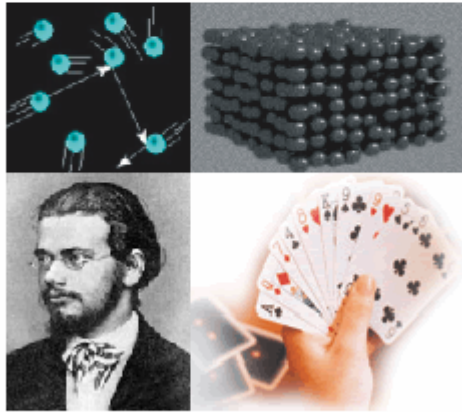


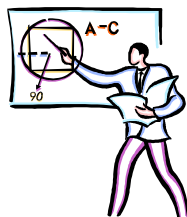
Introduction to Thermodynamics and Kinetics

F31ST1



School of Physics & Astronomy

Lecture Notes *Set 1: Introduction to* *States of Matter*



1.1 States of Matter: Forces & Potentials



Fig. 1.1 RP Feynmann and, inset, an STM image showing individual silicon atoms

One important objective of this course is to illustrate how macroscopic quantities and variables such as pressure, temperature and volume derive from the fundamental microscopic, or atomistic, properties of matter. Before we begin, let's consider the significance of our knowledge that solids, liquids and gases are made up of atoms and molecules. Fig.1 is a photograph of Richard Feynman, one of the 20th century's leading physicists. Feynman was of the opinion that the proposal and subsequent confirmation of the atomic nature of matter were the 'jewel in the crown' of all scientific activity across the ages:

"If, in some cataclysm, all of scientific knowledge were to be destroyed and only one sentence [could be] passed onto the next generation of creatures, what statement would contain the most information in the fewest words?"

"All things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another" . RP Feynman, *The Feynman Lectures in Physics*, Vol I (1963)

A large proportion of the *Thermal & Kinetic* module will be concerned with the properties of what are termed ideal gases – that is, hypothetical gases whose molecules do not attract each other *"when they are a little distance apart"*. However, in order to introduce a number of fundamental concepts in thermodynamics, it is helpful at first to consider the forces experienced by atoms in real gases, liquids and solids.

Solid matter is comprised of a very large number of interacting atoms and molecules. Can we construct an appropriate and physically reasonable model of those interactions which will give agreement with experimental data? A model somewhat similar to that proposed by Einstein in 1907 is shown in Fig. 2. Here the interatomic interactions are modelled by springs which couple the atoms together. Thus we have a system comprising very many *coupled oscillators*. Think back to the first laboratory report you did in the 1st year lab. last semester – just as you observed normal modes for simple pendula joined by a spring, the vibrations of atoms in the solid may also be analysed in terms of normal modes of vibration. We'll revisit this concept towards the end of the module, but for now let's consider a single simple harmonic oscillator....

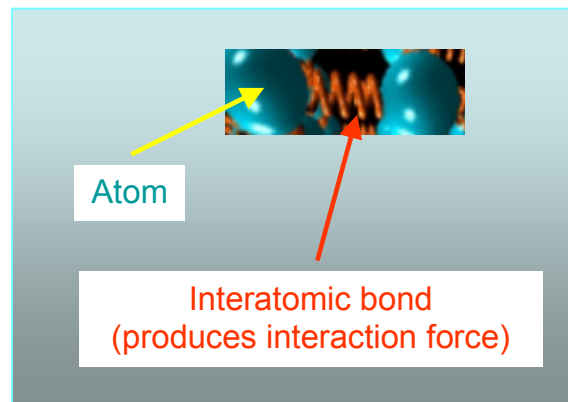
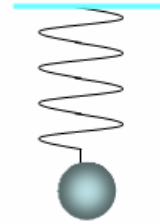


Fig. 2.1 Model of solid as a set of coupled oscillators (balls and springs). 3D model of solid taken from the "Matter & Interactions" website, Chabay and Sherwood.



Q1. Assuming simple harmonic motion, the force exerted by the spring on the ball depends:

- (a) *linearly*,
- (b) *quadratically*, or
- (c) *exponentially* on the displacement?

