

# Frontiers in Physics: Nano and Beyond

Philip Moriarty

*School of Physics and Astronomy, University of Nottingham*

`philip.moriarty@nottingham.ac.uk`

`http://www.nottingham.ac.uk/physics/people/philip.moriarty`

`http://www.youtube.com/Moriarty2112`

May 8, 2015

# Contents

Contents	i
<b>1 The Nanoworld: Where Size is Everything</b>	<b>2</b>
1.1 From nanotech to atomtech . . . . .	2
1.2 Defining nanoscience . . . . .	5
1.3 Size-dependence: An artificial periodic table? . . . . .	8
1.4 Reaching the atomic limit . . . . .	9
1.4.1 Atoms and bits: digital matter? . . . . .	12
1.4.2 A Matter Compiler? . . . . .	13
<b>2 Force and Potential at the Nanoscale</b>	<b>15</b>
2.1 Fundamental forces . . . . .	15
2.2 Forces and potentials . . . . .	16
2.3 Interatomic forces . . . . .	17
2.4 Modelling interatomic forces . . . . .	17
2.5 The Lennard-Jones potential . . . . .	21
2.6 Worked problem: Interacting hydrogen atoms . . . . .	23
2.7 Measuring interatomic & intermolecular forces . . . . .	24
2.8 The origin of interatomic and intermolecular forces . . . . .	28
2.9 van der Waals interactions . . . . .	29
2.10 Beyond physical attraction . . . . .	29
2.11 Tutorial video: Interatomic potentials – when do atoms touch? . . . .	31
2.12 Problems . . . . .	32

<b>3</b>	<b>Sticky, Goopy, and Bumpy: Scaling Down</b>	<b>33</b>
3.1	A Fantastic Voyage: Physics in a scaled-down world . . . . .	33
3.2	Scaling . . . . .	35
3.3	Fluid mechanics at the nanoscale . . . . .	36
3.4	Random walks in nanospace . . . . .	37
3.5	Problems . . . . .	41
<b>4</b>	<b>Introducing the Quantum</b>	<b>42</b>
4.1	Quantum mechanics: A gentle introduction . . . . .	42
4.2	Waves, particles, wavicles? . . . . .	42
4.3	The Schrödinger equation . . . . .	47
4.4	But what is it that's waving in a matter wave?! . . . . .	48
4.4.1	The wavefunction and probability . . . . .	49
4.5	Energy and time in the Schrödinger equation . . . . .	49
4.6	Waves on a string . . . . .	50
4.7	Schrödinger and the particle in a box . . . . .	52
4.8	Tutorial videos: Particle in a box . . . . .	54
4.9	When the uncertainty principle goes up to 11... . . . .	55
4.10	Worked problem: Particle in a palladium box . . . . .	56
4.11	Problems . . . . .	59
<b>5</b>	<b>Precision Probes</b>	<b>62</b>
5.1	Why can't a conventional microscope resolve atoms? . . . . .	62
5.2	Quantum mechanical tunnelling . . . . .	63
5.3	Tunnel current and the scanning tunnelling microscope . . . . .	64
5.4	STM imaging modes . . . . .	66
5.5	STM instrumentation . . . . .	67
5.5.1	Tip preparation . . . . .	68
5.5.2	Vibration isolation . . . . .	69
5.5.3	Piezoelectric elements . . . . .	70

5.5.4	Feedback loop and computer-based data collection . . . . .	70
5.6	Do we <i>really</i> see atoms? . . . . .	71
5.7	Bonding and anti-bonding orbitals . . . . .	73
5.8	Atomic force microscopy . . . . .	74
5.9	Non-contact AFM (aka dynamic force microscopy) . . . . .	75
5.9.1	Quality factor, damping, and the vagaries of vacuum . . . . .	78
5.10	Resolving single chemical bonds: From nanoscience to picoscience . . . . .	80
5.11	Atomic manipulation with scanning probes . . . . .	81
5.12	Tutorial video: How does an STM image and manipulate atoms? . . .	85
5.13	Problems . . . . .	86
<b>6</b>	<b>Atoms and molecules in motion</b>	<b>92</b>
6.1	The nanofactory revisited: Brute force vs self-assembly . . . . .	92
6.2	The crystal maze . . . . .	93
6.3	Crossing the barrier: atomic and molecular diffusion . . . . .	95
6.4	Worked Problem: Tracking Diffusion . . . . .	98
6.5	Tunnelling rather than hopping? . . . . .	99
6.6	Self-assembly: A question of balance . . . . .	100
6.7	From “hit-and-stick” to close-packing . . . . .	101
6.8	Problems . . . . .	104
	<b>Bibliography</b>	<b>110</b>



# Preface

This ebook brings together sets of lecture notes, videos, problems (and worked solutions), and YouTube videos developed over the last few years for the nanoscience component of the first year undergraduate *Frontiers in Physics* module at the University of Nottingham. As you might expect and hope, my aim is to combine all of these elements of the course in a seamlessly integrated manner. The bitter reality, however, is that it is almost certainly going to take a number of revisions before the book is anywhere near as coherent as both you and I would like. Therefore, please don't hesitate to contact me if you have suggestions for changes (or spot any errors): philip.moriarty@nottingham.ac.uk

One of the key motivations underpinning the *Frontiers in Physics* module is to introduce undergraduates to modern - preferably, state-of-the-art - physics in a number of fields. The aim is to couch these exciting developments in terms of first-year-level physics and maths. This ebook focuses on nanoscience research where there has been a wide variety of pioneering breakthroughs over the last decade. Nanoscience is now moving 'beyond nano' (as the title of this book suggests): single bond resolution is increasingly the norm, and scanning probe microscopes can now measure and manipulate on the piconewton and picometre scales.

A particular rationale for developing the *Frontiers* course material as an ebook is that, as compared to a print version of the textbook, it is straight-forward to modify the material so as to keep up with the latest developments in the field.

This ebook has been in gestation for far too long and I apologise profusely to the Nottingham undergrads for missing (more than once) my own self-imposed deadlines. I am fond of quoting Douglas Adams' opinion of deadlines: *I love deadlines. I love the whooshing sound they make as they go flying by..* Nonetheless, I will aim to be rather more disciplined when updating the book in future. (One near-term update will be the inclusion of more questions and problems at the end of each chapter.)

Finally, I have to note that this book could not have been brought to you without the endless patience of my wife, Marie, and my children, Niamh, Saoirse,

and Fiachra. They spent far too much of their time waiting for me to finish off “just one more” page or chapter...

Philip Moriarty  
Nottingham, April 2014.

# Chapter 1

## The Nanoworld: Where Size is Everything

*The air all around is full of micromachines. Robots the size of molecules.  
Nanogenes. Now that you're unprotected you're being rewritten.*

From Dr. Who, *Asylum of the Daleks* ©Steven Moffat; BBC Productions (2012)

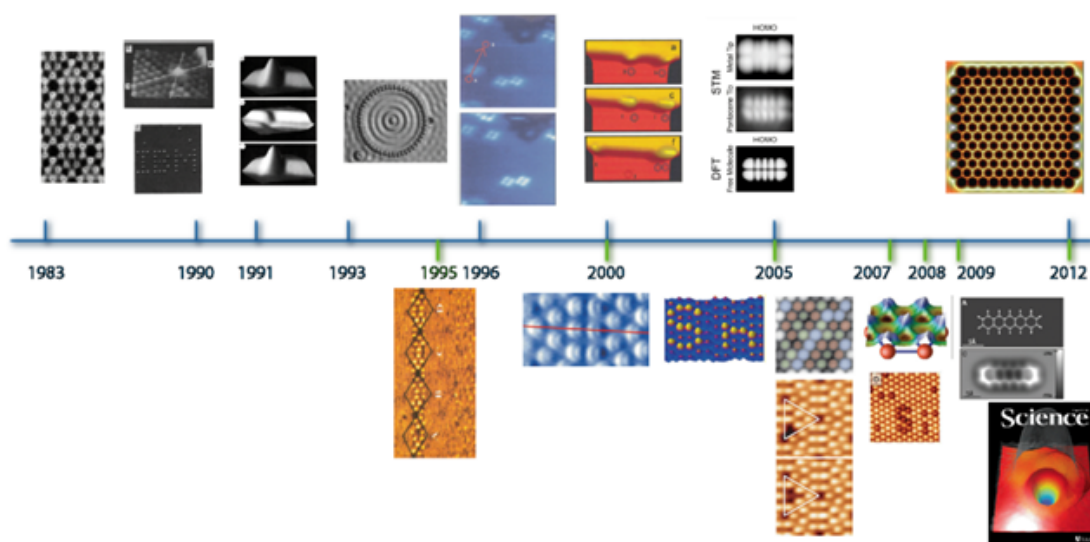
### 1.1 From nanotech to atomtech

It is now routine to image individual atoms and molecules on solid surfaces. Indeed, at the time of writing (spring 2014), the resolution of single *bonds* within molecules is being achieved by a growing number of researchers (including ourselves here at Nottingham). Controlled positioning of single atoms/molecules on surfaces is rather less routine but has been demonstrated for a relatively wide range of materials systems (see timeline in Fig. 1) spanning the seminal writing of the IBM logo in atoms of Xe on Ni by Eigler and Schweizwer in 1990[1], through the atom-by-atom synthesis of molecules demonstrated by both Lee and Ho, and Hla et al.[2, 3] in the late nineties/early 'noughties', to the measurement of the force required to move a single cobalt atom across a surface (Ternes *et al.*[4]).

The extent to which atom-scale engineering of this type can be exploited to build artificial nanostructures - or microstructures or, indeed, macroscopic objects - brings to mind a considerable number of compelling “gedanken” experiments. Eric Drexler proposed three decades ago[6, 7] that molecule-by-molecule construction

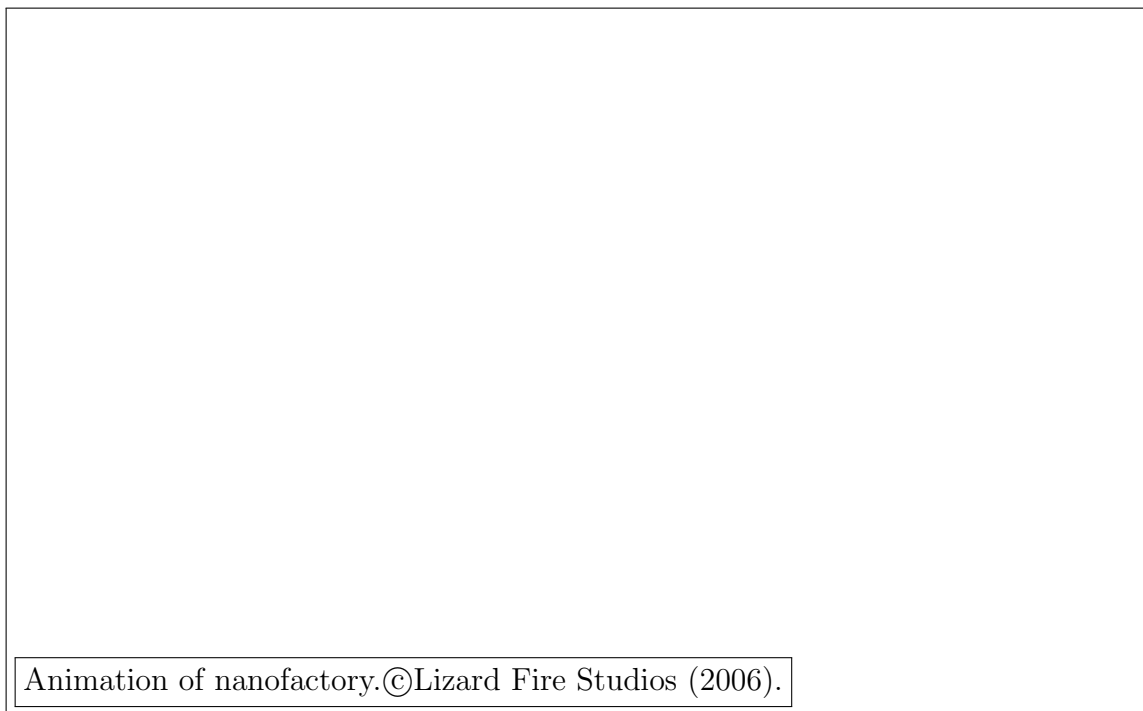
---

PowerPoint slides associated with this chapter are available [here](#).



**Figure 1.1** – A timeline of advances in atomic-scale imaging and manipulation of matter spanning the first images of a silicon surface captured by the scanning tunnelling microscope invented by Binnig et al.[5] in the early eighties, through the pioneering atomic manipulation experiments of Don Eigler and co-workers in the nineties, up to the exceptionally high resolution images of *intramolecular* structure achieved by Leo Gross and co-workers in 2009 and the observation of what has become known as 'sub-atomic' structure arising from the symmetry of atomic and molecular orbitals. Figure courtesy of Dr. Sam Jarvis, University of Nottingham and ©Royal Society of Chemistry (2012).

of practically any object would be possible via a nanoassembler- or nanofactory-based technology which relied for its operation on single molecule manipulation with atomic precision. One strategy for realising this concept is shown in the video below (although I stress that the video is an animation – *this type of technology does not exist and is unlikely to exist for, at best, a very long time*).



Although his ideas have been frequently disparaged - on sometimes less than scientific grounds - Drexler's molecular nanotechnology vision is worth exploring because, while the idea of a nanoassembler or nanofactory<sup>1</sup> is pure science fiction, the kernel of his concept, i.e. force-driven, computer-controlled chemistry with single atom precision, is demonstrably valid. We shall cover some of the latest developments in this area in later chapters.

Before moving on to consider the area known as “extreme nanotechnology” (i.e. the measurement and manipulation of matter with precision down to fractions of an atomic diameter), let's first consider just what is meant by the term *nanotechnology*.

---

<sup>1</sup>...or the type of 'nanogene' technology referred to in the quote from Dr. Who at the start of this chapter.

## 1.2 Defining nanoscience

Establishing a “universally agreed” definition of nanoscience (and/or nanotechnology) turns out to be remarkably difficult. Of course, the “nano” prefix refers to a nanometre (nm),  $10^{-9}$ m. Nanoscience, however, involves the study of structures and devices which can be much greater than 1 nm across. How then do we choose the upper (and, indeed, lower) size limits to distinguish nanoscience and nanotechnology from, say, microtechnology? Some have suggested that the upper “cut-off” for nanotechnology is 100 nm. This, however, is also fraught with difficulties because one could ask “Why not 101 nm or 99 nm?”.

Let’s first focus on some questions related to what a nanometre represents in terms of physical quantities and structures you’re perhaps familiar with from A-level and GCSE science.

**Q.** Which of the following is the closest to the wavelength of red light?

(A) 0.6 nm; (B) 6 nm; (C) 60 nm; (D) 600 nm; (E) 6,000 nm.

**Q.** Which of the following is closest to the size of a human red blood cell?

(A) 50,000 nm; (B) 5000 nm; (C) 50 nm; (D) 5 nm; (E) 0.5 nm

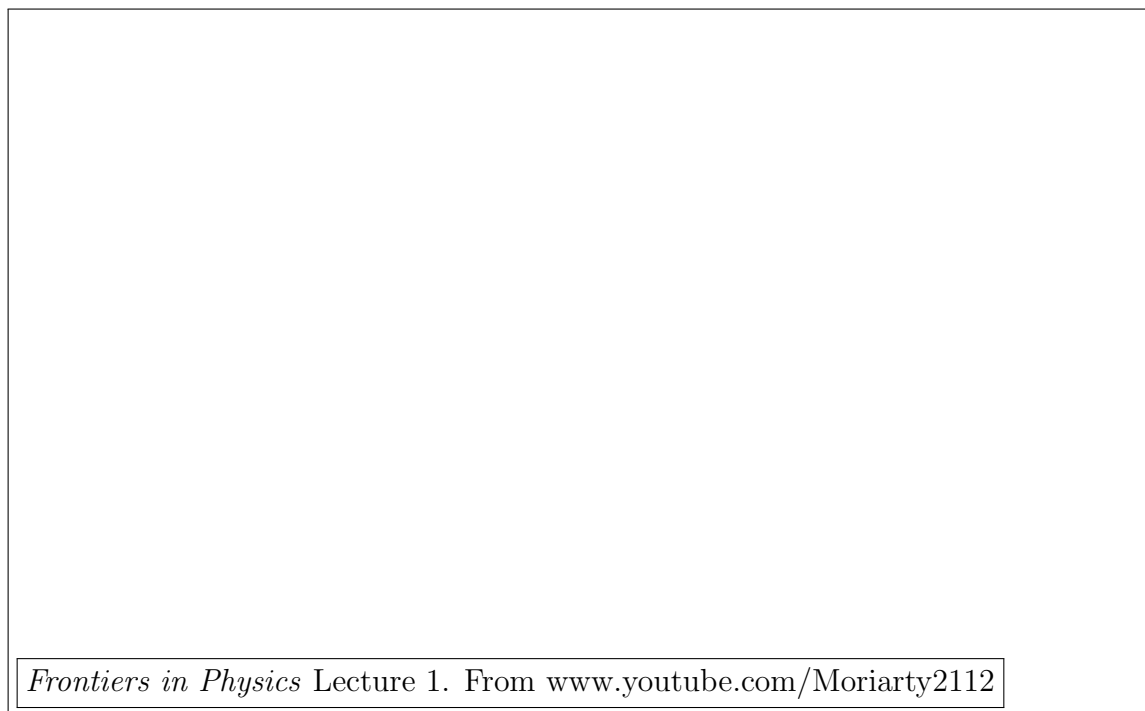
**Q.** The diameter of a gold atom is approximately (A) 3 nm; (B) 0.3 nm; (C) 0.03 nm; (D) 0.003 nm ?

