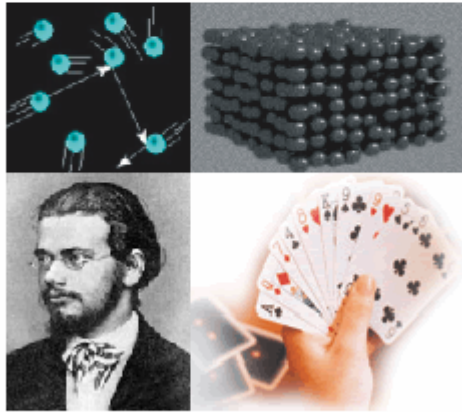


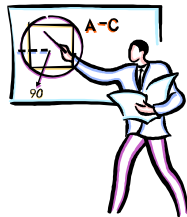
Introduction to Thermodynamics and Kinetics

F31ST1



School of Physics & Astronomy

Lecture Notes *Set 2a: Kinetic Theory I*



2.1 Distributions and Averaging

In this section of the module we will spend a considerable amount of time studying *distribution functions*. Not only is the form or shape of the distribution curve of interest but we will derive a number of fundamental quantities (including the average or mean value) from distribution functions. We'll begin by revising some of what you've learnt in the *Mathematical Modelling* module on distribution functions. You'll find that there is also some significant overlap of the mathematics discussed here with measurement theory, particularly with regard to *Gaussian* (or *normal*) distributions.

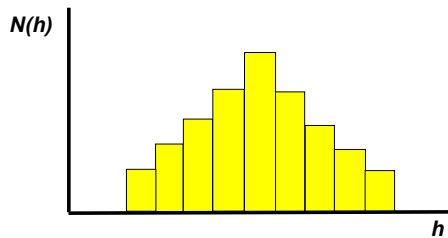


Fig. 2.1 A histogram of measurements of the maximum height to which a ball bounces when dropped from a given distance above the floor.

Fig. 2.1 shows a histogram of a set of measurements of the height to which a ball bounces when dropped from a set distance above the floor. Note that the measurements are placed in bins whose width is Δh . If the number of measurements is increased dramatically and the bin size correspondingly narrowed so that it becomes dh we get a *continuous curve* (Fig. 2.2).

The curve shown in Fig. 2.2 is a Gaussian distribution. (The first few weeks of the 1st year Physics laboratory are dedicated to demonstrations of – amongst other topics – the importance of Gaussian distributed variables). Later on in this section Gaussian functions will be shown to be of key importance when we consider the distribution of molecular velocities in a gas. **It is important to note that $N(h)dh$ is the number of measurements which yielded values between h and $h + dh$.**

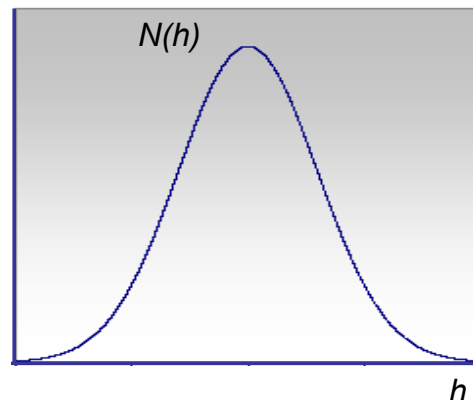


Fig. 2.2 By increasing the total number of measurements and correspondingly reducing the bin size to dh , we get a smooth, continuous curve.

? **Q. 2.1** Considering Fig. 2.2, write down an expression that gives the total number of times the measurement was made.

NOTES

Introduction to the Mathematics of Averaging

Let's now consider how we can determine the average value associated with a distribution function. First, we'll treat a system that can only exist in certain discrete states. A good example of this is the *quantum mechanical* simple harmonic oscillator (SHO). This is a system we will encounter a number of times later in this section and throughout the module. As opposed to the classical potential energy function for a SHO which we met in Section 1 - that is, $U(x) = \frac{1}{2}kx^2$ - a quantum mechanical SHO cannot have *any* value of energy. Just as the energy states of an electron in an atom are quantized, so too are the vibrational energies of a quantum mechanical oscillator (see Fig. 2.3). The energies are given by:

$$E_n = (n + \frac{1}{2})\hbar\omega_0 \quad (2.1)$$

where n is the quantum number associated with the energy level ($n = 0, 1, 2, 3, \dots$), \hbar is Planck's constant divided by 2π and ω_0 is the resonant frequency of the oscillator.

