, we can use the **equipartition theorem**:

> For a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

By a 'quadratic contribution' we mean a term that is proportional to the square of the momentum (as in the expression for the kinetic energy, $E_k=p^2/2m$) or the displacement from an equilibrium position (as for the potential energy of a harmonic oscillator, $E_p=\frac{1}{2}k_f x^2$). The theorem is strictly valid only at high temperatures or if the separation between energy levels is small because under these conditions many states are populated. The equipartition theorem is most reliable for translational and rotational modes of motion. The separation between vibrational and electronic states is typically greater than for rotation or translation, and so the equipartition theorem is unreliable for these types of motion.

Brief illustration B.8 Average molecular energies

An atom or molecule may move in three dimensions and its translational kinetic energy is therefore the sum of three quadratic contributions

$$E_{\rm trans}=\tfrac{1}{2}mv_x^2+\tfrac{1}{2}mv_y^2+\tfrac{1}{2}mv_z^2$$

The equipartition theorem predicts that the average energy for each of these quadratic contributions is $\frac{1}{2}kT$. Thus, the average kinetic energy is $E_{\rm trans}=3\times\frac{1}{2}kT=\frac{3}{2}kT$. The molar translational energy is thus $E_{\rm trans,m}=\frac{3}{2}kT\times N_A=\frac{3}{2}RT$. At 300 K

$$\begin{aligned}E_{\rm trans,m}&=\tfrac{3}{2}\times(8.3145\,{\rm J\,K^{-1}\,mol^{-1}})\times(300\,{\rm K})=3700\,{\rm J\,mol^{-1}}\\&=3.7\,{\rm kJ\,mol^{-1}}\end{aligned}$$

Self-test B.8 A linear molecule may rotate about two axes in space, each of which counts as a quadratic contribution. Calculate the rotational contribution to the molar energy of a collection of linear molecules at 500 K.

Answer: 4.2 kJ mol^{-1}

Checklist of concepts

☐ 1. **Newton's second law of motion** states that the rate of change of momentum is equal to the force acting on the particle.
☐ 2. **Work** is done in order to achieve motion against an opposing force.
☐ 3. **Energy** is the capacity to do work.
☐ 4. The **kinetic energy** of a particle is the energy it possesses as a result of its motion.
☐ 5. The **potential energy** of a particle is the energy it possesses as a result of its position.
☐ 6. The total energy of a particle is the sum of its kinetic and potential energies.
☐ 7. The **Coulomb potential energy** between two charges separated by a distance r varies as $1/r$.
☐ 8. The **First Law of thermodynamics** states that the internal energy is constant in a system isolated from external influences.
☐ 9. The **Second Law of thermodynamics** states that any spontaneous change in an isolated system is accompanied by an increase in the entropy of the system.
☐ 10. **Equilibrium** is the state at which the **Gibbs energy** of the system has reached a minimum.
☐ 11. The energy levels of confined particles are quantized.
☐ 12. The **Boltzmann distribution** is a formula for calculating the relative populations of states of various energies.
☐ 13. The **equipartition theorem** states that for a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

Checklist of equations

Property	Equation	Comment	Equation number
Velocity	$v = \mathrm{d}r/\mathrm{d}t$	Definition	B.1
Linear momentum	$p = mv$	Definition	B.2
Angular momentum	$J = I\omega$, $I = mr^2$	Point particle	B.3–B.4
Force	$F = ma = \mathrm{d}p/\mathrm{d}t$	Definition	B.5
Torque	$T = \mathrm{d}J/\mathrm{d}t$	Definition	B.6
Work	$\mathrm{d}w = -F\cdot\mathrm{d}s$	Definition	B.7
Kinetic energy	$E_k = \tfrac{1}{2}mv^2$	Definition	B.8
Potential energy and force	$F_x = -\mathrm{d}V/\mathrm{d}x$	One dimension	B.10
Coulomb potential energy	$V(r) = Q_1Q_2/4\pi\varepsilon_0 r$	Vacuum	B.14
Coulomb potential	$\phi = Q_2/4\pi\varepsilon_0 r$	Vacuum	B.16
Electric field strength	$\mathcal{E} = -\mathrm{d}\phi/\mathrm{d}x$	One dimension	B.18
Electrical power	$P = I\Delta\phi$	I is the current	B.19
Heat capacity	$C = \mathrm{d}U/\mathrm{d}T$	U is the internal energy	B.22
Enthalpy	$H = U + pV$	Definition	B.23
Gibbs energy	$G = H - TS$	Definition	B.24
Boltzmann distribution	$N_i/N_j = \mathrm{e}^{-(\varepsilon_i - \varepsilon_j)/kT}$		B.25a
Average speed of molecules	$v_{\text{mean}} = (8RT/\pi M)^{1/2}$	Perfect gas	B.26

C Waves

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➤ Why do you need to know this material?