**Q.** The wavelength of an electron (take the electron mass to be  $10^{-30}$ kg) travelling at  $10^6$  m/s is approximately:

(A) 0.01 nm; (B) 0.6 nm; (C) 20 nm; (D) 300 nm; or (E) 2112 nm?

(The speed of the electron is less than 1% of the speed of light so ignore relativistic effects).

You can find the answers to the questions on the previous page in the following video.



Instead of trying to define nanoscience in terms of particular length scales, the Royal Society, in an influential report[8], defined the field as follows:

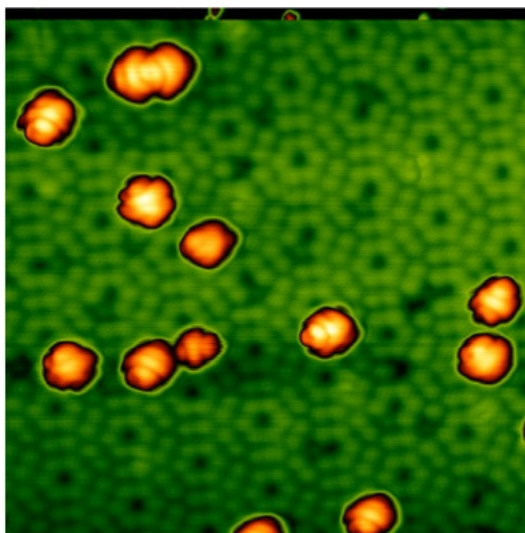
Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, **where properties differ significantly from those at a larger scale**. Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometre scale.

I have highlighted the phrase “where properties differ significantly from those at a larger scale” in bold because, although still somewhat vague, this cuts to the crux of what is special about nanoscience and nanotechnology. Simply by changing the size of an object (such as a small metal particle), one can radically change its properties. As we’ll cover later in this ebook, depending on the property in which we’re interested (e.g. electrical conductivity, optical absorption, mechanical strength, diffusivity etc...) the size-dependent change can be due to scaling laws which arise from classical physics or, when the size of the particle becomes comparable to the (de Broglie) wavelength of the electrons, quantum effects. As Jones

has pointed out[9], although the behaviour of matter at the nanoscale is often considered (particularly in popular science articles and books) as being solely due to quantum mechanical effects, one needs to be careful to distinguish when classical physics plays a role. We will cover both classical and quantum nanoscience in this book.

Although it is best to avoid definitions of nanoscience in terms of stringent length scale limits, a good “rule of thumb” to adopt is that if the structure or process in which you’re interested can’t be studied using conventional optical microscopy then it’s *nanoscopic* rather than microscopic. A technique at the very core of nanoscience - and which could be said to have given rise to the entire field - is scanning probe microscopy. This is a radically different form of microscopy as compared to that carried out using an optical microscope. In particular, scanning probe microscopes do not use lenses and do not suffer from the limitations which arise from lens-based instruments. Instead, a very sharp tip (atomically sharp for the highest resolution images) is moved back and forth across a surface, sensing some type of interaction (due to interatomic forces, or an electrical current, or electric or magnetic fields, etc...). The variation of this interaction is then mapped as a function of the position of the probe above the surface enabling atomic and molecular resolution images such as that shown in Fig. 1.2 to be acquired, where not only are the atoms of the substrate resolved but features arising from the orbital structure of the molecule can be distinguished. (We’ll discuss scanning probe microscopy in great detail in Chapters 4 and 5. In the meantime, you can find a short(-ish) introduction to the technique which I wrote for *Physics World* a few years ago [here](#)).





**Figure 1.2** – An SPM image of  $C_{60}$  molecules on silicon. Molecules are shaded in orange/yellow whereas the silicon is in green. The periodic pattern of the Si atoms is resolved, and many of the molecules show 'bands' due to their electronic structure. Image courtesy of A. Sweetman and P. Rahe, U. of Nottingham.

### 1.3 Size-dependence: An artificial periodic table?

A nugget of purest green? From Blackadder II. ©BBC Enterprises (1986).

E. Blackadder: *I don't want to be pedantic or anything but the colour of gold is gold. That's why it's called gold.*  
From “Money”, Episode 4 of Blackadder II (©BBC Enterprises, 1986).

The ability to dramatically modify the physical and chemical properties of a particle simply by changing its size has very important and exciting implications for the control of matter and the development of what have become known as “designer solids”. An idea that many nanoscientists have pursued is the development of an artificial periodic table where, instead of elements (and mixtures of elements), nanoparticles of different sizes (and shapes) are used to build up materials. The arrangements of electrons in these so-called nanostructured materials are then controlled by the properties of the nanoparticles (rather than by the chemical element(s) of which the nanoparticle is comprised).

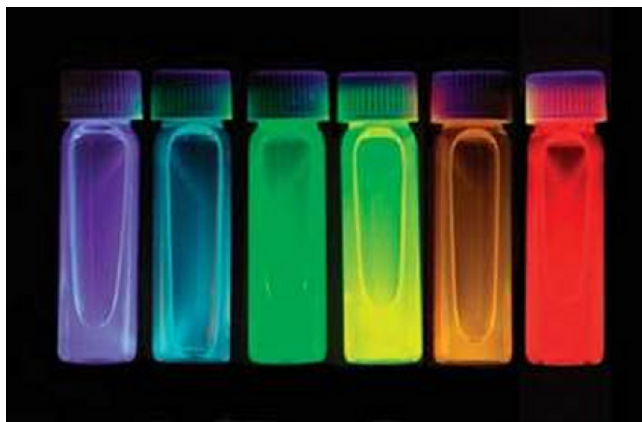
A particularly impressive example of the control of the electronic structure of a nanoparticle system simply by changing the size of the particles is shown in Fig. 1.3. Vials of CdSe nanoparticles (also called quantum dots, for reasons to be discussed in later chapters) illuminated by UV light emit different colours as a function of the size of the particles. The size range runs from 2 nm (blue) to 8 nm (red) from left to right. There is a lot of important quantum physics underpinning the colour changes seen in Fig. 1-3 and we shall explore this in some depth soon. For now, suffice it to say that by varying the size from 2 nm to 8 nm, the electronic structure of the nanoparticles changes (due to an effect known as quantum confinement). Changes in the electronic structure directly impact on the wavelengths of light emitted (and absorbed) by the particles. (See Chapter 4 for a discussion of how the size of a nanoparticle can affect its electronic, and thus optical, properties.).

By changing the size of the particle we vary the energy levels of the electrons (see Section 4.7). Once we can control the energies of the electrons we can *tune* the optical, chemical, and even magnetic properties of a nanoparticle. This coupling of the electronic, optical, and structural properties of nanoscale systems is something to which we will regularly return.

## 1.4 Reaching the atomic limit

*When we get to the very, very small world - say, circuits of seven atoms - we have a lot of new things that would happen that represent completely new opportunities for design. Atoms on a small scale behave like nothing on a large scale...*  
Richard P. Feynmann, from *There's Plenty of Room at the Bottom* (1959).

It's an unwritten rule that any discussion of nanoscience *must* cite Richard



**Figure 1.3** – Vials of CdSe nanoparticles illuminated by UV light. The size of the particles ranges from 2 nm on the left to 8 nm on the right. Note the change in the wavelength of light emitted by the particles. Photograph ©Felice Frankel. Taken from <http://www.laserfocusworld.com>

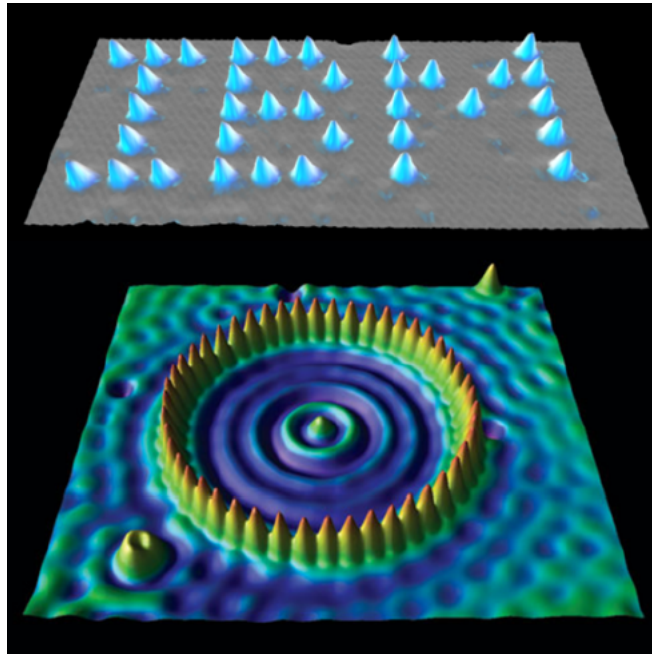
Feynmann’s “There’s Plenty of Room at the Bottom” talk to the American Physical Society in 1959. This is because Feynmann’s talk was both visionary and entertaining, and, for many scientists in the nanoscience and nanotechnology fields, he is considered the “godfather” of nanotech<sup>2</sup>. (There is, however, considerable debate about the precise origins of nanoscience and nanotechnology[10]).

In the quote from Feynmann above he stresses the wonderful new opportunities presented by an ability to form atomic-scale structures and circuits. Unfortunately Feynmann died in 1988 and, while he was fascinated by the development and capabilities of scanning probe microscopes, he did not live to see the pioneering atomic manipulation work of Don Eigler’s group at the IBM Almaden Laboratory in the early nineties (see Fig. 4). Using scanning probe microscopes, Eigler *et al.*<sup>3</sup> moved individual atoms on surfaces at very low temperatures ( $\sim 4$  K) and at very low pressures ( $\sim$  thirteen orders of magnitude below atmospheric pressure). The examples in Fig.1.4 show Xe atoms rearranged to spell out the IBM logo and Fe atoms manipulated to form a quantum corral [1, 11].

---

<sup>2</sup>I enthusiastically recommend all of Feynmann’s writings, including the three volume *Feynmann Lectures in Physics* set of undergraduate notes. While I would not recommend Feynmann’s lectures as a primary undergraduate text they are certainly very well worth reading as background material. The full text of “There’s Plenty of Room at the Bottom” is available in “The Pleasure of Finding Things Out” (Penguin Books (2000)). This book also contains, for example, Feynmann’s musings on the future of computing, the social and cultural value of science, and some memoirs of his work on the Manhattan Project. I guarantee that you will enjoy reading it!

<sup>3</sup>Note that “et al.” is the formal way of saying “and others” (from the Latin) in scientific papers and reports



**Figure 1.4** – Manipulation of single atoms using a scanning probe microscope. Upper image: Xe atoms on a nickel surface; lower image: corral comprising Fe atoms on copper.[1, 11].

It is also worth noting that Feynman’s dream of a “seven atom circuit” was realised (to some extent) in 2004 by Fölsch et al.[12] who measured the electronic properties of a chain of seven Cu atoms. We shall return to discuss the details of these fascinating and inspiring experiments in later chapters, but for now it’s worth enjoying the video below which shows the type of precision atomic control that’s possible with scanning probe microscopes operating at low temperatures and under ultrahigh vacuum conditions (where the pressure is comparable to that on the surface of the moon). The IBM research team who made this wonderful video describe it as the smallest stop-motion film ever made. Feynman would have loved the combination of the precise manipulation of matter with the plain *fun* of playing with atoms...



### 1.4.1 Atoms and bits: digital matter?

A rather interesting “back of an envelope” calculation we can do is to estimate the storage density possible if we could use each atom in, say,  $1 \text{ cm}^3$  of a solid to store a bit of information. We carry out this calculation in the *Frontiers* lectures each year. It’s worth attempting the calculation for yourself. You can check the video below for the answer (and the details of how to get to that answer.)

How many bits of information in 1 cm<sup>3</sup>? (*Frontiers* lecture 1)

### 1.4.2 A Matter Compiler?

Nanoscience and nanotechnology have a history of some controversy in both the scientific literature and in the popular press. A central figure in the debate has been Eric Drexler, who was introduced at the start of the chapter and who, in his books *Engines of Creation*[6] and *Nanosystems*[7], put forward what many consider an extreme and unrealistic vision of nanotechnology. Drexler adopted Feynmann's arguments regarding atomic scale engineering to argue that it would be possible to develop autonomous nanoassemblers, nano robots ("nanobots"), and nanofactories which would be able to "compile" matter so as "*to make virtually anything from common materials without labour, replacing smoking factories with systems as clean as forests*". This utopian vision has been dismissed time and time again as science fiction.

It is worth reading the debate between Drexler and the late Richard Smalley, a Nobel laureate and influential nanoscientist, in [Chemical and Engineering News from 2003](#)[13] to get an insight into just how acrimonious the dispute had become<sup>4</sup>.

---

<sup>4</sup>It is perhaps worth noting that while I agree to some extent with Smalley regarding the ultimate viability of nanobots and nanoassemblers, it is important to highlight that, as stated at the start of this chapter, a core element of Drexler's "vision" - the manipulation of single atoms and molecules using computer-controlled probes - is demonstrably valid. As we shall see in later lectures, although not quite a routine experimental technique just yet, an increasing number of

There are a number of other debates available online via important nanotechnology blogs [14, 15] which, although almost a decade old, flag up some of the key technical issues associated with computer-controlled manipulation of matter.

---

research groups (including the Nanoscience Group here at Nottingham) have demonstrated the capability to move atoms solely via short-range chemical forces. There remains significant scope for computer-controlled assembly of matter. Drexler's claim, however, that it will be possible to make "virtually anything" is clearly bunkum for the reasons outlined in Ref.[14].

# Chapter 2

## Force and Potential at the Nanoscale

*Magnetism is one of the six fundamental forces of the Universe, with the other five being Gravity, Duct Tape, Whining, Remote Control, and The Force That Pulls Dogs Toward The Groins Of Strangers.*

Dave Barry (1947 - )

### 2.1 Fundamental forces

Physicists classify forces into four fundamental types:

- Gravitational interactions;
- The strong force (responsible for intranuclear interactions);
- The weak force (changes one flavour of quark into another);
- Electromagnetic interactions.

At the nanoscale, we need only consider electromagnetic forces as these control the interactions between atoms, molecules, and nanoparticles. (We will, however, spend some time in the following sections considering how forces at the nanoscale compare with the gravitational force). Electromagnetic forces not only hold atoms together but determine just how they arrange to form molecules, clusters, and

---

PowerPoint slides associated with this chapter are available [here](#) and [here](#)



nanoparticles. It is worth doing a "back of an envelope" calculation to compare the Coulomb force for two protons with the gravitational force between them. You'll find that the Coulomb force not only dominates the gravitational interaction, it *overwhelms* it.

## 2.2 Forces and potentials

Before considering the details of interactions at the nanometre scale, let's spend a little time revising some fundamental principles related to force and energy. There is a very simple and powerful relationship between force,  $F(x)$ , and potential energy,  $U(x)$ :

$$F(x) = -\frac{dU}{dx} \quad (2.1)$$

In words, *force is the negative gradient of potential energy*<sup>1</sup>. The negative sign arises because it dictates the direction of the force. We'll consider this statement in the context of a force with which you are very familiar - the gravitational force - before moving on (and down) to the microscopic and nanoscopic levels. (As discussed in the lecture, it's important to carefully take into account the positive/negative sign in the expression for a force. See sections 11.5 and 11.6 of *Physics for Scientists and Engineers*, RD Knight, Third Edition).

**Q.** The gravitational potential,  $F_g(r)$  between two objects depends on their separation,  $r$ , as follows:

(A)  $F_g(r) \propto 1/r$ ; (B)  $F_g(r) \propto \log(r)$ ; (C)  $F_g(r) \propto \exp(r^2)$ ; or (D)  $F_g(r) \propto 1/r^2$

**Q.** If we take  $F_g(r) = Gm_1m_2/r^2$ , the gravitational potential (as defined by Equation 2.1 above) is given by:

(A)  $U_g = -2Gm_1m_2/r^3$ ; (B)  $U_g = 2Gm_1m_2/r$ ; (C)  $U_g = Gm_1m_2/r$ ; or  
(D)  $U_g = -Gm_1m_2/r$ ;

---

<sup>1</sup>For Eqn 2.1 I am assuming a very simple one-dimensional potential which varies only in the  $x$  direction. However, the statement that the force is the gradient of the potential is general and is equally valid in three spatial dimensions. Although we'll stick to one-dimensional potentials throughout this book (and for the Nanoscience component of *Frontiers*), in Year 2 you'll learn about vector calculus and the mathematical *grad* operator, denoted as  $\nabla$

During the lectures I sketched a number of graphs and asked which best represented the dependence of  $U_g$  on  $r$ . It's worth making sure that you can sketch the appropriate graph. If you get stuck, you'll find the answer in Knight, Section 13.5.