(An important observation here is that the lowest energy state ($n = 0$) for a quantum mechanical oscillator, unlike the classical SHO, *does not have zero energy*. Thus, at 0 K when all classical vibration is 'frozen out', quantum mechanical oscillators still have a *zero point energy*. We'll return to this point later.)

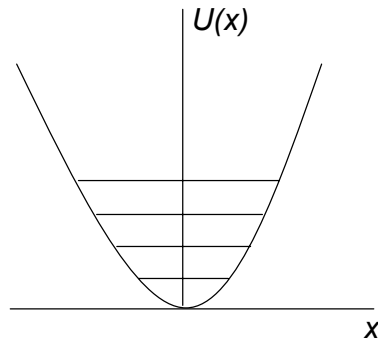


Fig. 2.3 The potential energy curve for a classical simple harmonic oscillator is continuous. A quantum mechanical oscillator can only take on certain quantized energy values as illustrated by the equally spaced lines in the diagram above.

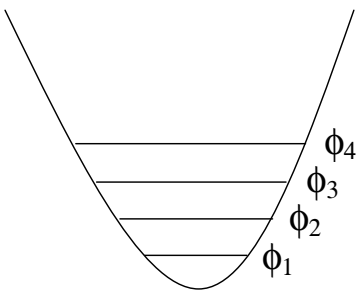


Fig. 2.4 The QM SHO vibrates in discrete states ϕ_i ($i=1,2,3, \dots$)

We label the quantum mechanical SHO states as ϕ_i (where $i = 0, 1, 2, \dots$). The probability of occurrence of each of these states is P_i . If the oscillator has energy E_i in each of these states then the *average* value of E (which we'll denote $\langle E \rangle$) is given by:

$$\langle E \rangle = \sum_i P_i E_i \quad (2.2)$$

However, this analysis is not limited to the quantum mechanical SHO. For *any* function which has discrete values (say, Q_i) when the system is in the states $i = 0, 1, 2, \dots$ etc... then the average value of Q is: $\langle Q \rangle = \sum_i P_i Q_i$ where P_i is again the probability of finding the system in the i^{th} state.

In other cases, instead of comprising a set of discrete states, the system is capable of existing in any one of a continuous range of states. The state of the system is represented by a coordinate, x

? *Q. 2.2 What's the probability of finding this continuous system in a specified, individual state, x ?*

There is a certain probability associated with finding the system in a state lying within a range x to $x + \delta x$. This probability is given by $f(x)\delta x$. The quantity Q considered for the discrete function above is now a function of the continuous variable, x and should thus be written $Q(x)$. The average value of Q is given by:

$$\langle Q \rangle = \sum_i Q(x) f(x) \delta x \quad (2.3)$$

In the limit $\delta x \rightarrow dx$, $\langle Q \rangle$ is given by the following integral:

$$\langle Q \rangle = \int Q(x) f(x) dx \quad (2.4)$$

Note that the function $f(x)dx$ is a probability and hence: $\int f(x)dx = 1$

NOTES

2.2 The Ideal Gas Law

Having introduced distribution functions, we can now move on to derive *the ideal gas law* - a cornerstone of kinetic theory and thermal physics. From a consideration of the motions of the molecules comprising an idealized gas (i.e. the microscopic structure of the gas), the relation $PV = nkT$ will be derived (where P , V , n , k , and T are pressure, volume, number of molecules, Boltzmann's constant and temperature respectively). This simple law underlies a large amount of the physics we'll cover in this module and illustrates convincingly how a consideration of the microscopic structure of a system allows the prediction of relationships between macroscopic variables.

Consider a gas confined in a large square box (wall area: A , side length: a). In deriving the ideal gas law we make a number of important assumptions:

- (i) the molecules comprising the gas are featureless points, occupying negligible volume;
- (ii) there are no forces between the molecules (i.e. no intermolecular interactions);
- (iii) all molecules move independently making elastic collisions;
- (iv) the molecules obey Newton's laws of motion.

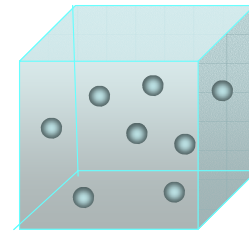


Fig. 2.5 Cartoon of ideal gas molecules in a container. Note the distribution of velocities (different vector lengths)

This hypothetical gas is termed, perhaps unsurprisingly, an *ideal gas*. A monatomic gas such as He or Ne *at low pressures* shows approximately ideal gas behaviour. Later in this section some of the differences in the behaviour of *real* and ideal gases will be covered.