Several important investigative techniques in physical chemistry, such as spectroscopy and X-ray diffraction, involve electromagnetic radiation, a wavelike electromagnetic disturbance. We shall also see that the properties of waves are central to the quantum mechanical description of electrons in atoms and molecules. To prepare for those discussions, we need to understand the mathematical description of waves.

➤ What is the key idea?

A wave is a disturbance that propagates through space with a displacement that can be expressed as a harmonic function.

➤ What do you need to know already?

You need to be familiar with the properties of harmonic (sine and cosine) functions.

A wave is an oscillatory disturbance that travels through space. Examples of such disturbances include the collective motion of water molecules in ocean waves and of gas particles in sound waves. A **harmonic wave** is a wave with a displacement that can be expressed as a sine or cosine function.

C.1 Harmonic waves

A harmonic wave is characterized by a **wavelength**, λ (lambda), the distance between the neighbouring peaks of the wave, and its **frequency**, ν (nu), the number of times per second at which its displacement at a fixed point returns to its original value (Fig. C.1). The frequency is measured in *hertz*, where $1\,\mathrm{Hz} = 1\,\mathrm{s}^{-1}$. The wavelength and frequency are related by

$$\lambda\nu = v \qquad \text{Relation between frequency and wavelength} \tag{C.1}$$

where v is the speed of propagation of the wave.

First, consider the snapshot of a harmonic wave at $t=0$. The displacement $\psi(x,t)$ varies with position x as

$$\psi(x,0) = A\cos\{(2\pi/\lambda)x + \phi\} \qquad \text{Harmonic wave at } t=0 \tag{C.2a}$$

where A is the **amplitude** of the wave, the maximum height of the wave, and ϕ is the **phase** of the wave, the shift in the location of the peak from $x=0$ and which may lie between $-\pi$ and π (Fig. C.2). As time advances, the peaks migrate along the x-axis (the direction of propagation), and at any later instant the displacement is

$$\psi(x,t) = A\cos\{(2\pi/\lambda)x - 2\pi\nu t + \phi\} \qquad \text{Harmonic wave at } t>0 \tag{C.2b}$$

A given wave can also be expressed as a sine function with the same argument but with ϕ replaced by $\phi + \frac{1}{2}\pi$.

If two waves, in the same region of space, with the same wavelength, have different phases then the resultant wave, the sum of the two, will have either enhanced or diminished amplitude. If the phases differ by $\pm\pi$ (so the peaks of one wave coincide with the troughs of the other), then the resultant wave, the sum of the two, will have a diminished amplitude. This effect is called **destructive interference.** If the phases of the two waves

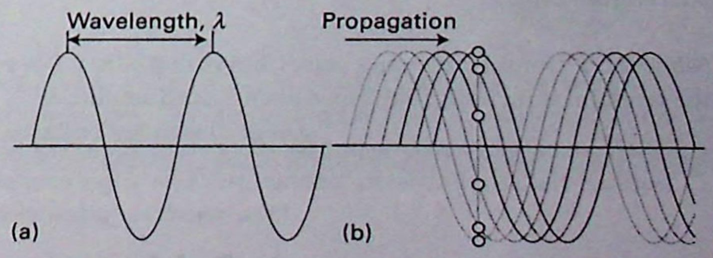

Figure C.1 (a) The wavelength, λ, of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed v. At a given location, the instantaneous amplitude of the wave changes through a complete cycle (the six dots show half a cycle) as it passes a given point. The frequency, ν, is the number of cycles per second that occur at a given point. Wavelength and frequency are related by $\lambda\nu = v$.

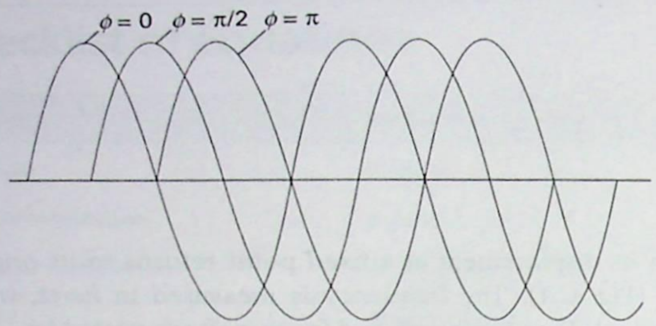

Figure C.2 The phase ϕ of a wave specifies the relative location of its peaks.

are the same (coincident peaks), the resultant has an enhanced amplitude. This effect is called **constructive interference.**

Brief illustration C.1 Resultant waves

To gain insight into cases in which the phase difference is a value other than ±π, consider the addition of the waves $f(x)=\cos(2\pi x/\lambda)$ and $g(x)=\cos\{(2\pi x/\lambda)+\phi\}$. Figure C.3 shows plots of $f(x)$, $g(x)$, and $f(x)+g(x)$ against x/λ for $\phi=\pi/3$. The resultant wave has a greater amplitude than either $f(x)$ or $g(x)$, and has peaks between the peaks of $f(x)$ and $g(x)$.