## 2.3 Interatomic forces

Richard Feynman once posed the following question [see the *Feynman Lectures in Physics*, Vol I (1963)]:

*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?*

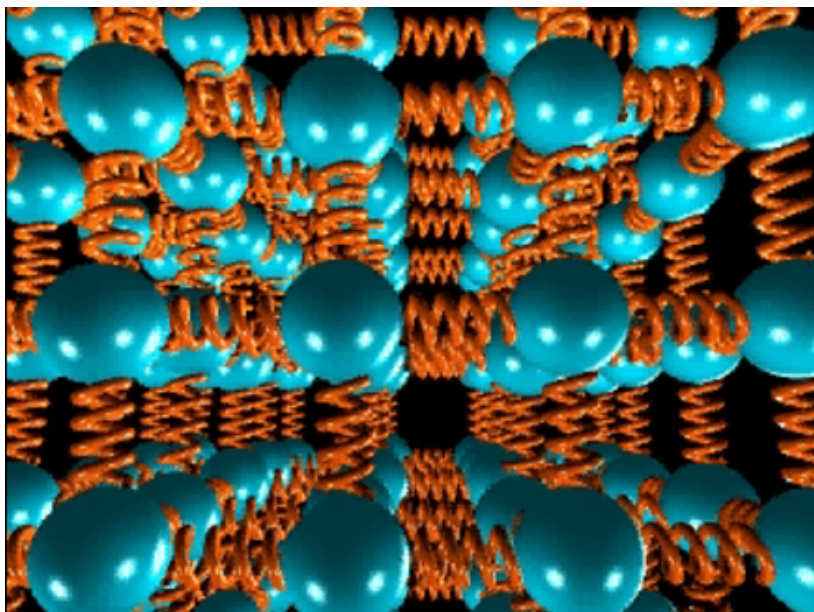
What was Feynmann's answer? It wasn't based on Newton's laws, relativity, or the principles of quantum mechanics (well, not explicitly). Rather, he suggested the following:

*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.*

This is a wonderfully concise and elegant statement. We need to ask, however, just why it is atoms attract each other "when they are a little distance apart" and why they repel when they are "squeezed into one another". The answers to these questions are at the very core of nanoscience.

## 2.4 Modelling interatomic forces

Consider a solid such as silicon or diamond. The atoms in the crystal are held in place via strong interatomic bonds. How might we model those bonding interactions? The approach that Einstein adopted at the start of the 20<sup>th</sup> century was to consider the atoms as balls and the interatomic bonds as springs (see the video below - you may need to click on it to (kick-)start it). This simple picture can - under the appropriate circumstances - give us a remarkable degree of insight into the behaviour of matter on the atomic, molecular, and nanometre scales. Treating interatomic forces as springs (with the bond strength proportional to the spring constant) leads us naturally to the subject of simple harmonic motion. We will see that this particular topic pops up time and time again throughout the module.



**Figure 2.1** – Still from a video animation showing a solid represented by balls and springs. Taken from the downloadable material available for *Matter and Interactions*, Ruth Chabay and Bruce Sherwood, John Wiley & Sons, Inc. (2002)

Let’s first revisit some A-level physics related to simple harmonic oscillators:

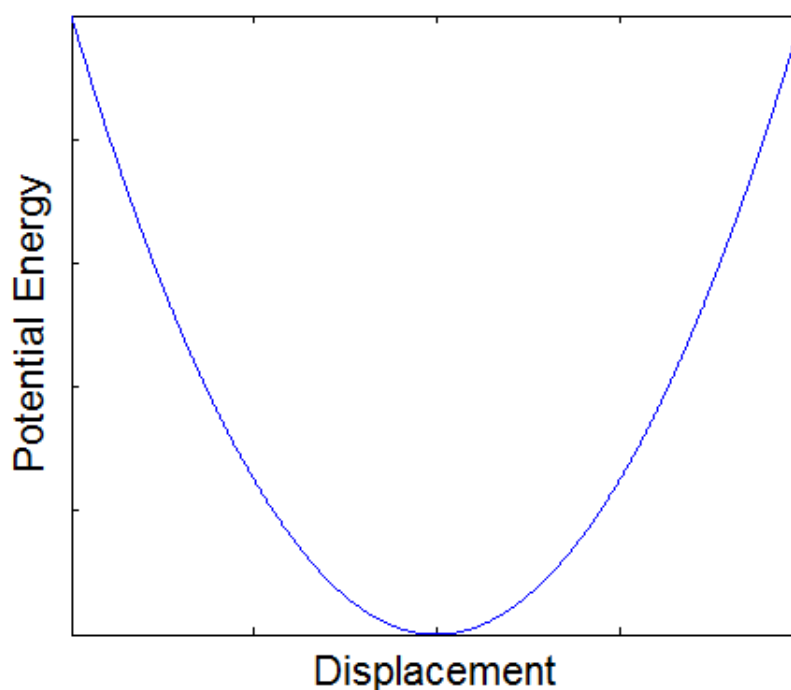
**Q.** Assuming simple harmonic motion, the restoring force exerted by a spring on a ball depends: **(A)** linearly; **(B)** quadratically; **(C)** exponentially; **(D)** logarithmically on the displacement.

**Q.** If the force is given by  $F = -kx$  (where  $k$  is the spring constant), the potential energy is given by: **(A)**  $kx^{1/2}$ , **(B)**  $k/x^2$ , **(C)**  $\cos(kx)$ , **(D)** None of these.

The answer to the preceding question is “None of these”. Instead, for a simple harmonic oscillator the potential depends *parabolically* on the displacement. That is,

$$U(x) = \frac{1}{2}kx^2 \quad (2.2)$$

where  $x$  is the displacement from the equilibrium position and  $k$  is the spring constant. We say that the potential is “harmonic” (see Fig. 2.2).



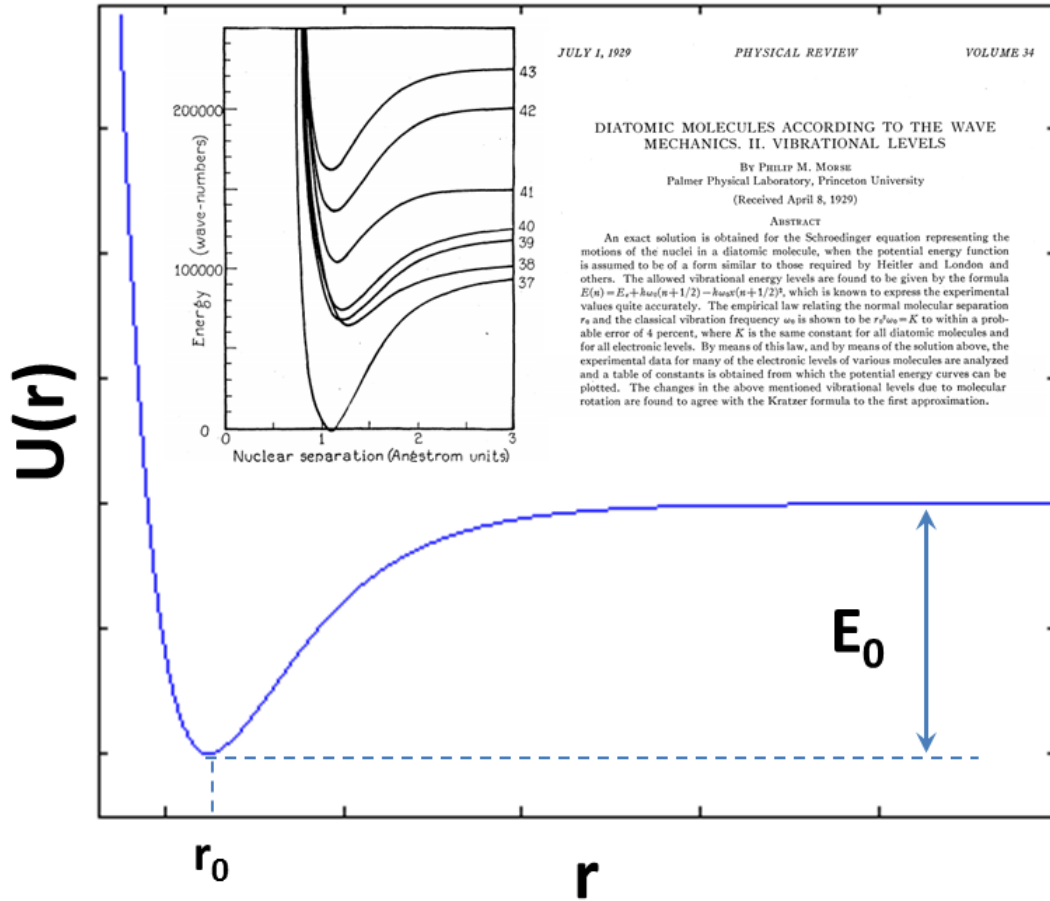
**Figure 2.2** – Parabolic potential energy curve associated with a simple harmonic oscillator.

Given that I have suggested above that we can approximate interatomic interactions with a simple ball-and-spring model, we need to consider carefully whether a harmonic potential of the type shown in Fig. 2.2 is indeed appropriate to model the forces between atoms in a solid. Consider what happens to  $U$  as the interatomic separation is increased. In the limit that the separation is infinite, what can we say about the potential energy? Does this make sense? The potential must go to zero as we increase the separation between the atoms to the point where they do not interact.

We need a function that will fall off smoothly to zero as the interatomic separation is increased. In addition, the potential energy function should increase for interatomic separations which are smaller than the equilibrium separation. That is, it costs energy to push two atoms together so they are separated by a distance smaller than the natural bond length. (This is fundamentally due to the Pauli exclusion principle which prohibits electrons from “collapsing” into the same quantum state - more on this principle soon.) A function which is commonly used to approximate the potential energy variation for two neutral atoms is the Morse curve:

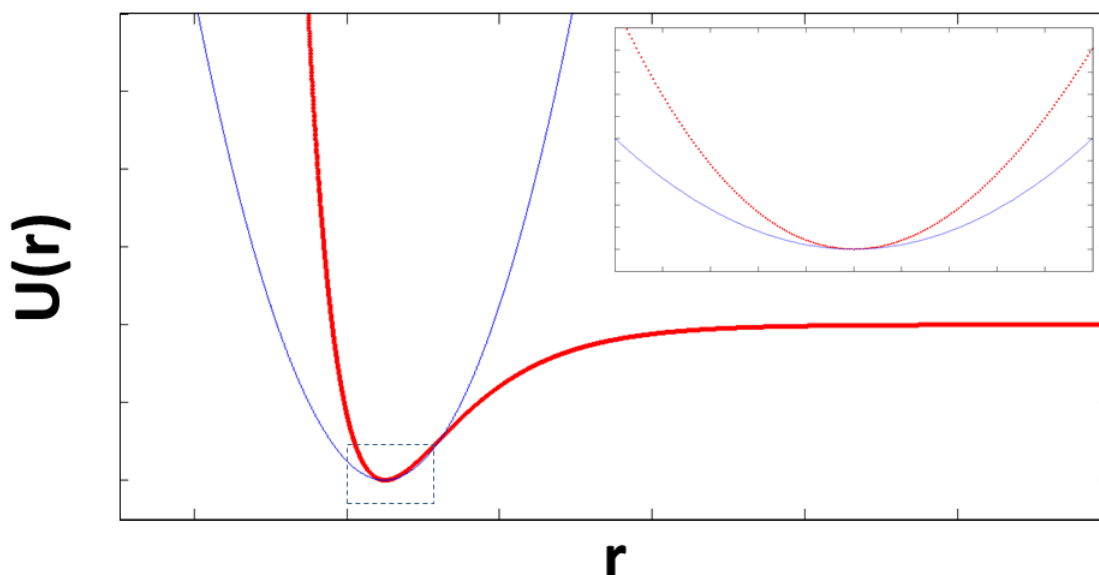
$$U = E_0[1 - \exp(-\alpha(r - r_0))]^2 - E_0 \quad (2.3)$$

This function is sketched in Fig. 2.3. Note that the expression in Equation 2.3 describes a *potential well* whose depth is given by  $E_0$  and where the position of the minimum is given by  $r_0$ , the equilibrium separation of the atoms.



**Figure 2.3** – Morse potential commonly used to model the potential energy of interaction of two atoms. The insets show (left) a number of Morse curves for nitrogen calculated by Morse himself in 1929, and (right) the abstract from Morse’s 1929 paper where he first described the potential [Phys. Rev. 34 57 (1929)].

Why is it that we can use a simple harmonic oscillator (SHO) model (Fig. 2.2) to treat interatomic interactions when it's clear that the SHO model breaks down as we increase the interatomic separation (compare Fig. 2.2 and Fig. 2.3)? The key point is that if we are interested in only very small displacements from the equilibrium separation (e.g. atoms vibrating in a solid at temperatures much, much smaller than the melting temperature) then, as shown in Fig. 2.4, the simple harmonic oscillator model is a good *approximation* to the potential energy curve. For larger separations, the SHO model fails because the true potential is *anharmonic*.



**Figure 2.4** – Comparison of simple harmonic potential (blue line) to the Morse potential (red line). The inset shows a magnified region of the graph about a small range of values close to the equilibrium separation. For very small separations, the harmonic oscillator potential arising from the simple ball-and-spring model is a good approximation to the Morse potential. (Note that a different choice for the spring constant for the simple harmonic potential could be used to produce better agreement over a larger, but still relatively small, range of values in this case.)

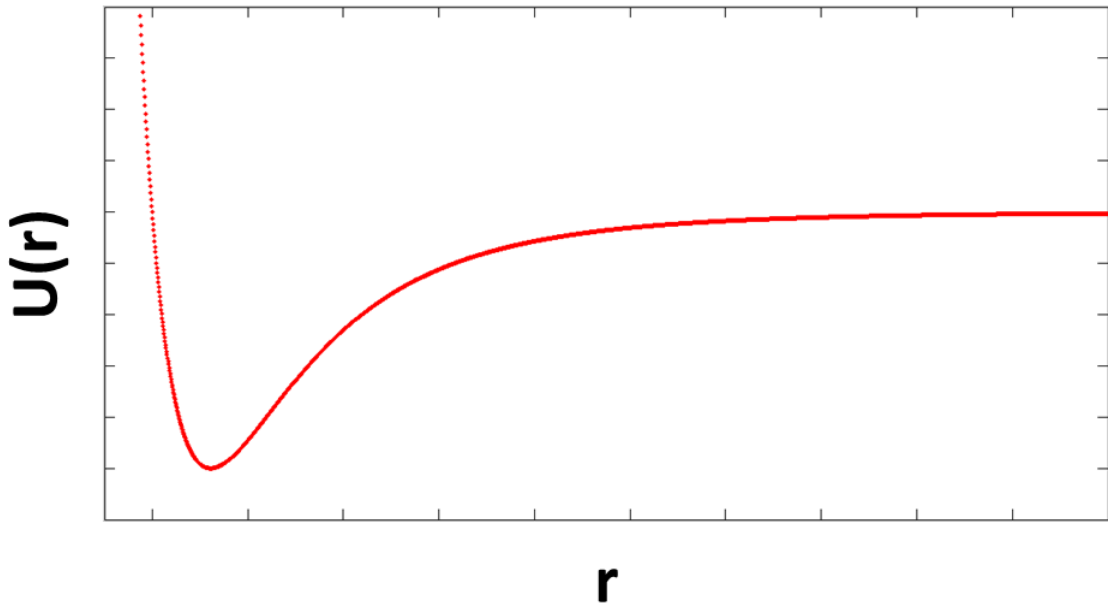
## 2.5 The Lennard-Jones potential

Another choice of function to represent interatomic interactions is the Lennard-Jones potential (Fig. 4). The Lennard-Jones potential has qualitatively the same general shape as the Morse potential but the functional form is quite different, being based around power law, rather than exponential, functions:

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \quad (2.4)$$

where  $r$  is the distance between the atoms,  $\epsilon$  is the depth of the potential well, and  $\sigma$  is a parameter which controls the shape of the function.

The  $r^{-6}$  term in the Lennard-Jones potential models the attractive forces between the atoms whereas the  $r^{-12}$  term accounts for the repulsive interactions. Later in this chapter we shall discuss the physical origin of these two terms.



**Figure 2.5** – Lennard-Jones potential for two atoms.

## 2.6 Worked problem: Interacting hydrogen atoms

**P2.1** The interaction of two hydrogen atoms can be described using the Morse potential,  $U_{Morse}(r)$ :

$$U_{Morse}(r) = U_0 [1 - \exp(-\alpha(r - r_0))]^2$$

where the parameters  $U_0$ ,  $\alpha$  and  $r_0$  are selected so as to best model interatomic interactions. ( $U_0$  is the energy required to break the  $H_2$  bond, dissociating the molecule into separate atoms)<sup>a</sup>.

(i) Show that  $r_0$  is the equilibrium separation **{3}**.