Molecular velocities

To derive the ideal gas law we need to consider the distribution of molecular velocities. We'll start with a question:

? **Q. 2.3** *What's the average velocity of a molecule?*

We could assume that all the molecules move parallel to the x -, y - or z -axis and all have the same speed. However, this is a *very* big assumption and goes somewhat 'against the grain' because it neglects the distribution of molecular speeds and velocities which are at the core of thermal physics. In the following we will take into account the appropriate distributions.

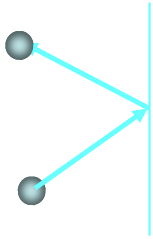


Fig. 2.6 Specular reflection of molecules

The molecules are *specularly* reflected at the walls – that is, the angle of incidence equals the angle of reflection. The momentum change a molecule suffers on colliding with a wall which, as shown in Fig. 2.6, is perpendicular to the x-axis, is therefore $2mv_x$. (Make sure you understand why).

To determine the rate of change of momentum due to the collisions of the molecules with a wall, the frequency of collisions needs to be determined. Only those molecules within a distance v_x of the wall will collide with it within 1 second (see Fig. 2.7). This will be a fraction v_x/a of the total number of molecules in the box.

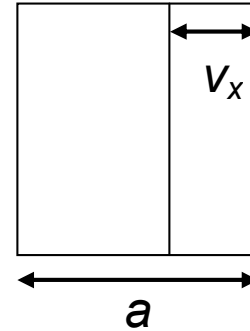


Fig. 2.7 Only those molecules within v_x of the wall will collide with it within 1 second.

Furthermore, the fraction of all molecules which have their x component of velocity in the range v_x to $v_x + dv_x$ is given by: $f(v_x)dv_x$. Here $f(v_x)dv_x$ represents a *probability*. The total number of molecules having their x -component of velocity in this range is: $Nf(v_x)dv_x$.

Hence, the total change of momentum per second due to molecules within the given velocity range is:

$$2mv_x \frac{v_x}{a} Nf(v_x)dv_x \quad (2.5)$$

To get the total change of momentum due to molecules of *all* velocities (in the x direction) hitting a wall, integrate over all velocities:

$$\int_0^{\infty} 2mv_x \frac{v_x}{a} Nf(v_x)dv_x \quad (2.6)$$

? **Q. 2.4** Why are the integral limits $(0, \infty)$?

By symmetry, $f(v_x) = f(-v_x)$ and hence the integrand is symmetrical about $v_x=0$.

$$\Rightarrow \int_0^{\infty} 2m \frac{v_x^2}{a} Nf(v_x)dv_x = \frac{mN}{a} \int_{-\infty}^{\infty} v_x^2 f(v_x)dv_x \quad (2.7)$$

The value of the integral is simply the mean value of v_x^2 which is denoted $\langle v_x^2 \rangle$. Hence, the total change of momentum per second is:

$$\frac{mN}{a} \langle v_x^2 \rangle \quad (2.8)$$



Show that Equation 2.8 can be written $PV = mN \langle v_x^2 \rangle$.

By symmetry, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$.

So, $\langle v_x^2 \rangle = (1/3) \langle v_x^2 + v_y^2 + v_z^2 \rangle = (1/3) \langle v^2 \rangle$

Thus: $PV = \frac{1}{3} mN \langle v^2 \rangle$ (2.9)

$\langle v^2 \rangle$ is the *mean square speed* of the molecules.

NOTES

Free expansion: the Joule effect

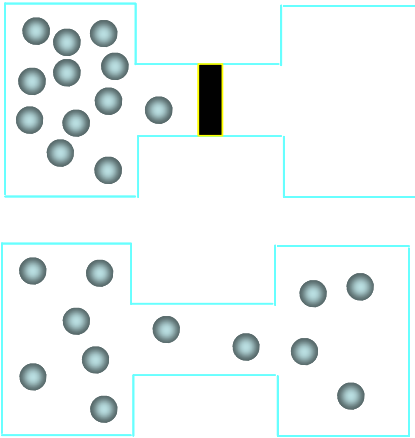


Fig. 2.8 Free expansion of a gas into a vacuum. In the upper sketch the gas is confined to the chamber on the left by the valve. On opening the valve the gas expands into the chamber on the right. This process is carried out adiabatically – there is no heat flow into or out of the gas.