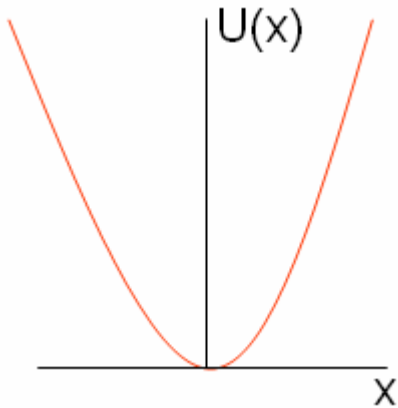


Q2. For a simple harmonic oscillator (spring constant k), the potential energy is:

- (a) kx^2 , (b) k/x^2 , (c) $\cos(kx)$, (d) none of these.

[NB Don't just simply look up the answer if you don't know it already.

Calculate the potential energy from the equation for the force (answer to Q1).]



Q3. Is this an appropriate potential to use to describe interatomic interactions under all conditions? Why?

Fig. 3 Potential energy curve for simple harmonic oscillator

NOTES

The Morse potential

So, we need to suggest a more physically reasonable function to describe the potential energy between two atoms. The Morse potential shown to the right is an *approximation* to the interatomic potential that yields a potential energy vs separation dependence that has roughly the correct form. The mathematical expression for the potential is:

$$U(r) = E_0[1 - \exp(-\alpha(r - r_0))]^2 \quad 1.1$$

where E_0 is the depth of the potential well, α is a parameter which controls the width of the well, and r_0 is the equilibrium separation of the atoms.

The depth of the well depends on the strength of the bond between the atoms and can vary from a few tenths of an electron volt (eV)[†] up to ~ 10 eV for the strongest interactions. From last semester's *Mathematical Modelling* module – and elsewhere – you will know that the force is given by the negative of the gradient of the potential (with respect to separation in this case). It is interesting to consider the direction of the force when an atom is moved from its equilibrium position, r_0 , to either shorter or longer distances.

? Q4. What is the direction of the force on an atom at a separation greater than the equilibrium separation?

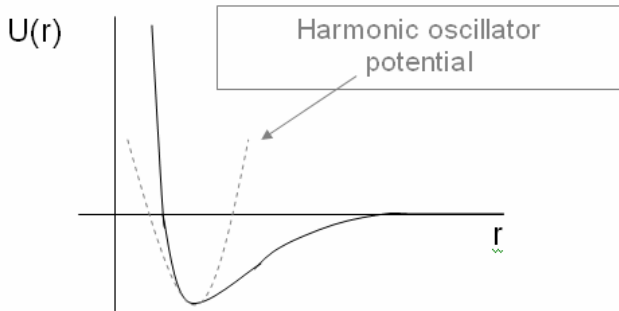


Fig. 1.4 The bottom of the Morse potential energy curve may be approximated by a harmonic potential.

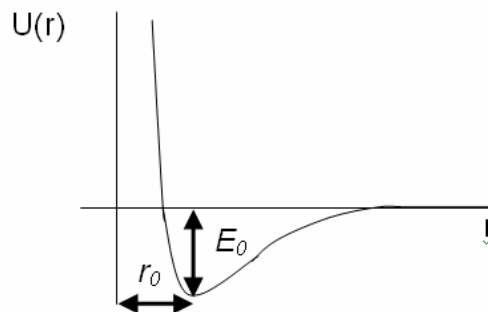


Fig. 1.3 The Morse potential energy function. $U(r)$ is the potential energy of two neutral atoms.

You could now argue – correctly – that this curve is pretty different from the potential energy curve for a simple harmonic oscillator (we say the curve – and the behaviour of the atoms – is *anharmonic*). So why did we spend time discussing simple harmonic oscillators? Well, if we consider only small deviations from the equilibrium separation (as may be the case for thermal vibrations of atoms in a solid, for example) then we can *approximate* the potential energy curve around the equilibrium point to that of a simple harmonic oscillator. This is shown graphically in Fig. 1.4.

[†] Get used to thinking in terms of electron volts – we'll be using them a lot in this module.