(ii) For the hydrogen molecule, the values of  $U_0$  and  $\alpha$  are 4.79 and 19.3, respectively. The units of  $U_0$  are eV. If the units of  $r$  are nm, what are the units of  $\alpha$ ? **{2}**

(iii) Show that near equilibrium, the hydrogen-hydrogen bond can be described as a spring of stiffness 571 N/m. **{6}**

(iv) In quantum mechanics the energy of a simple harmonic oscillator is quantized such that  $E_n = (n + 1/2)\hbar\omega$ . Assuming that the hydrogen molecule can be accurately described as an harmonic oscillator with an angular frequency,  $\omega_0$  of  $8.3 \times 10^{14}$  rad/s, at what vibrational quantum number will the molecule dissociate?

---

<sup>a</sup>A version of this question appeared on the 2012-2013 *Frontiers in Physics* exam paper. The numbers in braces represent the marks allocated for each question.

(i) At equilibrium,

$$F = -\frac{dU}{dr} = 0$$

$$\frac{dU}{dr} = 2U_0 [1 - \exp(-\alpha(r - r_0))] \alpha \exp(-\alpha(r - r_0))$$

$$\Rightarrow dU/dr = 0 \text{ when } r \rightarrow \infty \text{ and when } r = r_0$$

(ii) Exponent must be dimensionless. Therefore  $\alpha$  has units  $\text{nm}^{-1}$

(iii) Near equilibrium  $\Rightarrow (r - r_0)$  is small. Assume  $\alpha(r - r_0) \ll 1$

$$\Rightarrow U_{Morse} \sim U_0 [1 - (1 - \alpha(r - r_0))]^2$$



Let  $r - r_0 = x$  (displacement)

$$\begin{aligned}\Rightarrow U_{Morse}(x) &\sim U_0(\alpha x)^2 \\ \Rightarrow U_{Morse} &\sim U_0\alpha^2 x^2\end{aligned}$$

This is a parabolic dependence of potential energy on displacement – so an harmonic oscillator potential. Equate the approximate expression for  $U_{Morse}$  above to  $U = \frac{1}{2}kx^2$ ,

$$\begin{aligned}\frac{1}{2}k &= U_0\alpha^2 \\ \Rightarrow k &= 2U_0\alpha^2\end{aligned}$$

Plugging in the values for  $U_0$  and  $\alpha$ , we find that  $k = 571\text{N/m}$

$$\text{(iv)} \quad \omega = 8.3 \times 10^{14} \text{ rad/s} \Rightarrow \hbar\omega = 0.54 \text{ eV}$$

$$\begin{aligned}E_n &= (n + \frac{1}{2})\hbar\omega \\ \Rightarrow n &= \frac{E_{vib}}{\hbar\omega} - \frac{1}{2}\end{aligned}$$

$$\Rightarrow n = 8.3$$

This means that the molecule will dissociate at  $n = 9$ .

## 2.7 Measuring interatomic & intermolecular forces

Over the last decade or so, it has become possible to measure the potential between two atoms or two molecules using an atomic force microscope (AFM). We'll cover the operating principles of the AFM in quite some detail in Chapter 5 (it's a remarkable instrument at the very heart of nanoscience) but, for now, it's enough to say that an AFM is capable of measuring the gradient of the force between two atoms - one at a sample surface, and the other at the end of an atomically sharp tip which is used as a probe - as their separation is varied. From this force gradient we can, by integration, determine the force, and by integrating once more, the potential energy. (Recall Equation 2.1). Thus, an AFM allows us to measure potential-vs-separation curves which we can compare to the theoretical Morse and Lennard-Jones potentials (amongst others).

The video below briefly describes just how the AFM works; how it can be used to image atoms, molecules, and bonds; and how the instrument can be exploited to measure interatomic and intermolecular forces. (Please excuse the truly awful guitar playing in the middle of the video, however...)

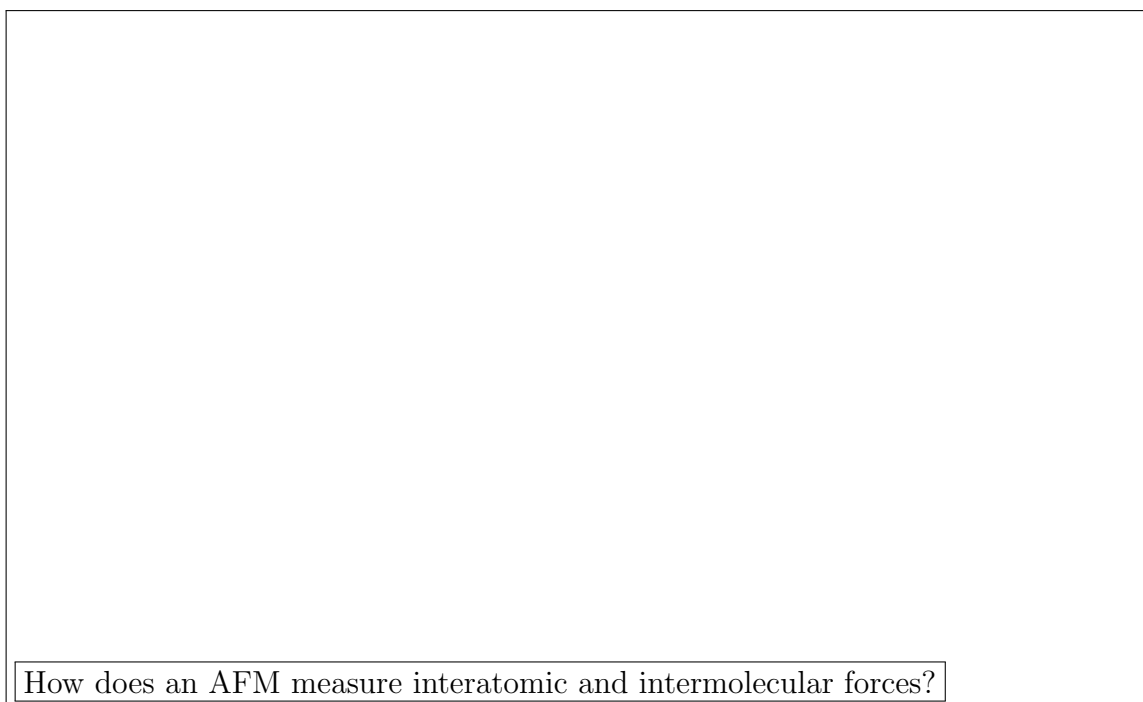
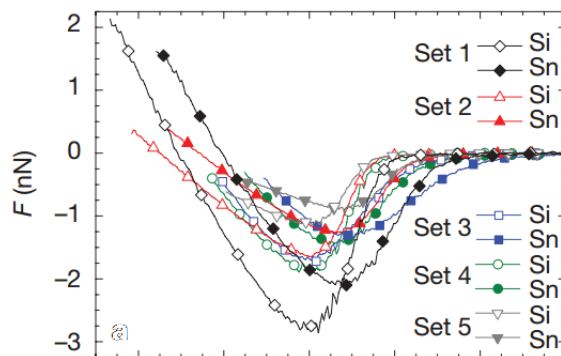


Fig. 2.6 shows force-separation curves for a number of different combinations of atoms, taken from the work (published in 2007) of Oscar Custance and co-workers at Osaka University in Japan [Y. Sugimoto et al., *Nature* **446** 64 (2007)]. You need not be concerned with the details of these curves. The important thing to note is that the shape of the curves is similar to that of the Morse and Lennard-Jones potentials. (Note, however, that Fig. 2.6 shows force vs. separation, rather than potential energy vs. separation graphs. That the force vs separation curves should have a similar overall shape to the potential vs separation curves is not unexpected: the Morse potential is based around an exponential function, and the Lennard-Jones potential comprises two inverse power law functions with high values of the powers.)

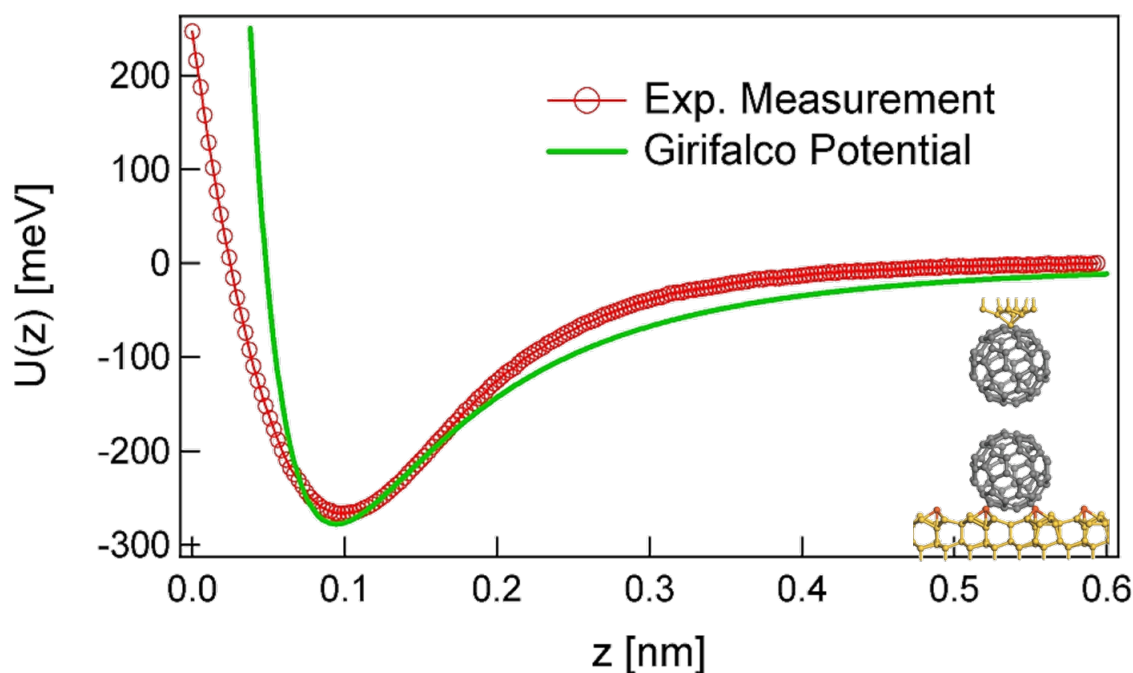


**Figure 2.6** – Force vs separation curves for two atoms, measured using an atomic force microscope. In each case, the force between an atom at the surface of a sample and an atom at the apex of a tip has been derived from experimental measurements. Two different types of atom at the surface have been studied: tin (Sn) and silicon (Si). A variety of different tips (denoted by Set 1 -5) have been used, giving rise to the range of force vs separation curves seen in the figure. Data taken from Y. Sugimoto et al., *Nature* **446** 64 (2007). ©Nature Publishing Group (2007).

You can watch (and listen to) a measurement like that shown in Fig. 2.6 being made in the video below.

Measuring an interatomic force curve using AFM.

In addition to being able to measure interatomic interactions, the AFM is also increasingly being exploited to probe intermolecular interactions. To do this, a molecule from the surface can first be transferred to the tip (this is easier said than done!). Then another molecule adsorbed on the surface is located and the separation between the molecule at the tip, and the molecule at the surface adjusted in order to determine the intermolecular force and potential. An example of the data which can result from probing intermolecular interactions in this way is shown in Fig. 2.7, taken from the work of the [Nanoscience group here in Nottingham](#). Note once again the similarity of the potential energy curve to the Morse and Lennard-Jones potentials shown in Figs. 2.3 and 2.5 respectively. The depth of the potential well (in this case, approximately 0.3 eV) is a measure of the strength of the intermolecular interaction.



**Figure 2.7** – Experimental potential energy curve for two  $C_{60}$  molecules (red circles) compared to a theoretical potential for the  $C_{60}$ - $C_{60}$  system (green line). The experimental measurements were made by first attaching a  $C_{60}$  molecule to the tip of an atomic force microscope, and then this tip-adsorbed  $C_{60}$  molecule was approached to another  $C_{60}$  molecule on the surface of a silicon sample. The inset shows the experimental geometry. The  $z$  value on the graph represents the displacement of the tip molecule. Data from C. Chiutu et al., *Physical Review Letters* **108** 268302 (2012)

## 2.8 The origin of interatomic and intermolecular forces

The Morse and Lennard-Jones potentials discussed in the preceding sections describe the variation of the potential energy of interaction of two neutral atoms (or molecules/nanoparticles) as a function of their separation. It's worth taking a moment to sketch the Lennard-Jones potential as a function of  $r$ , the interatomic/intermolecular separation (see if you can do this from memory). Label the position of the minimum in the potential as  $r_0$ .

We can break the potential energy curve up into two regimes:

- $r < r_0$  In this regime the atom-atom interaction is increasingly dominated by repulsive forces (remember that the force is given by the negative gradient of the potential). The fundamental origin of this repulsion is the Pauli exclusion principle. This principle - which lies at the heart of the behaviour of all matter - states that no two electrons can exist in precisely the same quantum state. You will study the Pauli exclusion principle in the context of quantum statistics next year but, for now, the aspect of the Pauli exclusion principle that is most important when considering the interaction of atoms and molecules is simply that if an electron is in a given state, it excludes all other electrons. That is, the increasing overlap of electron orbitals as two atoms are pushed past their equilibrium separation leads to a strong repulsive force, which, in the Lennard-Jones potential is described by a steeply rising  $\frac{1}{r^{12}}$  function. Precisely the same fundamental quantum mechanics prevents neutron stars and white dwarf stars from collapsing<sup>2</sup>.
- $r > r_0$  In this regime the attractive force dominates. This attractive force can arise from bond formation (e.g. covalent or ionic bonding, as described below) but even in the absence of chemical bond formation there is a physical attraction between atoms (or molecules or nanoparticles): the *van der Waals* force.

---

<sup>2</sup>For those of you who may have heard of Bose-Einstein condensates, the Pauli exclusion principle often doesn't hold for the atom clouds studied in those experiments. Those atoms can be prepared as *bosons* - particles which, unlike electrons, have integer spin. Electrons instead have a spin of  $\pm\frac{1}{2}$ . Do not be too concerned for now with what is meant by spin - it is one of four quantum mechanical parameters (quantum numbers) which describe the state of an electron. These quantum numbers are described in Chapter 42 of Knight

## 2.9 van der Waals interactions

The van der Waals force arises from interactions between atoms or molecules which do not involve the sharing or transfer of electrons and is due to the interaction of dipoles. A dipole is a separation of positive and negative charge and can be of three types: permanent, instantaneous, and induced. A permanent dipole exists in molecules such as HCl. Two HCl molecules can interact via a dipole-dipole force where the positive “end” of one molecule is attracted to the negative “end” of another. We say that the molecule is *polar*. A dipole can also be *induced* in an atom or molecule which does not originally have a dipole moment (i.e. a non-polar molecule). The electrons in the non-polar molecule feel the influence of the dipole of the polar molecule, leading to an asymmetric charge distribution, i.e. a dipole.

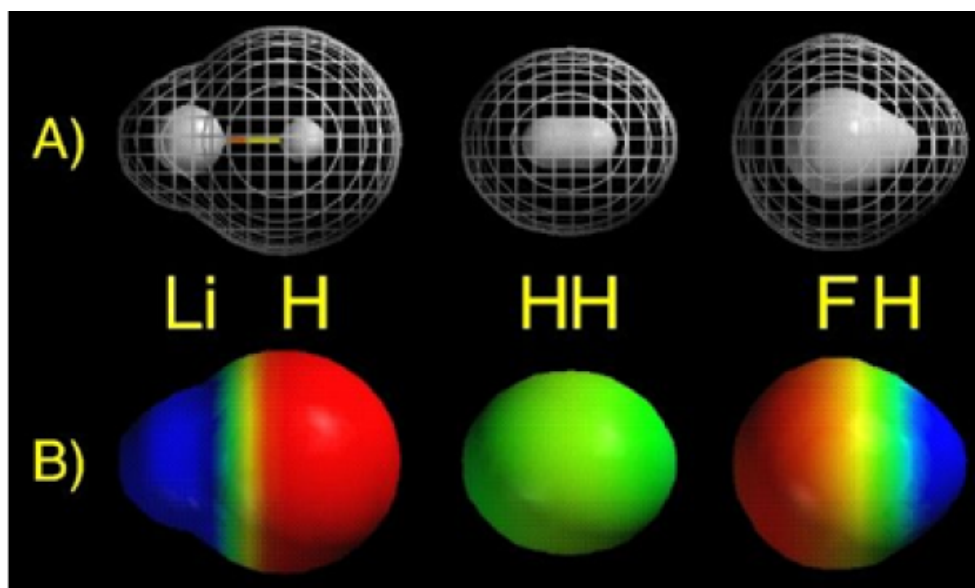
It is also possible to have *instantaneous* dipoles due to rapidly changing distributions (fluctuations) of electron charge around a non-polar atom or molecule. At a given instant of time, a non-symmetric distribution of charge produces a dipole on a given atom. As described above, this dipole induces a dipole on another atom. These two dipoles then attract each other. The force that arises from this interaction of instantaneous dipoles is known both as the van der Waals force and, slightly more rigorously, as the London dispersion force. The  $\frac{1}{r^6}$  component of the Lennard-Jones potential models the van der Waals force due to fluctuating dipoles.