The mean square speed of the molecules, $\langle v^2 \rangle$, and thus the total molecular kinetic energy ($\frac{1}{2} Nm\langle v^2 \rangle$) are greater the higher the temperature. The question now arises as to whether $\langle v^2 \rangle$ is also a function of pressure or volume? Joule attempted to address this issue in 1845 by allowing gas to expand into a vacuum *adiabatically*. An adiabatic process occurs when the system is completely isolated from its surroundings – *there is no heat flow into or out of the system*.

Take an ideal monatomic gas – that is, a gas where all the ‘molecules’ are single atoms (eg. He, Ar, Ne, Hg vapour). In this case there are no internal motions of the gas molecule (eg vibrations, rotations).

In common with very many textbooks I’ll use the term ‘molecule’ and ‘atom’ interchangeably to describe the constituents of an ideal gas even though the ‘molecules’ comprise only one atom.

Furthermore, the gas is ideal so there are no intermolecular interactions. Hence, no work is done during a *free adiabatic expansion* of an ideal gas (because we don’t need to put any work in to break intermolecular ‘bonds’).



NB It is easy to get confused here. In this case we are concerned with the *free adiabatic expansion* of the gas. There is no mechanism (for example, a piston) by which work could be done on the gas or the gas could do work. We will discuss situations involving those types of adiabatic work in detail in Section 3 of the module.

So no work is done and there is no heat energy flowing into or out of the gas (remember, this is an adiabatic process) – thus, *the total energy (U) of an ideal gas remains unchanged during a free expansion*. That is, $dU = 0$.

Writing U as U(T,P), the following relationship holds:

$$dU = \left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP \quad (2.10)$$

If no temperature change takes place (i.e. $dT = 0$) in a free expansion ($dU = 0$) then it follows that:

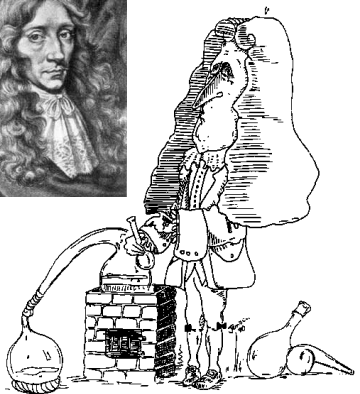
$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \quad (2.11)$$

or, to put Eqn. 2.11 into words, U – the internal energy – does not depend on P . You should use similar arguments to convince yourself that a lack of a temperature change in a free expansion also implies that U does not depend on V . Joule did not detect a temperature change[†] during the free expansion of the gas used in his experiments and hence he used this as proof of the following statement.



The internal energy of an ideal gas depends only on temperature.

Boyle's law and mean kinetic energy



Writing the internal energy of the ideal gas as $U = \frac{1}{2}m\langle v^2 \rangle$, Equation 2.9 can be rewritten as:

$$PV = 2U/3 \quad (2.12)$$

As U is a function of T only for an ideal gas we find:

$$PV = \phi(T) \text{ or, in other words, } PV = \text{constant for a given temperature}$$

This is ***Boyle's law***.

Since the temperature T is proportional to the mean kinetic energy we can write:

$$\begin{aligned} \langle E_K \rangle &\propto T \Rightarrow \\ \frac{1}{2} m \langle v^2 \rangle &= cT \text{ (where } c \text{ is a constant)} \end{aligned}$$

Choosing the constant, c as $3kT/2$ we get the following important relation:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT \quad (2.13)$$

where k is Boltzmann's constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$). Hence, there is a constant conversion factor $3k/2$ between the mean kinetic energy of a molecule and a unit of temperature (the Kelvin).

[†] In fact, we now know that Joule's measurement apparatus was insufficient to measure the small temperature change that was present because the gas used (air) is *not* an ideal gas. This need not concern us at the moment, although it is somewhat fortuitous that Joule's experiment was flawed as it is likely that the progress of kinetic theory would have been slowed somewhat if a temperature change *had* been measured.

Finally, the ideal gas law.....

“Why have you decided to choose the constant of proportionality as $3k/2$?”

Bear with me..! We'll see why the constant has that particular value later in the module.

Accepting that $\langle E_K \rangle = 3kT/2$, we can rewrite $PV = (1/3)Nm\langle v^2 \rangle$ (Eqn. 2.9) as:

$$PV = NkT \quad 2.14$$

For 1 mole of gas, $N = N_A$ (Avogadro's number). Equation 2.14 can then also be written as:

$$PV = RT \quad 2.15$$

where R is the universal gas constant.

Don't confuse N (total no. of molecules) with n (no. of moles)

NOTES

When is a gas an ideal gas?