We can write a simple expression for this harmonic potential:

$$U_{approx} = \frac{1}{2}k_{bond}r^2 + U_0 \quad \mathbf{1.2}$$

In this expression U_0 arises from the value of the potential at the bottom of the Morse potential energy curve and we have included the harmonic potential for an interatomic bond with a spring constant of k_{bond} . Hence, we model the solid as a collection of balls and springs.

(*An important aside:* it is worth noting here that the idea of approximations about a minimum in a function were also covered in some depth in the *Mathematical Modelling* course (see, for example, <http://www.nottingham.ac.uk/~ppxada/minima.pdf>). Similarly, throughout your degree, try to see the *links* between the material you cover in each of the modules. Each module is part of an interconnected ‘whole’.)

NOTES

1.2 Introducing temperature and changes of phase

A disclaimer regarding this section.....

You intuitively know that increasing the temperature of a solid, liquid or gas will increase the average energy of the atoms/ molecules comprising the state of matter. An important aim of this module will be to show you that the concept of temperature is rather more involved than this and, for a proper definition of temperature, we need to consider both *thermal equilibrium* and *entropy* in some detail. Similarly, in the following, the idea of a *change of phase* will be introduced in a somewhat qualitative fashion. We will revisit these important concepts in detail later in the module.

An interesting question that we can address using the simple arguments outlined in Section 1.1 is: why does a solid expand as the temperature is increased? First note that as we increase the temperature, we increase both the kinetic energy *and* the potential energy of the atoms that comprise the solid.

? Q5. Why does the *potential* energy increase?

Increasing the temperature increases the average stretch of the interatomic bonds (or ‘springs’) holding the solid together. As the interatomic potential (e.g. the Morse curve) is not symmetric about the equilibrium point - it is *anharmonic* and not harmonic – then the average separation will increase.

If you think carefully, however, there is a problem with this argument. In the interior of the solid, each atom experiences forces due to all of its neighbours (the Morse curve describes the potential of a *pair* of atoms or molecules) and thus the overall potential curve is, in fact, symmetric. However, at the surface of the solid the atoms have lost some of their neighbours, the potential becomes asymmetric again, and the argument put forward in the caption to Fig. 1.5 is again valid. The bond lengthening thus starts at the surface and propagates into the bulk of the solid. (This is just one example of the importance of *surfaces*. There is an entire branch of science (called, not surprisingly, *surface science*) devoted to the properties of - and processes that occur at – surfaces.)

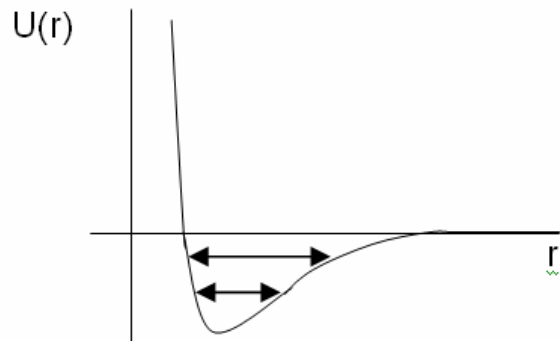


Fig. 1.5 As the temperature of the solid increases, the average stretch increases and, because the potential is anharmonic, the equilibrium separation changes.

Phase changes

Let's keep increasing the energy input so that the total energy (kinetic + potential) reaches the point where the atoms are no longer bound to fixed positions and the solid undergoes a *phase change* to become a liquid. The key question is: *what happens to the temperature of the solid at the phase transition?* We can address this question by attempting to explain a few apparently simple phenomena:



**TRY TO ANSWER THE FOLLOWING QUESTIONS
BEFORE TURNING THE PAGE!**



Q6. If you add a small amount of hot water (at, say, 50°C) to ice water at 0°C , will the temperature of the mixture initially: (a) rise to 25°C , (b) stay at 0°C , (c) rise to 50°C , (d) none of these?

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Q7. A kettle of water takes a shorter time to reach boiling point than for the water to boil away. Why?

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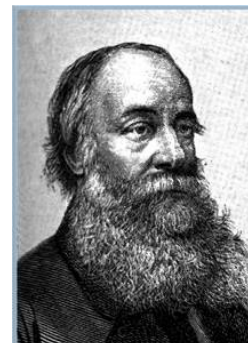
Q8. Years ago, my grandmother used to spray water over the vegetables in the cellar to protect them from frost. Is this simply an 'old wives' tale' or can the presence of water help protect the vegetables?