## 2.10 Beyond physical attraction

Although van der Waals interactions are not chemical bonds, they can still give rise to quite strong forces at the nanometre and sub-nanometre scales. This makes objects at the nanoscale very “sticky” - atoms and molecules will stick to surfaces and to each other due to the ubiquitous van der Waals force (and we will return to this topic in the next chapter). Chemical bonding interactions are, however, even stronger. To highlight this distinction between physical and chemical adsorption at surfaces, the terms *physisorption* (due to physical van der Waals forces) and *chemisorption* (due to chemical bonding) are used. van der Waals bonding is extremely important in self-assembly, a subject discussed in detail in the Year 2 and Year 3 nanoscience modules.

There are two major classes of chemical bonds of interest for now: covalent bonding (involving electron orbital overlap and electron sharing) and ionic bonding (charge transfer). It is important not to think that there is a well-defined division between these two classes and that all bonds are rigidly one type or another. A pure covalent and a pure ionic bond represent extremes of bonding. In many cases there is a combination of both electron sharing and charge transfer. This is illustrated

nicely by the charge distributions shown in Fig. 2.8 for a LiH, a H<sub>2</sub>, and an HF molecule (taken from the organic chemistry website of Texas A & M University). The upper part of the figure (Fig. 1(A)) shows meshes which indicate the variation in electron density across the molecule at a distance quite far from the nuclei. Note how the size of the electron orbital above hydrogen is much greater for the LiH molecule as compared to the HF molecule. Lithium donates electronic charge to hydrogen, whereas fluorine (a more electronegative element) takes electronic charge from hydrogen. In the H<sub>2</sub> molecule there is an equal sharing of electrons. The solid surfaces inside the meshes show how the electron charge is distributed at a distance much closer to the nuclei. For LiH, there is very little charge density between the nuclei - an indication of a strongly ionic bond. H<sub>2</sub> and HF, however, have a significant amount of electron density between the nuclei, indicating covalent character. The plots shown in Fig. 1(B) (which are in colour in the online version of the notes) represent the variation in the electrostatic potential across the molecule. Red regions are “electron rich” and blue regions are “electron poor”.



**Figure 2.8** – Electron charge distributions for three molecules: LiH, H<sub>2</sub>, and HF. Figure taken from <http://www.chem.tamu.edu/organic/>

## 2.11 Tutorial video: Interatomic potentials – when do atoms touch?

Interatomic potentials: When do atoms touch?



## 2.12 Problems

**P2.1** The potential energy of interaction,  $U$ , between two nanoparticles as a function of their separation,  $r$ , can be modelled using the Lennard-Jones function,

$$U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2.5)$$

where  $\epsilon$  is the depth of the potential well and  $\sigma$  is a parameter which describes the range of the potential. In this case,  $\epsilon = 4.80 \times 10^{-21}$  J and  $\sigma = 2.68$  nm.

- (a) Determine an expression for  $F(r)$ , the force between the nanoparticles as a function of their separation **{3}** and hence calculate the equilibrium separation of the nanoparticles **{3}**.
- (b) What is the maximum attractive force of interaction between the nanoparticles and at what separation does it occur? **{6}**
- (c) For small displacements about the minimum of  $U(r)$  we can use a simple harmonic approximation for the potential energy vs separation function.
  - (i) Perform a Taylor series expansion to second order of  $U(r)$  about  $r_0$ , the equilibrium separation of the nanoparticles. **{5}**
  - (ii) Show that your Taylor series expansion can be written in the form  $U = \frac{1}{2}kx^2 + \text{constant}$  where  $k$  is a spring constant and  $x$  is the displacement from the equilibrium separation. **{4}**
  - (iii) Hence calculate the value of the “spring constant” associated with the interaction of the two nanoparticles. **{4}**

See also Problem P5.4 at the end of Chapter 5.

## Chapter 3

# Sticky, Goopy, and Bumpy: Scaling Down

*Any intelligent fool can make things bigger, more complex, and more violent. It takes a touch of genius – and a lot of courage – to move in the opposite direction.*

Quote attributed to Albert Einstein  
(possibly apocryphally, like quite a few other Einstein quotes...)

### 3.1 A Fantastic Voyage: Physics in a scaled-down world

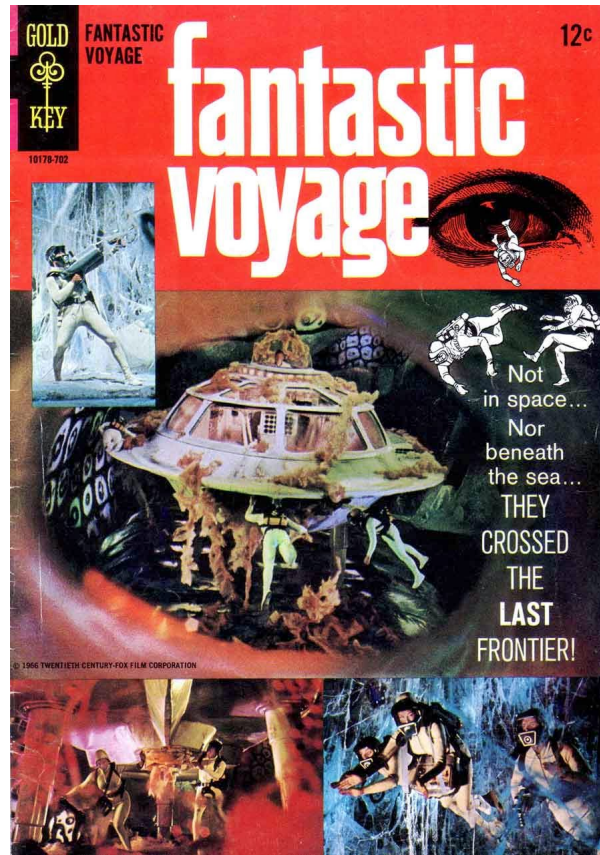
In the film “Fantastic Voyage” (released in 1966 - browse YouTube to find the trailer), the U.S. and the Soviet Union have developed technology that allows macroscopic objects (e.g. people and submarines) to be miniaturized<sup>1</sup>. An assassination attempt on one of the scientists working on this process leaves him comatose with a life-threatening blood clot in his brain. A team of five board a submarine (the *Proteus*) which is then shrunk to one micrometre in size and injected into the scientist. The crew of the *Proteus* are then expected to travel through the bloodstream, find the blood clot, and destroy it using a laser.

Although there are a number of not-entirely-insignificant holes in the plot (and in the science underlying the plot) the premise of *Fantastic Voyage* makes for a

---

PowerPoint slides associated with this chapter are available [here](#) and [here](#)

<sup>1</sup>The “Fantastic Voyage” discussion in this section is based very heavily on Chapter 4 of “Soft Machines”, RAL Jones, Oxford University Press (2004). I strongly recommend this book as a readable and entertaining introduction to nanoscience and nanotechnology.



**Figure 3.1** – Front cover of a *Fantastic Voyage* comic from 1966 (re-released the same year as the film of the same name). Taken from <http://farfuturehorizons.blogspot.co.uk/2014/03/fantastic-voyage.html>.

very useful “gedanken” experiment. What differences in the behaviour of everyday objects might we expect if we scale them down to the micron, sub-micron, and nanometre scales? The technology and engineering with which we are familiar is based on physical principles which are important in the macroscopic world. At the “nanoscopic” level, different physics becomes important. This is not to say, as is regularly suggested in popular science accounts of nanotechnological developments, that the conventional laws of physics fail at the nanoscale and that this requires the adoption of a revolutionary new set of concepts. Rather, it is that different aspects of known physics become important; our experience and intuition, derived from the behaviour of objects in the macroscopic world, are generally not valid at the nanometre level.

## 3.2 Scaling

A very helpful way of highlighting differences between the macroworld and the nanoworld is to consider scaling laws. A scaling law is simply a statement of how a property of an object or a force varies as a function of the size of the object. Moreover, scaling laws provide a simple method of comparing the behaviour (or performance) of a system at two different length scales.

Let's consider an object which has a length ("linear dimension")  $L$ . This means that if we change  $L$ , the surface area of the object,  $S$ , varies as  $L^2$ , and the volume varies as  $L^3$ . In other words,

$$S \sim L^2 \quad (3.1)$$

$$V \sim L^3 \quad (3.2)$$

Let's try a couple of questions:

**Q.** How does mass scale with  $L$ ?  
**(A)**  $m \sim L^2$ ; **(B)**  $m \sim L$ ; **(C)**  $m \sim L^3$ ; **(D)**  $m \sim L^{1/2}$

**Q.** How does pressure scale with  $L$ ?  
**(A)**  $P \sim L$ ; **(B)**  $P \sim L^{-1}$ ; **(C)**  $P \sim L^2$ ; **(D)**  $P \sim L^3$

The van der Waals force discussed in the previous section scales with the area of the contact. That is, if we have two objects of linear dimension  $L$ , the van der Waals force,  $F_{vdW}$ , between them will scale as:

$$F_{vdW} \sim L^2. \quad (3.3)$$

This means that

$$F_{vdW}/F_g \sim L^{-1} \quad (3.4)$$

From this simple analysis we have uncovered an important result: as we make  $L$  smaller, the quantity  $F_{vdW}/F_g$  gets larger. In other words, at small values of  $L$ , the adhesion force between two surfaces due to the van der Waals interaction dominates gravity. Gravitation may be neglected at small values of  $L$ . It's sticky in

the nanoworld! The Proteus would very quickly get covered in proteins (unless the surfaces were engineered somehow to prevent adhesion of unwanted molecules<sup>2</sup>).

### 3.3 Fluid mechanics at the nanoscale

Let's assume that we can engineer around the problem of the surface of the Proteus becoming "clogged up" with proteins. How effectively would a scaled down version of a submarine travel through water? During one of the lectures you saw an impressive example of a "belly flop" into a swimming pool. The reason that a belly flop can be so painful is that the inertia of the water means that it doesn't "get out of the way" quickly enough. There are two key impediments to motion under water: inertia and viscosity. Viscosity is the "gooiness" of a fluid - it's a measure of resistance to flow (e.g. honey is more viscous than water). A quantity known as the Reynolds number,  $Re$ , provides a measure of the ratio of inertial to viscous forces:

$$Re = \frac{\rho v L}{\eta} \quad (3.5)$$

where  $\rho$  is the density of the fluid,  $v$  its velocity,  $L$  the linear dimension of the object (e.g. diameter), and  $\eta$  is the viscosity.

Let's consider how the inertial and viscous forces scale with size. The force due to inertia,  $F_{in}$ , arises because we have to move a volume of fluid, imparting momentum to it. If we work out the rate of change of momentum then we immediately know the force (via Newton's second law). The volume of fluid moved out of the way per second by an object of area  $A$  travelling at a speed  $v$  is proportional to  $vA$  (note how the quantity  $vA$  is *dimensionally correct*, i.e. it has units  $m^3s^{-1}$ ). Volume and mass are related by  $m = \rho V$  (where  $\rho$  is the density of the fluid), which means that the change of the momentum of the fluid per second, i.e. the inertial force,  $F_{int}$ , is proportional to  $\rho v^2 A$ .

For reasons I won't go into here, the viscous force does not depend on the mass of the fluid. It instead depends on the viscosity of the fluid and the rate at which the velocity of the fluid changes with distance. This means that we can write:

$$F_{visc} \sim \eta A v / L, \text{ i.e. } F_{visc} \sim \eta v L \quad (3.6)$$

---

<sup>2</sup>This is a tricky surface science problem that many nanoscience research groups are tackling. (For applications rather less exotic, it must be admitted, than controlling the rate of protein attachment to miniaturised submarines containing a shrunken crew working against time to destroy a blood clot with a microlaser...)

This in turn means that,

$$F_{int}/F_{visc} \sim vL \quad (3.7)$$

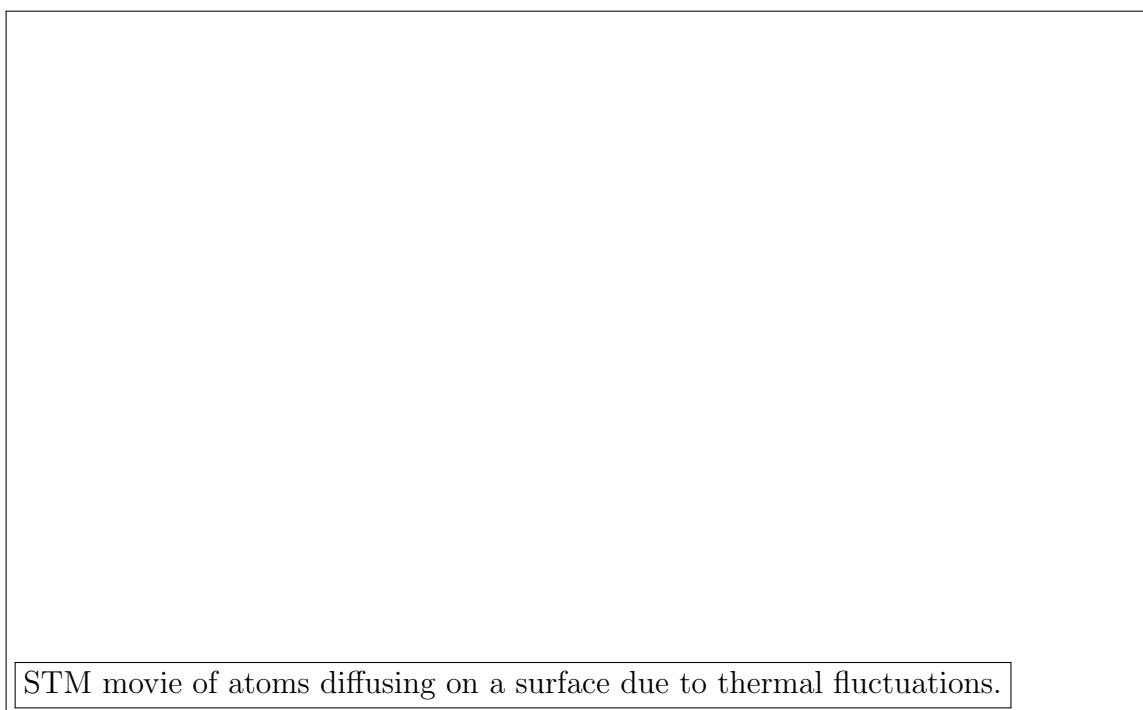
In other words, viscosity dominates at small values of  $L$ . The Proteus submarine in the “Fantastic Voyage” movie would, when scaled down to the micron level, have great difficulty moving through the bloodstream due to this domination of viscosity at the micro- and nanoscale. Interestingly, and as Jones has pointed out, evolution has found a neat solution to the problem of moving microscale objects (such as bacteria) through fluids: twisting flagella, as Prof. Eaves discusses in the following [Sixty Symbols](#) video on the Reynolds number.

The Reynolds number. (From Sixty Symbols).

### 3.4 Random walks in nanospace

Atoms and molecules are associated with translational, vibrational, and rotational motions (or “degrees of freedom”). This means that at room temperature - and, indeed, for some systems, down to very low temperatures - thermal energy produces a great deal of movement at the nanoscale. An example with which you’ll be familiar is the Brownian motion of pollen grains due to their constant buffeting by water molecules. The motion (diffusion) of the pollen grain and, more importantly for

our purposes, an individual water molecule, can be described by a *random walk*. However, it is important to realise that this “buffeting” process is not necessary to generate a random walk: single atoms and single molecules will similarly follow a random walk on a surface due to their motion being driven by thermal fluctuations, and their motion can be monitored by a scanning probe microscope as shown in the following short video clip[I. Brihuega et al., *Physical Review Letters* **98**, 156102 (2007)]. (There’s much more on atomic and molecular diffusion in Chapter 6.)



We can treat the diffusion of any molecule as a random walk. Imagine following the motion of an individual molecule in the air and plotting its path as it is constantly buffeted by the other gas molecules, or similarly consider a single molecule hopping across a surface as a result of thermal energy (as shown in the preceding video). The path the molecule follows will resemble something like that shown in the following video. (The computer algorithm used to simulate random walks is known as a Monte Carlo program, after a casino in Monaco - a fitting name because the operation of a casino, assuming that it’s run honestly(!), is also due to series of random events.)



Plotting the random walk of a molecule undergoing Brownian motion.

Let's now determine how far the molecule travels after a certain number of steps. First, think about the following question:

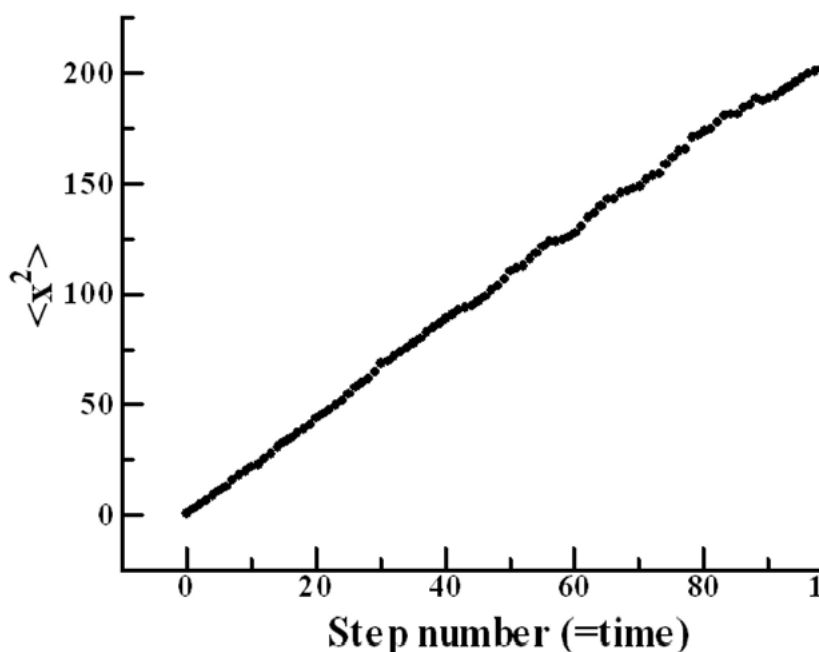
**Q.** What is the average displacement of a molecule following a random walk?