Before moving on to the next section I'd like to both summarise what we've covered thus far (see below) and to reiterate that an ideal gas is exactly what its name suggests: an *idealisation*. No real gas behaves exactly like an ideal gas: first, molecules are not pointlike and, second, all molecules interact to some degree. However, a key point to realise is that the ideal gas law (Equation 2.14 or Equation 2.15) is a good approximation to the behaviour of real gases *at low pressures*.

Summary thus far

To recap: we have derived the ideal gas law from a microscopic picture of the gas. This should not be taken too lightly – remember, throughout this module “*we assert that the gross properties of matter should be explainable in terms of the motion of its parts*” (RP Feynmann, Lectures on Physics, Vol I, p. 49-1). However, we need to go much further. We've so far only considered the average speed of the molecules and know little if anything about the details of the distribution of speeds and the positions/ arrangements of the molecules comprising the gas. A key question to clear up is just why we can say that $\frac{1}{2} m \langle v^2 \rangle = 3kT/2$. Considering the *distributions* rather than solely the average quantities will provide us with a much better insight into what temperature represents.

NOTES

2.3 Boltzmann factors



“Available energy is the main object at stake in the struggle for existence and the evolution of the world”, Ludwig Boltzmann

“At thermal equilibrium all microscopic constituents of a system have the same average energy”, Grant & Philips, “The Elements of Physics”, p.421

Instead of the average energy we’re now going to consider the *distribution* of energy in a system. For a system in thermal equilibrium at a certain temperature, the components are distributed over available energy states to give a total internal energy, U (see Fig. 2.9). However, what is the *probability* of finding a molecule (or a particle, or another component of the system) in a given energy state?

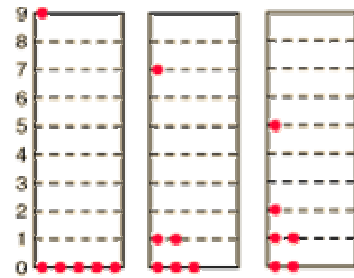


Fig. 2.9 Sample distributions of the components of a system amongst the available energy states.

Boltzmann’s law

The probability of finding a component of a system (eg an atom) in an energy state, ϵ , is proportional to the Boltzmann factor: $\exp(-\epsilon/kT)$

This elegant and simple law underlies a vast amount of physics. You’ll find it useful to **commit the law to memory.**

“Where did the exponential term come from?”

Derivation of Boltzmann’s law

Let’s revisit our picture of molecular motion in a gas. We imagine making the molecules subject to a force pointing along the x-direction. This could be an electric field acting on charged molecules, or an attraction to a wall, or something – *it doesn’t matter*. Now, consider two planes in the gas separated by a distance dx (as shown in Fig. 2.10). There is a pressure change, dP between the planes.

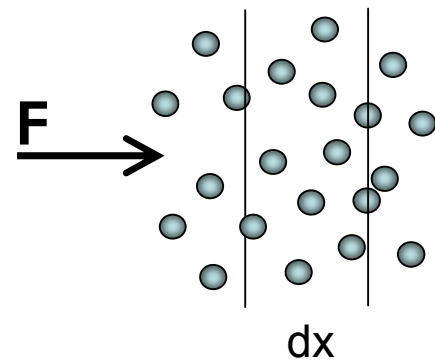


Fig. 2.10 Molecules subject to a force pointing in the +x direction. We consider the pressure difference across the ‘slice’ of gas of width dx .

$$dP = \text{force on each atom} \times \text{no. of atoms per unit vol} \times ?$$

? From a consideration of the unit of pressure, can you suggest what the final term in the equation above might be?

So:

$$\begin{aligned} dP &= F(N/V)dx \\ &= Fn'dx \end{aligned} \quad 2.16$$

However, from Equation 2.14 dP can also be written as:

$$dP = n'kT \quad 2.17$$

n' ($=N/V$) is a different quantity to n .

Equating 2.16 and 2.17;

$$Fdx = kT \frac{dn'}{n'} \quad 2.18$$

Solving this differential equation (see your Mathematical Modelling and/or General Maths notes):

$$\int Fdx = kT \int \frac{dn'}{n'} \quad 2.19$$

$$\Rightarrow -\varepsilon = kT \ln(n') + C \quad 2.20$$

In equation 2.20, ε is the potential energy (remember $F = -dU/dx$, hence $U = -\int Fdx$). Equation 2.20 can be rewritten as:

$$n' = \alpha \exp(-\varepsilon / kT) \quad 2.21$$

Here, α is a constant whose value can be determined by considering the number density when the potential energy is 0.