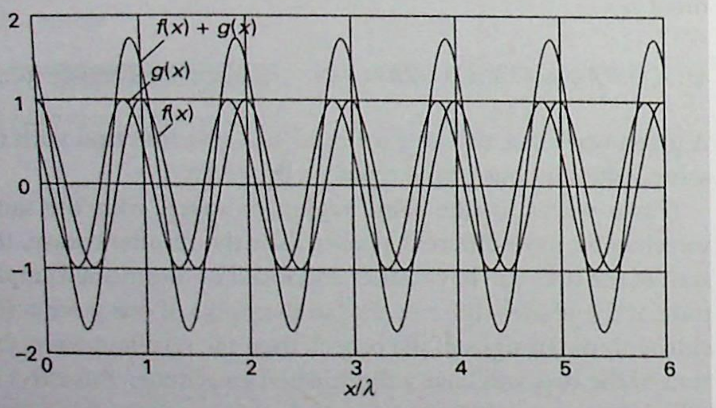

Figure C.3 Interference between the waves discussed in *Brief illustration* C.1.

Self-test C.1 Consider the same waves, but with $\phi=3\pi/4$. Does the resultant wave have diminished or enhanced amplitude?

Answer: Diminished amplitude

C.2 The electromagnetic field

Light is a form of electromagnetic radiation. In classical physics, electromagnetic radiation is understood in terms of the **electromagnetic field**, an oscillating electric and magnetic disturbance that spreads as a harmonic wave through space. An **electric field** acts on charged particles (whether stationary or moving) and a **magnetic field** acts only on moving charge particles.

The wavelength and frequency of an electromagnetic wave i a vacuum are related by

$$\lambda\nu=c$$

Electromagnetic wave in a vacuum Relation between frequency and wavelength (C.

where $c=2.997\,924\,58\times10^{8}\,\mathrm{m\,s^{-1}}$ (which we shall normall quote as $2.998\times10^{8}\,\mathrm{m\,s^{-1}}$) is the speed of light in a vacuum When the wave is passing through a medium (even air), it speed is reduced to c' and, although the frequency remain unchanged, its wavelength is reduced accordingly. The reduce speed of light in a medium is normally expressed in terms o the **refractive index**, n_r, of the medium, where

$$n_{\mathrm{r}}=\frac{c}{c'}$$

Refractive index (C.4

The refractive index depends on the frequency of the light, an for visible light typically increases with frequency. It also depend on the physical state of the medium. For yellow light in water a 25 °C, $n_r=1.3$, so the wavelength is reduced by 30 per cent.

The classification of the electromagnetic field according to it frequency and wavelength is summarized in Fig. C.4. It is ofte desirable to express the characteristics of an electromagneti wave by giving its **wavenumber**, $\tilde{\nu}$ (nu tilde), where

$$\tilde{\nu}=\frac{\nu}{c}=\frac{1}{\lambda}$$

Electromagnetic radiation Wavenumber (C.5

A wavenumber can be interpreted as the number of complet wavelengths in a given length (of vacuum). Wavenumbers ar normally reported in reciprocal centimetres ($\mathrm{cm^{-1}}$), so a wavenumber of $5\,\mathrm{cm^{-1}}$ indicates that there are 5 complete wavelengths in 1 cm.

Brief illustration C.2 Wavenumbers

The wavenumber of electromagnetic radiation of wavelength 660 nm is

$$\tilde{\nu}=\frac{1}{\lambda}=\frac{1}{660\times10^{-9}\,\mathrm{m}}=1.5\times10^{6}\,\mathrm{m^{-1}}=15\,000\,\mathrm{cm^{-1}}$$

You can avoid errors in converting between units of $\mathrm{m^{-1}}$ and $\mathrm{cm^{-1}}$ by remembering that wavenumber represents the number of wavelengths in a given distance. Thus, a wavenumber expressed as the number of waves per centimetre and hence in units of $\mathrm{cm^{-1}}$ must be 100 times less than the equivalent quantity expressed per metre in units of $\mathrm{m^{-1}}$.

Self-test C.2 Calculate the wavenumber and frequency of red light, of wavelength 710 nm.

Answer: $\tilde{\nu}=1.41\times10^{6}\,\mathrm{m^{-1}}=1.41\times10^{4}\,\mathrm{cm^{-1}}$, $\nu=422\,\mathrm{THz}$ ($1\,\mathrm{THz}=10^{12}\,\mathrm{s^{-1}}$)