Therefore, it makes much more sense to consider the mean square displacement of the molecule. But as this is a random process, we also need to consider the statistics associated with the problem - just considering one walk is not enough. Figure 3.2 is a graph of the mean square displacement vs the number of steps (each step represents an increment of time  $dt$ ) for a random walker. Each point on the graph is the average mean square displacement measured from 1000 different random walks. Note that  $\langle x^2 \rangle$  varies linearly with time and, hence, the root-mean-square (rms) displacement varies as  $\sqrt{t}$ .

**Q.** How does the displacement of the random walker compare with the displacement of a single free molecule traveling with a speed  $v$  that doesn't undergo collisions? Is the random walker faster or slower?

In Chapter 5 I'll discuss the use of scanning probe microscopes to manipulate individual atoms and molecules. A key aspect of much (though, importantly, not





**Figure 3.2** – Mean square displacement,  $\langle x^2 \rangle$ , for a random walker as a function of the number of steps.

all) of the atomic and molecular manipulation work done to date has been the use of low temperatures (in many cases as low as 5K) to “freeze out” diffusion. For certain systems, including noble gas atoms adsorbed on metal surfaces (e.g. the Xe on Ni system used by Eigler and Schweizer in the generation of the atomic IBM logo discussed in Chapter 1), the energy barriers for diffusion are so low that for temperatures much above 5K the atoms gain enough energy to diffuse readily across the surface. This means that the atomic arrangement put in place with the scanning probe is “washed away” due to thermal excitations. Alternatively, it is possible to use a scanning tunnelling microscope or atomic force microscope to actively follow the diffusion of an atom as a function of temperature and thus determine the energy barrier for diffusion.

### 3.5 Problems

**P3.1(a)** A conducting component of length  $L$  and cross section  $A$  has an electrical resistance  $R = \frac{\rho L}{A}$  where  $\rho$  is the resistivity.

- (i) Assuming that  $\rho$  remains constant, how does  $R$  scale with the linear size of the component?
  - (ii) A voltage is applied to the conductor and a current,  $I$ , flows. How does  $I$  scale with the linear size of the component?
  - (iii) How does the power dissipated by the component scale with  $L$ ?
  - (iv) A large number of the components are packed onto the surface of a chip. How does the power dissipated per unit area scale with  $L$ ?
- (b) Consider a parallel plate capacitor. How do each of the following scale with the length,  $L$ , of the capacitor: (i) the capacitance, (ii) the charge stored on the capacitor plates, and (iii) the energy stored in the capacitor?

# Chapter 4

## Introducing the Quantum

*There isn't a way things should be. There's just what happens, and what we do.*

Terry Pratchett, from *A Hat-full of Sky*

### 4.1 Quantum mechanics: A gentle introduction

My aim in this chapter is to introduce the core concepts in quantum mechanics that are required to understand many of the physical properties of nanostructures. A particular focus will be the “particle in a box” problem and its relationship to quantum confinement in nanoparticles but I will also cover other aspects of quantum physics which underpin key areas of nanoscience. Mathematics is the language of quantum physics - and, more broadly, it's the *lingua franca* of physics and science in general - and therefore a certain amount of mathematical detail is essential. Moreover, the same type of mathematics appears time and time again in different, apparently disparate, physical situations which you will encounter throughout your degree course and I will aim to draw links between these areas (e.g. the simple harmonic oscillator, the wave equation and Fourier analysis, eigenfunction and eigenvalue problems...).

### 4.2 Waves, particles, wavicles?

In nanoscience we deal with the physics of the ultrasmall (i.e. atoms, molecules, and nanoparticles) where properties and behaviour can be dictated by quantum mechanics. We shall see that many aspects of quantum physics are counter-intuitive

---

PowerPoint slides associated with this chapter are available [here](#), and [here](#), and [here](#)

and difficult largely because they challenge our common-sense ideas of how objects and particles should move and behave. To start, I should define just what I mean by the term “particle”. By **particle** I mean an object which has a definite, well-defined, momentum, kinetic energy, and, importantly, position in space. (We say that a particle is *localised*). Take, for example, a ball on a snooker table - we can accurately calculate, using Newton’s laws of motion, the position of the centre of mass of the ball before and after it is hit by another ball.

A **wave**, on the other hand, is not something that we can “pin down” to a specific location. We say that a wave is *delocalised*. If one thinks of waves on the surface of a lake, there is a transfer of energy from one position to another but there is no net movement of the water (unlike the motion of the snooker ball). The Oxford English dictionary defines a wave as follows: “*A periodic disturbance of the particles of a substance which is propagated without net movement of the particles, as in the passage of undulating motion or sound.*”

In quantum mechanics the distinction between particle and wave is blurred and it is this blurring that produces the surprising behaviour of matter at the nanoscale<sup>1</sup>. We speak of *matter waves* or *wave-particle duality* rather than particles - electrons, atoms, and molecules can all exhibit behaviour we attribute to waves such as interference and diffraction. Louis de Broglie hypothesised that the wavelength of a particle is inversely proportional to its momentum:

$$\lambda = h/p \quad (4.1)$$

where  $\lambda$  is the wavelength,  $h$  is Planck’s constant, and  $p$  is the momentum of the particle. If we consider particles with non-relativistic velocities (i.e. velocities which are much less the speed of light) then we can write Eqn. 4.1 as:

$$\lambda = h/mv \quad (4.2)$$

where  $m$  is the mass of the particle and  $v$  is its velocity.

**Q.** You are walking down the street at a speed of  $1.5 \text{ ms}^{-1}$ . Calculate your de Broglie wavelength.

The answer to the question above will give you a good insight into why everyday objects do not exhibit wave-like properties.

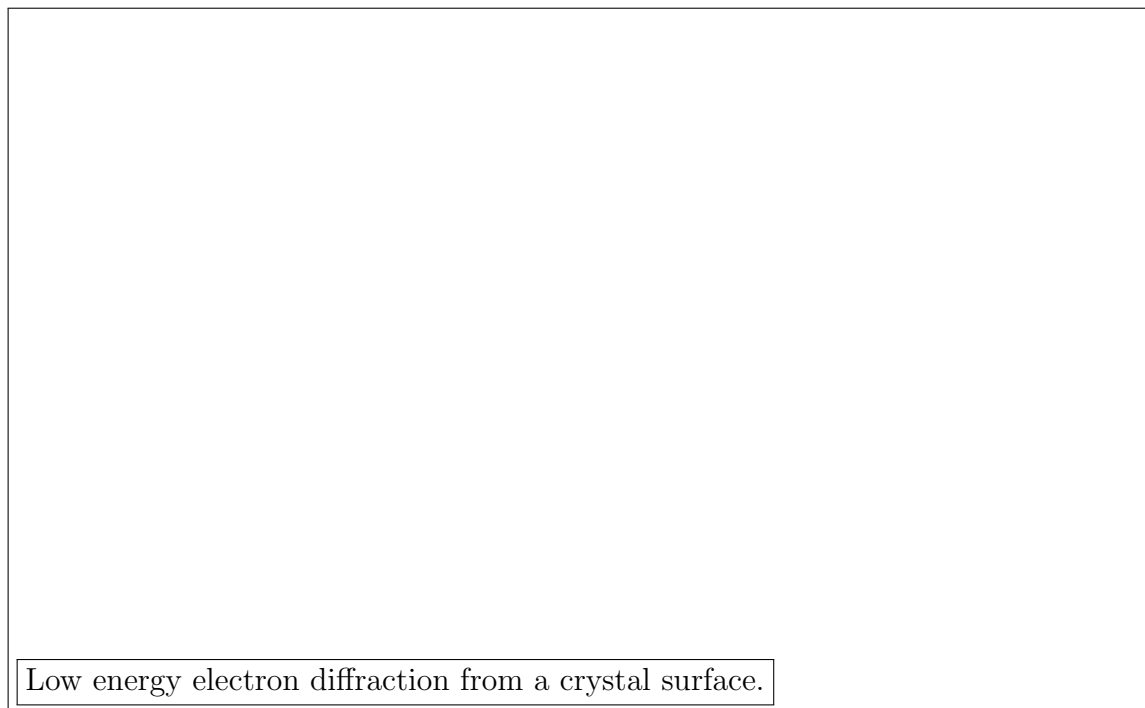
---

<sup>1</sup>It is very important, however, that you do not think of *the particle itself* as spreading out like a wave. As we’ll see soon, quantum mechanics is not as ‘simple’ as this...

**Q.** An important unit of energy used throughout quantum physics is the electron volt (abbreviated as eV). An electron volt is equal to the change in energy of an electron which has moved through a potential difference of one volt and is approximately  $1.602 \times 10^{-19}$  joules. Calculate the de Broglie wavelength of an 100 eV electron.

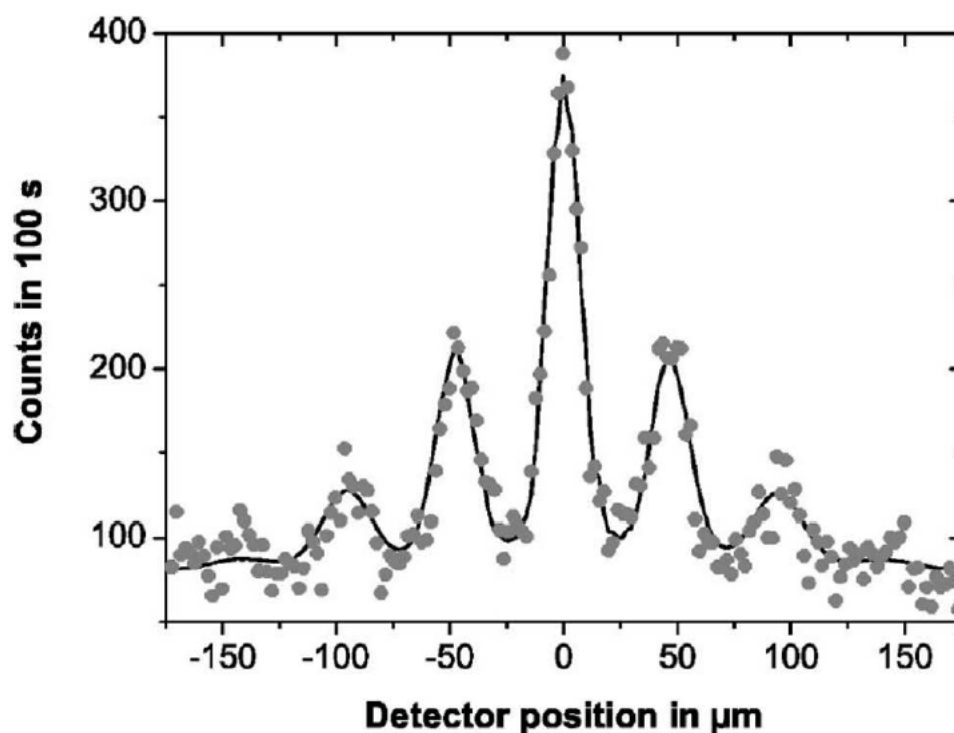
You should find that the wavelength of an 100 eV electron is comparable to interatomic distances in solids. When the wavelength of a wave is comparable to the size of an object in its path, the wave will be strongly *diffracted* by the obstacle. (Diffraction also occurs for objects which are very much larger than the wavelength of the impinging wave but its effects are significantly more difficult to observe - see the discussion of  $C_{60}$  diffraction below.) Diffraction arises from the *interference* of waves and one of the more common examples is the “rainbow” of colours that is observed on a CD or DVD due to diffraction from the features on the disc used to encode the information. Davisson and Germer first observed diffraction patterns for (low energy) electrons scattered from clean, atomically flat surfaces in 1927. Low energy electron diffraction (LEED) is now a very well-established technique in surface science and nanoscience because analysis of the diffraction pattern provides a great deal of information about the diffracting object (i.e. the crystal surface).

The video below shows a LEED system in action.



Low energy electron diffraction from a crystal surface.

Fig.4.6 shows a double slit diffraction pattern [from Nairz *et al.* *American Journal of Physics* **71**, 319 (2003)] for buckminsterfullerene ( $C_{60}$ ), a molecule with a diameter of  $\sim 1$  nm. It is worth comparing this with the pattern observed for laser light diffracted from a pair of slits shown in Fig.4.2. You will see that there are very strong similarities. (The precise details of the pattern in each case are best understood in the context of Fourier analysis - a topic you will cover in Year 2). The diffraction pattern can be calculated (and compared to experiment) by considering the de Broglie wavelength of the  $C_{60}$  molecules which impinge upon the slits.

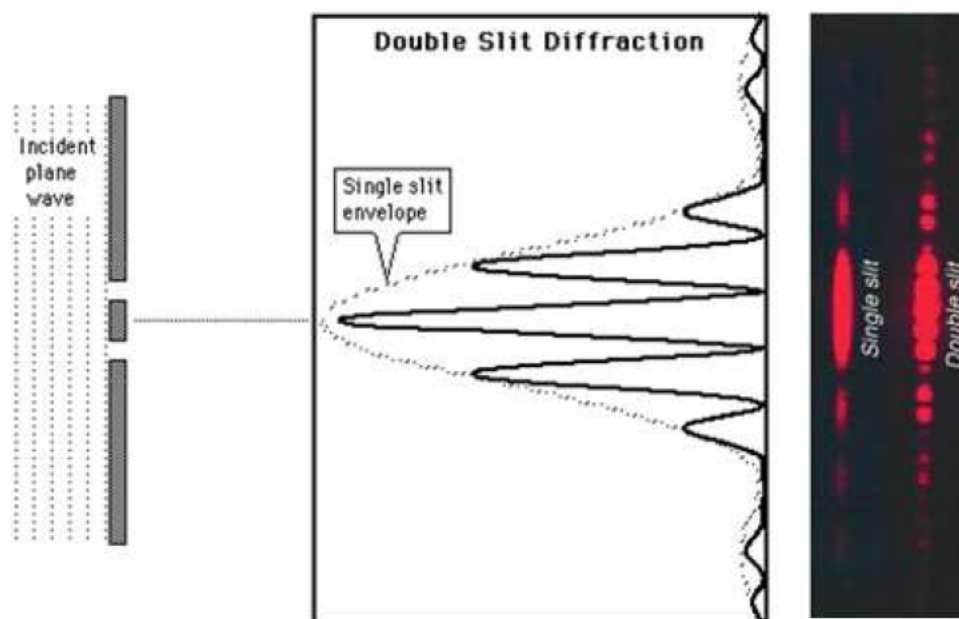


**Figure 4.1** – A double slit diffraction pattern for  $C_{60}$  molecules with a mean velocity of 117 m/s. Full circles represent the experimental data. The full line is a numerical model based on diffraction theory. From Nairz *et al.*

**Q.** Calculate the de Broglie wavelength of a  $C_{60}$  molecule which is travelling with a speed of  $200 \text{ ms}^{-1}$ .


Note that the wavelength you have calculated is (or should be!) *much* smaller than the width of the slits used in the experiment of Fig.4.6 (55 nm). This means that the angles through which the fullerene molecules are diffracted are *tiny*. It's worthwhile attempting to calculate the value of the angle at which you'd expect to

see first order diffraction. (See [the Hyperphysics website](#) for a discussion of orders of diffraction. See also the problems at the end of this chapter.



**Figure 4.2** – A double slit diffraction pattern for laser light. Compare to Fig. 4.1. Taken from [Hyperphysics](#)

A remarkable aspect of the diffraction of matter - among very many other remarkable aspects - is that when the double slit experiment is performed such that only a single particle is in the apparatus at any given time, *the diffraction pattern still appears*. This was elegantly shown by Akira Tonomura of Hitachi Research Labs. back in the eighties, who, in the video below, shows the stunning results of the experiment he carried out.



Tonomura (Hitachi) double slit experiment with single electrons.

### 4.3 The Schrödinger equation

The wavelike behaviour described in the previous section is of paramount importance in determining the properties of nanostructures (and matter in general). Of course, the obvious question to ask is: what is it that waves in a matter wave? Before we address this question, we need to consider the pioneering efforts of Erwin Schrödinger. Schrödinger, building on de Broglie's work relating the wavelength and momentum of a particle, developed an elegant mathematical framework to describe matter waves.