NOTES

Boltzmann factors and probability

Equation 2.21 is a simple but exceptionally important expression. Remember that at the start of the derivation we said that *any* force was appropriate. This is almost but not quite correct. For Eqn. 2.21 to be valid the force must be *conservative* – that is, the elements of the system (the molecules in this case) are not subject to friction or any other type of process that dissipates energy. Thermal equilibrium cannot exist if the forces on the atoms are not conservative. However, Eqn. 2.21 doesn't depend on the *type* of conservative force and hence is a general expression.



Fig. 2.11 A Boltzmann factor is responsible for the fact that diamond does not spontaneously decay into graphite.

Boltzmann factors appear *everywhere* in physics (and chemistry and biology and materials science and.....). Why? Primarily because the Boltzmann expression (Eqn. 2.21) underlies the population of energy states and thus controls the rate of a process.

A key example is that of diamond. Graphite is more thermodynamically stable than diamond and represents the ground state of crystalline carbon. Given enough time, diamond will decay to graphite. The key reason why diamond is (relatively) prevalent in our world is that it represents what is termed a *kinetically hindered* state of the system. To see more clearly what this means, the potential energy curve shown in Fig. 2.12 is useful.

Stability, metastability and instability

The potential energy curve shown in Fig. 2.12 includes both a *metastable* and a *stable* state. There is a 'hill' (if we were considering a gravitational potential then this would literally be a hill) between the metastable and the ground state. The system will only surmount the hill when it gains enough energy. If we are relying on thermal fluctuations for this to happen the energy input may be very low (see below). Diamond is *metastable* with respect to graphite.

The probability of surmounting the barrier is proportional to $\exp(-\Delta E/kT)$

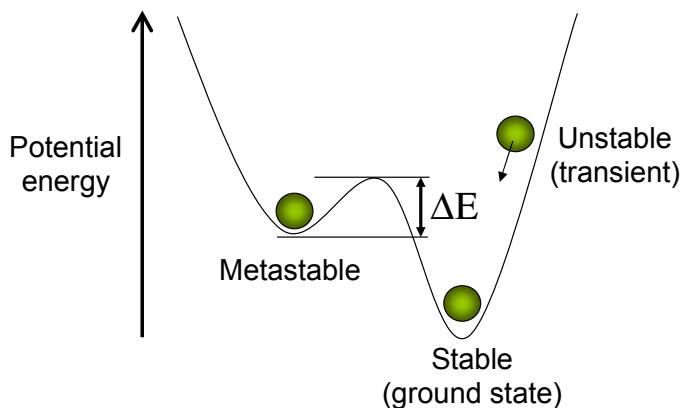


Fig. 2.12 A schematic potential energy curve illustrating time invariant stable and metastable states, and a transient unstable state.



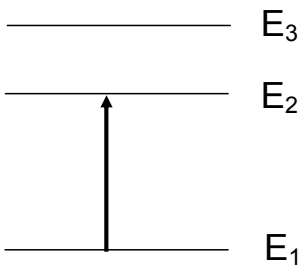
It is possible to have a time invariant unstable state. Can you sketch the form of the potential energy curve associated with this state?

NOTES

The statement in bold at the bottom of the preceding page is so important I'm going to repeat it again (in a slightly different form):



The probability of finding a system in a state with energy ΔE above the ground state is proportional to: $\exp(-\Delta E/kT)$



PROBLEM: Electrons in atoms are restricted to occupying certain quantized energy states. The hydrogen atom can exist in its ground state (E_1) or in an excited state (E_2, E_3, E_4 etc...). At a temperature T , what is the relative probability of finding the atom in the E_3 state as compared to finding it in the E_2 state?

- (a) $\exp(E_3/kT)$
- (b) $\exp(E_2/kT)$
- (c) $\exp((-E_3+E_2)/kT)$, or
- (d) $\exp((-E_2-E_3)/kT)$



The value of kT at room temperature (293 K) is 0.025 eV.

This is a very important value to memorise as it gives us a ‘handle’ on what processes are likely to occur at room temperature.



The first excited state of the hydrogen atom lies ~ 10.2 eV above the ground state. What is the probability of the hydrogen atom being in the first excited state at room temperature (in the absence of any energy input other than thermal energy)?

Remember that molecular vibrations and rotations are also *quantized* and Boltzmann factors can be used to determine the relative populations of the quantized energy levels associated with these motions.