NOTES

Heat capacity

Joule (pictured to the right) found that it takes 4.2 J of energy to raise the temperature of 1 g of water by a temperature of 1 K[†]. That is, the *specific heat capacity* of water (the heat capacity *per unit mass*) is 4.2 J K⁻¹ g⁻¹. Most often, specific heat capacities are quoted in terms of moles of substance.



? **Q9.** Given that the atomic weight of hydrogen is 1 *amu* and that of oxygen is 16 *amu*, write down the value of the specific heat capacity of water in units of J K⁻¹ mol⁻¹.

NOTES

(You should also know how many molecules are in 1 mole of a substance).

The definition of specific heat capacity given above is rather qualitative. The following is a more general and mathematically precise definition:

“If a small amount of heat, dQ , raises the temperature of an object of mass m by an amount dT , the heat capacity of the object is dQ/dT . The specific heat capacity (C) is the heat capacity per unit mass: $(dQ/dT)/m$ ”

Comparisons of experimental data for heat capacities against theoretical predictions from atomistic models played a large role in establishing the validity of both kinetic and quantum theory and we will spend a lot of time in Sections 2 and 3 of this module discussing heat capacities in detail. Note that specific heats can vary somewhat with temperature (see Fig. 12.6 of Grant and Phillips) and, furthermore, as we’ll also see in Sections 2 and 3, the value derived from the measurement of a specific heat depends critically on how the experiment was carried out: was the volume constant?; was the pressure constant?; was there a magnetic field on the sample?

? **Q10.** Taking the heat capacity of water from the answer to question 9, calculate the temperature rise of 100 g of water when 1 kJ of heat is added.

[†] We’ll usually use Kelvin as units of temperature in this module. Just how this unit is defined - and how the Kelvin scale is calibrated - will be covered in detail in a later lecture. For now, note that to convert degrees Celsius to Kelvin, simply add 273.15 (...we’ll also return to an explanation of that 273.15 figure!). In addition, it is worth bearing in mind at this point that 1 K is roughly equivalent to an average molecular energy of 10⁻²³ Joules. (*What is this value in eV?*)

Latent heat

Let's return to the questions posed on the page before last. All the questions can be answered by appreciating that ice and water have large *latent heats* of melting and vaporization respectively. Our original question at the start of the section on phase changes was what happens to the temperature at the phase transition. In order to answer this question we'll take a block of ice at a temperature of 250 K as our starting point.

Imagine adding heat at a constant rate to the block of ice. Its temperature will rise until it reaches a temperature of 273.15K (i.e. 0°C). At that point *the ice stops heating up* and starts to melt. Why, despite the fact that we're pouring in energy in the form of heat, does the temperature of the system not rise? Simply because the heat is not going to increase the thermal energy of the molecules, it's instead being used to break the intermolecular bonds. *The ice-water mixture remains at 273.15K until all the ice has melted.*

The heat used to transform a solid into liquid without changing its temperature is called the ***latent heat of melting*** or ***the latent heat of fusion***. As the intermolecular bonds in water are quite strong, water has a very large latent heat of melting: $333 \text{ kJ K}^{-1} \text{ kg}^{-1}$. (It's worthwhile calculating the rise in temperature that would result if 333 kJ of heat were added to water at room temperature.) Note that if we instead start with water and remove heat to freeze it, at 273.15 K the heat expelled leads to the solidification of the water (hence, latent heat of *fusion*) rather than a reduction in temperature. The heat energy released during the transformation of water to ice arises from the change in potential energy associated with the molecules binding together (see Fig. 1.3 – there is a potential well associated with the bonded molecules (of depth E_0)).

Returning to heating – rather than cooling – the water, we continue to raise the temperature of the liquid until it reaches 373.15 K. At this point additional heat input goes to evaporating the water so that it becomes steam. Water also has a high ***latent heat of evaporation*** or ***latent heat of vaporisation*** (the heat needed to convert unit mass of water to unit mass of steam at 373.15 K).