At the core of Schrödinger's theory is the concept of a *wavefunction*. If we have waves on a guitar string then the wavefunction,  $y(x, t)$  describes the displacement of the string as a function of position ( $x$ ) and time ( $t$ ). Similarly, we can write down a wave function for an electromagnetic wave (such as light) which describes the behaviour of the electric field as a function of position and time. In both cases the wavefunction represents a solution to the *wave equation*. It's worth writing down the wave equation for both these systems so you can see the similarities:

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \quad (4.3)$$

where  $v$  is the speed of the wave. For electromagnetic waves:



$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} \quad (4.4)$$

where  $c$  is the speed of light and  $E$  is the electric field.

Equations 4.3 and 4.4 are *second order partial differential equations*. That is, they involve partial derivatives (derivatives of functions of more than one variable) and those derivatives are “double derivatives” (i.e. second order). You will see that the equation for a wave on a string and for an electromagnetic wave are very similar indeed.

Schrödinger realised that if matter indeed behaves in some sense like a wave then it should be possible to describe its behaviour using a wave equation. He considered matter to be described by a *wavefunction*, which is conventionally represented by the Greek symbol,  $\psi$ . For reasons we shall discuss below, the wave equation required to describe how  $\psi$  behaves as a function of position and time (i.e. Schrödinger’s equation) is not quite of the form given in 4.3 and 4.4 above. Although, as for equations 4.3 and 4.4, Schrödinger’s equation involves the second derivative of the wave function with respect to position, this is proportional not to the second, but to the *first* derivative of the wave-function with respect to time. In other words (and, for simplicity, considering only one spatial dimension,  $x$ ):

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = \alpha \frac{\partial \psi(x, t)}{\partial t} \quad (4.5)$$

## 4.4 But what is it that’s waving in a matter wave?!

Now we ask: what does  $\psi(x, t)$  in Schrödinger’s equation represent? This is a tricky question which has involved a considerable amount of philosophical debate! Importantly, and confusingly, the wavefunction is not something we can measure directly in experiment - we say that it is not an *observable* quantity. This is essentially because the Schrödinger equation is fundamentally based on a description of matter waves in terms of complex functions. We can write any complex number,  $z$ , in terms of its modulus ( $|z|$ ) and phase angle ( $\phi$ ) as:  $z = |z| \exp(i\phi)$  where  $|z|$  **is a real number**. The quantity we can observe in experiment,  $\psi\psi^*$ , represents the modulus squared of the wavefunction,  $|\psi|^2$ .

### 4.4.1 The wavefunction and probability

Summarising, the wavefunction,  $\psi(x, t)$  itself has no physical meaning - it is a *complex-valued* function and therefore can contain an imaginary component. However, the product of the wavefunction and its complex conjugate,  $\psi\psi^*$  (which is equal to the modulus squared, i.e.  $|\psi|^2$ )) is a real function and can be measured in an experiment.  $|\psi|^2$  is directly proportional to the probability of finding a particle between  $x$  and  $x + dx$  (i.e. in an infinitesimally narrow range of positions in space).  $|\psi|^2$  is a *probability density*. To determine the probability of finding a particle in a region of space between  $x$  and  $x + dx$ , we take the probability density and multiply it by  $dx$  to get the probability.

*This* is the physical interpretation of the solutions to Schrödinger's equation:  $\psi$  does not have a physical meaning but  $|\psi|^2 dx$  is a measure of the probability of finding a particle in a particular region of space.

The total probability of finding a particle anywhere in space must equal 1. (It makes no sense to talk of a probability greater than 1). That is,

$$\int_{-\infty}^{+\infty} P(x, t) dx = 1 \quad (4.6)$$

where  $P(x, t)dx$  is the probability of finding the particle between  $x$  and  $x + dx$ . (We integrate between  $-\infty$  and  $+\infty$  because we want to cover all space.) The amplitude of the wavefunction can always be chosen so that the condition represented by Equation 4.6 holds by ensuring that:

$$\int_{-\infty}^{+\infty} |\psi(x, t)|^2 dx = 1 \quad (4.7)$$

This process is called *normalisation* and a wavefunction for which Equation 4.7 is true is said to be **normalised**.

## 4.5 Energy and time in the Schrödinger equation

Recall that we had written down the basic form of the Schrödinger equation for matter waves:

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = \alpha \frac{\partial \psi(x, t)}{\partial t} \quad (4.8)$$

It turns out that to define the constant  $\alpha$ , we need to bring in the imaginary number  $i$ . (For those of you who are interested in knowing why this is the case, please refer to Chapter 2 of *Quantum Mechanics*, Alastair I.M. Rae (Taylor & Francis (2002)) for a discussion. Note, however, that you will not be examined on this particular aspect of quantum mechanics in the *Frontiers* examination.). The wave equation for free particles becomes:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (4.9)$$

Equation 4.9 is the *time-dependent* Schrödinger equation for a *free* particle. By “free”, we mean that the particle does not move under the influence of a potential,  $V$ . However, we are more generally interested in the behaviour of matter waves when they are subject to a potential (an electron in a nanoparticle, for example). A potential energy term therefore needs to be included in the equation. This is done as follows:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (4.10)$$

It turns out that very many cases involve a potential which does not change with time. We therefore don’t need to consider the time dependent term in Equation 4.10 and can instead use the ***time-independent*** Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V\psi = E\psi \quad (4.11)$$

where  $E$  is the total energy of the particle. [See Chapter 40 of Knight]. Note that the first term on the left-hand side of Eqn. 4.11 represents the kinetic energy of the electron: the greater the curvature (second derivative) of the wavefunction, the higher the electron energy. The reason for this relationship between wavefunction curvature and the kinetic energy of the electron will become clear(er) in the following section.

## 4.6 Waves on a string

We now come to a simple problem which rather remarkably illustrates many of the key features of quantum physics: if we have a string fixed at both ends, at what frequencies do we observe - or, more correctly, hear - standing waves? As a fundamental premise of quantum mechanics is that matter can be described in terms of waves, the solution to this problem also describes the allowed energies of

a quantum mechanical particle confined to a nanoscale box - say, an electron in a nanoparticle. We shall cover the physics of the problem from a classical wave perspective.

First, we need to define what we mean by a *standing wave*. Let's take a guitar string as a good example. The string is fixed at either end. When we pluck the string, waves are reflected from its ends and *interfere* to produce a wave whose nodes (i.e. the positions of zero displacement) are fixed in space: this is a standing wave. Of key importance for the discussion below, the standing waves have well-defined and, for the ideal waves-on-a-string problem, simply-related frequencies. In particular, because the vibrations of the string must have a node at either end (as the string is fixed there), this puts an important constraint on the frequencies of the standing waves.

Fig.4.4 shows that the relationship between the frequencies of the various standing waves is straight-forward to determine. We call the lowest frequency standing wave, which has only one antinode (i.e. position of maximum displacement) at the centre of the string, the first *harmonic* (or the fundamental mode of vibration). The second harmonic has a frequency which is double that of the first, the third harmonic has a frequency three times that of the first, etc... Thus, each of the harmonics has a particular resonant frequency. If we consider the set of all harmonics/resonant frequencies, this is called the frequency *spectrum*.

From Fig.4.4, the wavelength of the first harmonic,  $\lambda_1$  is  $2L$  (where  $L$  is the length of the string),  $\lambda_2 = L$ ,  $\lambda_3 = 2L/3$ , etc... That is:

$$\lambda_n = 2L/n \quad (4.12)$$

where  $n = 1, 2, 3, \dots$

Or, in terms of frequency (remember that for a wave  $v = f\lambda$  where  $v$  is the speed of the wave,  $f$  is its frequency, and  $\lambda$  is its wavelength):

$$f_n = \frac{nv}{2L} = nf_1 \quad (4.13)$$

From a quantum mechanical perspective, an electron - i.e. a matter wave - trapped in a nanoparticle is remarkably similar to the standing waves which form on a string held between two fixed points. If we consider a 1D "nanoparticle" and assume that the electron is confined perfectly within the particle, the edges of the nanoparticle represent the fixed ends of the string. Using the de Broglie relationship between wavelength and momentum (Eqn 4.1), and considering only the wavelengths of the standing waves that form on the string (i.e. within the nanoparticle), we can determine the energy of an electron confined within the particle.

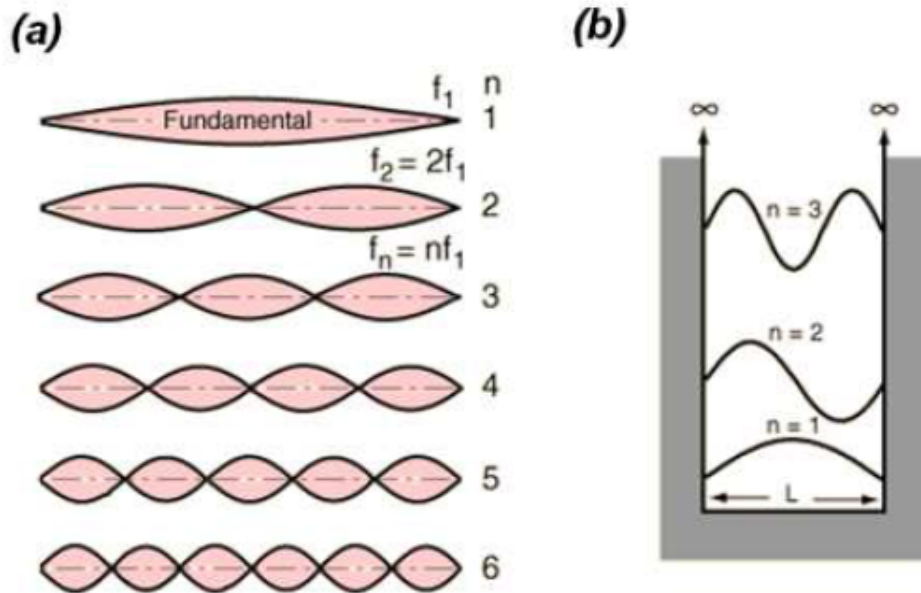
**Q.** Using the de Broglie relationship,  $p = h/\lambda$ , the relationship between energy and momentum,  $E = p^2/2m$ , and the expression for wavelength given in Equation 4.12, show that  $E_n = n^2 h^2 / 8mL^2$ .

## 4.7 Schrödinger and the particle in a box

How do we apply Schrödinger's equation to the particle in a box (i.e. waves on a string) problem? We first consider that the electron is trapped in a potential well where outside the well the potential is infinite whereas inside the box the potential is zero. Outside the box, the particle cannot exist (because the potential is infinite) whereas inside the box we can write down the Schrödinger equation as follows:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (4.14)$$

If we define



**Figure 4.3** – (a) Illustration of standing wave formation on a string fixed at both ends. Note relationship of the frequencies of the harmonics. (b) Standing wave formation for a matter wave (e.g. an electron) confined to a box of width  $L$ . [Both illustrations taken from [Hyperphysics](#)]

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (4.15)$$

then

$$\frac{d^2\psi}{dx^2} = -k^2\psi \quad (4.16)$$

As the potential energy term in the Schrödinger equation is zero, the particle is essentially free within the box. It is, however, subject to *boundary conditions*. Just as for the wave on a string, the value of the wavefunction must be zero at the edges of the box, i.e. at  $x = 0$  and at  $x = L$ . From the Schrödinger equation and the boundary conditions we can deduce the form of the wavefunction. Note that, from Eqn. 4.16 we require a function which when differentiated twice we get the original function. A sine or a cosine function fulfils this criterion<sup>2</sup>.

Without going into the details of how to solve second order differential equations, the general solution for the Schrödinger equation inside the box is:

$$\psi(x) = A \cos(kx) + B \sin(kx) \quad (4.17)$$

We now impose the boundary conditions. We know that at  $x = 0$ ,  $\psi(x) = 0$ . Therefore, substituting into Eqn. 4.17:

$$0 = A \cos(k0) + B \sin(k0) \Rightarrow A = 0 \quad (4.18)$$

This means that  $\psi(x) = B \sin(kx)$ . We also know, however, that  $\psi(x) = 0$  when  $k = L$ . Thus:

$$B \sin(kL) = 0 \quad (4.19)$$

The function  $\sin(x)$  equals zero when  $x = n\pi$  (where  $n$  is an integer). Hence, for Eqn. 4.19 to be true requires  $kL = n\pi$ , i.e.

$$k = n\pi/L \quad (4.20)$$

**Q.** Using equations 4.15 and 4.20, determine an expression for the allowed energy values,  $E_n$ .

---

<sup>2</sup>We could also use an exponential function...

## 4.8 Tutorial videos: Particle in a box



Video tutorial: Particle in a box I.



Video tutorial: Particle in a box II.

Note that, just as the string can't form standing waves of any arbitrary wavelength/frequency, an electron is restricted to taking up particular values of energy. We say that its energy is *quantised*<sup>3</sup>. This represents a fundamental difference as compared to classical physics where energies are not restricted to particular discrete values but are continuous functions. The simple waves-on-a-string model described above allows us to make a reasonable estimate of the energy of an electron confined to a nanoscale region of space (in, for example, a nanoparticle). The following question asks you to carry out the appropriate calculation.

**Q.** For an electron confined to a box which is 10 nm wide, calculate the value of  $E_1$ , i.e. its lowest energy state. (You should quote your answer in units of electron volts (eV)).

## 4.9 When the uncertainty principle goes up to 11...

Your First Year textbook, Knight, does an excellent job of explaining the Heisenberg uncertainty principle and I am not going to repeat the discussion here. I **strongly** recommend that you read Section 39.6, which makes the distinction between the uncertainty principle and the measurement problem in quantum mechanics - which are often confused - very clear. (Indeed, you should ensure that you read *all* of Chapter 39 and Chapter 40 of Knight because these cover all of the quantum physics you will require for the nanoscience component of *Frontiers*.)

The confusion in some textbooks between the uncertainty principle and the role of measurement in quantum mechanics is a particular bugbear of mine, as this caused me a great deal of, errmm, uncertainty (sorry) and confusion as an undergraduate many moons ago. The uncertainty principle also acts as a bridge between two particular interests of mine: heavy metal and quantum physics, as discussed in [this blog post](#) for the Institute of Physics' *physicsfocus* site<sup>4</sup>.

---

<sup>3</sup>It is important to note that the Schrödinger equation can be written as an eigenvalue problem:  $\hat{H}\psi = E\psi$  where the wavefunctions,  $\psi$  represent the eigenfunctions (eigenvectors) and the energy values,  $E$ , are the eigenvalues.  $\hat{H}$  is called the Hamiltonian operator and comprises the kinetic energy and potential energy terms of Eqn. 4.11. You will see a great deal more of this eigenvalue-eigenfunction approach to quantum mechanics in Year 2.

<sup>4</sup>Note: The links between heavy metal and the uncertainty principle do not form part of the examinable syllabus for *Frontiers in Physics*



## 4.10 Worked problem: Particle in a palladium box

The scanning probe microscope was introduced in Chapter 1 and its capabilities are described at length in Chapter 5. The first type of SPM which was invented, the scanning tunnelling microscope (STM), exploits quantum mechanical tunnelling to image surfaces with atomic resolution. Of key importance is that an STM essentially provides a map of probability density for a nanostructured or atomic-scale system. The worked problem below <sup>5</sup> illustrates this for a simple real-world particle in a box example.

**P4.1A** Fig. 4.4(A) shows the step-by-step assembly, using a scanning tunnelling microscope, of a linear chain of twenty palladium atoms (Pd<sub>20</sub>). The Pd chain acts as a confining potential for electrons. Assuming that the potential can be treated as zero inside the chain and infinite outside, write down the Schrödinger equation for an electron inside the Pd<sub>20</sub> nanostructure {2} and sketch the wavefunctions for the four lowest energy states {2}.

As discussed in Section 4.7, we can write down the Schrödinger equation inside the Pd 'box' as follows (because the potential there is zero):

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (4.21)$$

The wavefunctions for the lowest four energy states are simply the waves on a string resonances shown in Fig. 4.3.

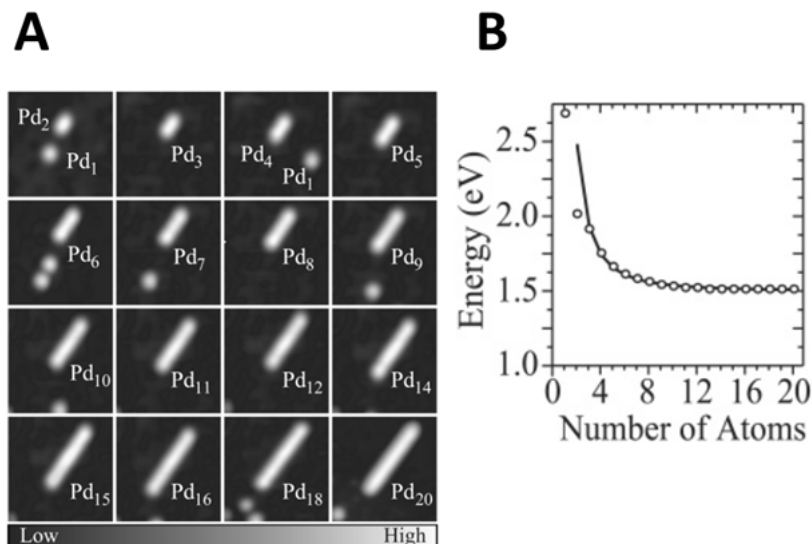
**P4.1B** It was found that the energy of the ground state of the well,  $E_1$ , varied with the length,  $L$ , of the Pd chain as shown in Fig. 4.4(B). From a consideration of (i) the Schrödinger equation {2}, and (ii) the Heisenberg uncertainty principle {2} explain why  $E_1$  decreases with increasing  $L$ .