However, there is much more to evaporation and the liquid:gas change of phase than this.....

NOTES

1.3 Vapours, evaporation and vapour pressure

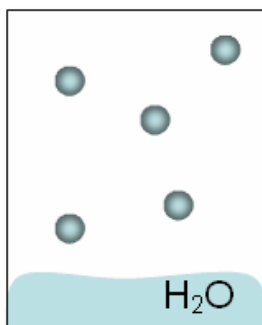


Fig. 1.6 Liquid water coexisting with its vapour in a sealed container.

Two ‘limiting’ cases need to be considered when discussing vapours and evaporation. First, take a closed container which is partially filled with water at, say, 300 K (Fig. 1.6). Water vapour at a pressure termed the *saturated vapour pressure* fills the space in the container above the surface of the water.



Q.11 The temperature of the water is 300 K. This is a little over room temperature but very much less than the boiling point of water, 373.15 K. Why is there water vapour in the container?

NOTES

In the container, molecules not only leave the surface of the liquid to contribute to the vapour but molecules from the vapour phase hit the surface of the water and undergo energy exchanges with the liquid phase molecules. A state of *thermal equilibrium* is established where the rate of molecules leaving the surface is exactly balanced by the rate of molecules returning to the liquid from the vapour phase. “*In thermal equilibrium with its vapour at any given temperature, water has a unique saturated vapour pressure*” (Grant & Phillips, p. 418). This statement obviously holds true for *any* liquid but you might be surprised to find that every *solid* material also has an associated vapour pressure. This may be extremely small (particularly at room temperature) but there is still a chance that some atoms from the solid can pass directly into the gas phase (a process called *sublimation*). It is important to remember that the saturated vapour pressure for a given material is a function of temperature.

Now consider the second case, as shown in Fig. 1.7, where the container has been removed and the water droplet is exposed to the environment. Now when water molecules enter the vapour phase, there is a net loss of water, leading to a gradual disappearance of the droplet. The rate at which the water evaporates will obviously increase as the temperature is raised *and*, perhaps less obviously, is related to the *relative humidity* of the atmosphere. The relative humidity depends on both the temperature and the density of water vapour in the air.

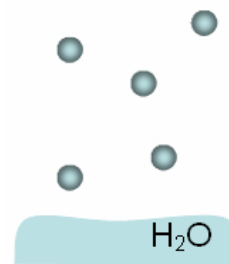


Fig. 1.7 A droplet of water in an open environment.



Q. 12 What happens to the temperature of the droplet as the water evaporates?

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As more heat is put in, the temperature of the water increases until the saturation vapour pressure of the water equals the external (e.g., atmospheric) pressure. At that temperature (373.15 K at normal atmospheric pressure), the water *boils*. Boiling is a special type of evaporation, where the evaporation occurs not at the surface but within the bulk of the liquid. At boiling point, the heat input goes to overcome intermolecular interactions and does not raise the temperature of the system until all the water has turned to steam.



Q. 13 Why does it take longer to cook an egg at the top of a 3000m high mountain?

NOTES

1.4 Drinking ducks



During one of the lectures associated with the *Thermal & Kinetic* module you'll be shown a type of bird that used to be quite common but unfortunately seems to have become almost completely extinct in recent years (although it has been spotted on an episode of "*The Simpsons*"). This seemingly magical bird bobs back and forth for hours – or even days – on end, sipping a glass of water with no apparent input of energy. In Section 1 of the module we have covered everything you need to explain the operation of the bird. Try to do so!

NOTES



References for Lecture Notes Set 1

The discussions in this set of notes borrow heavily from:

The Elements of Physics, Grant & Phillips, Chapter 12

Matter & Interactions, Chabay & Sherwood, Chapters 4 and 5

The Feynman Lectures on Physics, Vol. I, RP Feynman, Chapter 39

How Things Work: The Physics of Everyday Life,

LA Bloomfield, John Wiley & Sons Inc, ISBN 0-471-59473-3

(I don't recommend that you purchase this book as it is designed to give qualitative explanations of physical phenomena and in that regard is not suitable for this module. However, as a pointer towards appreciating physics in everyday life, it cannot be matched!)