(i) As  $L$  increases, the curvature of the wavefunction,  $\frac{d^2\psi}{dx^2}$ , decreases. This means that the kinetic energy of the wavefunction decreases (because the kinetic energy is given by  $\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2}$ ).

(ii) The Heisenberg uncertainty principle can be written as  $\Delta x \Delta p_x \geq \frac{\hbar}{2}$ .

---

<sup>5</sup>The question is taken from the *Frontiers in Physics* exam paper for 2012-2013. The numbers in braces show the marks allocated to each part of the question



**Figure 4.4** – (A) Pd chains of different length (ranging from 1 to 20 atoms) fabricated using a scanning tunnelling microscope. (B) Variation of ground state electron energy within a Pd chain as a function of the length of the chain. Figures taken from N. Niluis et al., J. Phys. Chem. B 109 20657 (2005). ©. American Chemical Society.

Increasing  $L$  means that the uncertainty in position increases (because the well is wider and so  $\Delta x$  is larger), with a corresponding reduction in momentum from the uncertainty principle. As  $E = \frac{p^2}{2m}$  there is a corresponding decrease in electron energy<sup>6</sup>.

**P4.1C** The graph in Fig. 4.4(B) was linearised by plotting  $\log E$  vs  $\log L$ . What is the slope of this linear graph? **{2}**

$$\begin{aligned}
 E_n &= \frac{n^2 h^2}{8mL^2} \\
 \Rightarrow E_1 &= \frac{h^2}{8mL^2} \\
 \Rightarrow E_1 &= \frac{C}{L^2}
 \end{aligned}$$

where  $C$  is a constant.

<sup>6</sup>A number of you have contacted me by e-mail to ask a very perceptive and important question about this aspect of applying the uncertainty principle, namely how is it possible to equate the uncertainty in momentum with the momentum itself? That is, how can we write  $\Delta p \sim p$ ? See Appendix A for an explanation.

$$\Rightarrow \log E_1 = -2 \log L + \log C$$

Therefore, the slope of the graph is -2.

**P4.1C** The wavefunction,  $\psi_1$ , for the ground state of the well is

$$\psi_1 = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

where  $L$  is the length of the well. The  $\text{Pd}_{20}$  chain is 6 nm in length. What is the probability of finding an electron in the ground state between  $x=0$  (i.e. the end of the  $\text{Pd}_{20}$  chain) and  $x = 1$  nm?

$$\begin{aligned} \psi_1 &= \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \\ \Rightarrow P &= \int_0^l |\psi_1|^2 dx \\ \Rightarrow P &= \frac{2}{L} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx \\ \Rightarrow P &= \frac{2}{L} \left[ \frac{x}{2} - \frac{\sin(2\pi x/L)}{4\pi/L} \right]_0^l \\ \Rightarrow P &= \frac{l}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi l}{L}\right) \end{aligned}$$

The Pd chain is 6 nm long, so  $L = 6$  nm, and the question asks for the probability of finding the electron between the end of the chain and  $x = 1$  nm, therefore  $l = 1$  nm.

If we plug these values for  $L$  and  $l$  into the expression for  $P$  given above we find that  $P = 0.029$ .

## 4.11 Problems

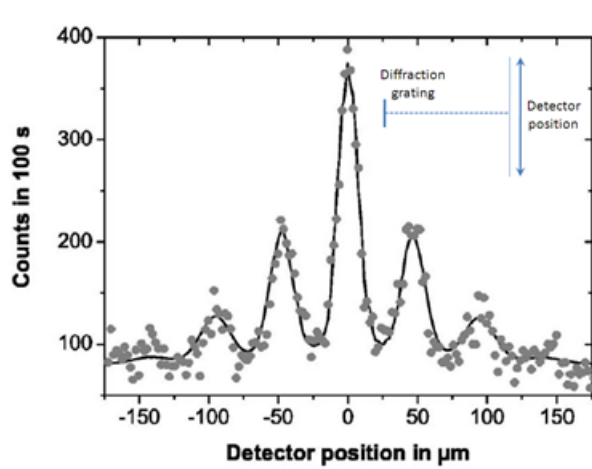
**P4.1** [Question from the 2011-2012 *Frontiers in Physics* exam paper.]

Assume that we can treat a nanoparticle as an infinite 1D potential well for electrons.

- (i) Taking a nanoparticle diameter of 4 nm, calculate the energies and sketch the wavefunctions for the four lowest confined states of an electron in the particle.
- (ii) What is the probability of finding an electron at the centre of the nanoparticle for the  $n=4$  state?
- (iii) What wavelength of light is emitted for an electronic transition from the  $n=4$  level to the ground state?

**P4.2** [Tutorial problem] Fig. 4.5 below shows a diffraction pattern for  $C_{60}$  molecules travelling with a mean velocity of 117 m/s which have been diffracted by a diffraction grating with a grating constant of 100 nm [taken from Nairz et al., *American Journal of Physics* **71**, 319 (2003)]. A  $C_{60}$  detector placed 1.2 m away from the grating produced the spectrum shown in Fig. 4.5.

- (i) Calculate the de Broglie wavelength of a  $C_{60}$  molecule travelling at a speed of 117 m/s.
- (ii) Determine the angle through which the  $C_{60}$  molecules are deflected for the first order diffraction peak. Does your estimate agree with the data shown in Fig. 4.5?



**Figure 4.5** – A diffraction pattern for  $C_{60}$  molecules diffracted by a grating with a period of 100 nm. The graph shows the change in the number of molecules measured as a function of the detector position. (See inset for schematic of experimental geometry.) From Nairz *et al.* *American Journal of Physics* **71**, 319 (2003)

**P4.3** A group of researchers at the University of California at Irvine (N. Nilius, TM Wallis, and W. Ho) have constructed one dimensional Au chains of various lengths using a

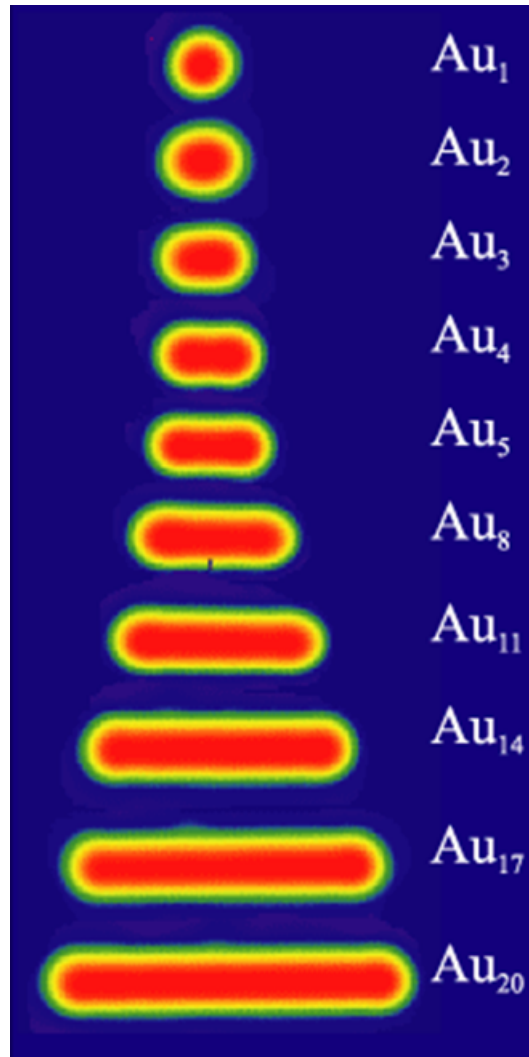
scanning tunnelling microscope to position individual atoms (see Fig. 4.6). These gold chains, ranging from a single atom to twenty atoms in length, represent one-dimensional confining potentials and their electronic properties can be understood using the simple 1D particle-in-a-box model which has been covered in the *Frontiers* lectures. With the STM, the researchers could measure the probability density and energy of a wide variety of electron states in the Au chains<sup>7</sup>.

[In the following, assume that: (i) the Au chains can be modelled as a 1D rigid box, i.e. where the potential inside the box is zero and that outside the box is infinite; (ii) the mass of the electron is  $9.11 \times 10^{-31}$  kg]

- (i) Write down an equation for the normalised ground state wavefunction (i.e. the  $n = 1$  state) of a Au chain **{1}**, and then sketch the probability density for the  $n = 1$  state of the Au<sub>5</sub> and Au<sub>20</sub> chains, respectively. The sketches should be on the same graph axes. **{3}**
- (ii) It was found that the energy difference between the  $n = 1$  and  $n = 2$  states for a Au<sub>10</sub> chain was 0.135 eV. From this result, determine the length of the Au<sub>10</sub> chain. **{5}**
- (iii) A single gold atom in a chain is 0.29 nm in diameter. For the  $n = 1$  state of the Au<sub>10</sub> chain, what is the probability of finding an electron confined to a single gold atom at the end of the chain? **{8}**
- (iv) The STM tunnel current was measured at the centre of the Au<sub>10</sub> chain for the  $n = 1$ ,  $n = 2$  and  $n = 3$  states. For which of these measurements was the tunnel current lowest in value? Why? **{3}**
- (v) The Heisenberg uncertainty principle can be written as  $\Delta x \Delta p_x \approx \hbar$ . Taking a (very rough) estimate of  $\Delta x$  to be  $L/2$ , where  $L$  is the length of a Au chain, compare the value of the ground state energy (again for the Au<sub>10</sub> chain) determined using the uncertainty principle with the value of  $E_1$  derived from the solutions to the Schrödinger equation for the infinite potential well. **{5}**

---

<sup>7</sup>This question currently forms a coursework exercise for the *Frontiers* module. Numerical answers to the problems are therefore not given at the end of the book.



**Figure 4.6** – A series of quantum well structures formed by manipulation of Au atoms using a scanning tunnelling microscope (see Chapter 5 for a discussion of the STM). The Au atoms have been positioned to form chains ranging in length from  $\text{Au}_2$  to  $\text{Au}_{20}$ . From T. M. Wallis, N. Nilius, and W. Ho, *Phys. Rev. Lett.* **89**, 236802 (2002). ©American Physical Society (2002).

# Chapter 5

## Precision Probes

*Where the telescope ends, the microscope begins.  
Which of the two has the grander view?*

Victor Hugo, from *Les Misérables*

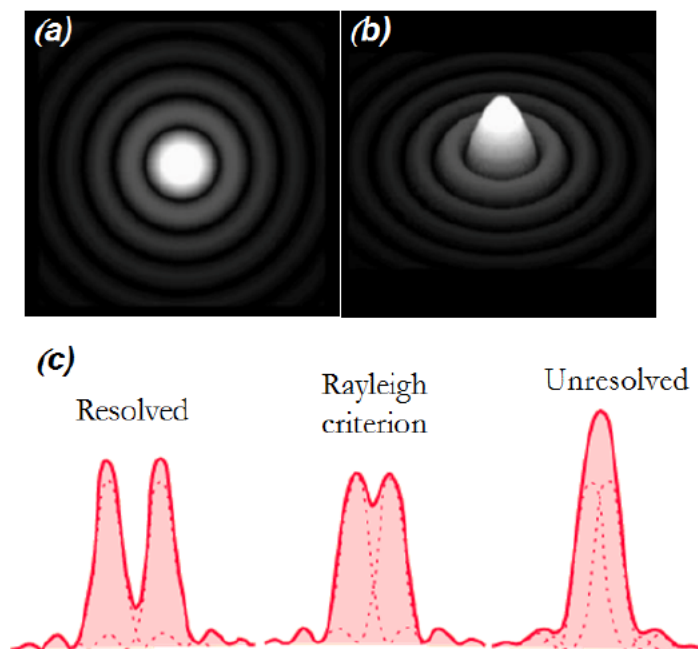
### 5.1 Why can't a conventional microscope resolve atoms?

Before describing how scanning probe microscopes work, let's take a moment to consider why "traditional" microscopes (i.e. those based on lenses, mirrors, or some sort of optical element) can't resolve atoms. The key limitation of an optical microscope arises due to *diffraction*. When the size of an object becomes comparable to the wavelength of the light used to image it then diffraction plays a key role in how the photons of light are scattered by the object. This sets a limit on the size of an object we can resolve given by (roughly)  $\lambda/2$ , where  $\lambda$  is the wavelength of the light used.

If we take a single point as our object, the point will appear as an Airy disc - a set of rings arising from the constructive and destructive interference of light (see Fig.5.1). The *Rayleigh criterion* (also illustrated in Fig. 5.1) defines the resolution limit associated with diffraction. If we take two point objects, each giving rise to an Airy disc, then the Rayleigh criterion (which defines the point at which the objects are *just* resolved) is reached when the central maximum of one Airy disc overlaps with the first minimum of the other disc.

---

PowerPoint slides associated with this chapter are available [here](#), and [here](#), and [here](#), and [here](#)



**Figure 5.1** – Reaching the diffraction limit. (a) and (b) show plots of the Airy disc - the image of a point source in an optical system. The peaks and troughs in intensity arise from the diffraction of light by the object. (Images taken from Wikipedia). (c) An illustration of the Rayleigh criterion. (Taken from the Hyperphysics website).

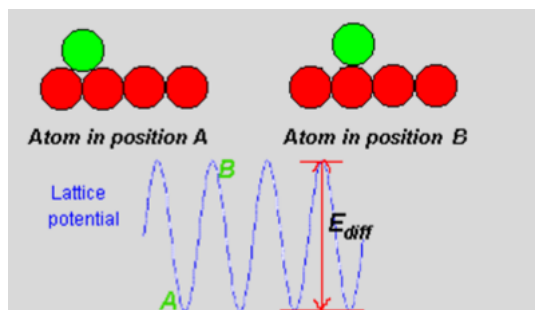
## 5.2 Quantum mechanical tunnelling

The scanning tunnelling microscope (STM) - an instrument whose invention many see as the “genesis” of nanoscience - relies for its operation on a remarkable and fascinating quantum mechanical effect known as *tunnelling*. There is no effect comparable to quantum mechanical tunnelling in classical physics. (Once again, your first year text book does a very good job of explaining the concept. See Section 40.10. In the following I’ll summarise the key physics concepts from a nanoscience perspective).

Consider a particle which encounters an energy barrier (a step in potential energy) - a good macroscopic analogy is that of a ball rolling towards a hill, i.e. a barrier in gravitational potential energy. In classical physics, if the ball doesn’t have sufficient kinetic energy it won’t traverse the barrier. At the nanoscale, however, where quantum mechanics can play a dominant role, a particle can cross the barrier *despite having an energy which is lower than the height of the barrier*.

Fig. 5.2 is a simple sketch of an energy barrier showing the energy of a particle in relation to the height of the potential barrier. The x-axis represents position and the y-axis is an energy scale. There are three regions: Region 1 where the particle is on the





**Figure 5.2** – Energy diagram for tunnelling process. The electron has an energy  $E$  and the height of the barrier is  $V_0$ .

left hand side of the barrier; Region 2, inside the barrier; and Region 3, where the particle is on the right hand side of the barrier. Classically, the particle, whose energy  $E$  is less than the barrier height  $V_0$ , could never be found on the right hand side of the barrier. Quantum mechanically, not only is there a finite probability of finding the particle on the right hand side of the barrier but the particle can also exist *inside* the barrier.

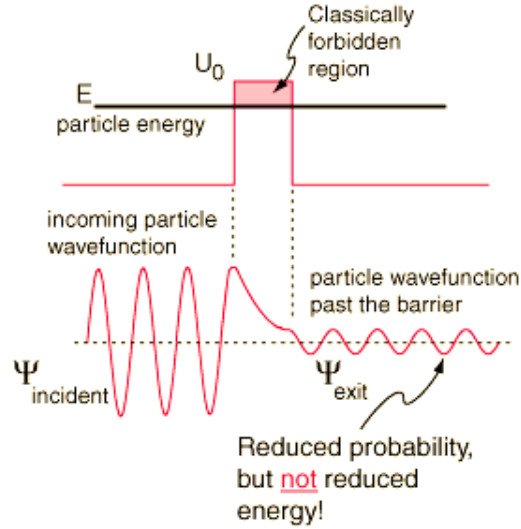
How is it possible for a quantum mechanical object to tunnel through an energy barrier in this fashion? The answer lies in the wave-like characteristics of electrons, atoms, and molecules described in Chapter 3. The wavefunction for an electron (or atom or molecule or other quantum object) can “leak through” the barrier as shown in Fig. 5.3 (taken from the Hyperphysics website). In Year 2 you will see how it’s possible to calculate the transmission coefficient (i.e. the ratio of the amplitude of the incoming (Region 1) and outgoing (Region 2) waves) for the tunnelling process. Here, you need only realise that the transmission coefficient is directly related to the flow of electrons across the barrier (from now on I will assume that we are considering electrons rather than any other quantum object<sup>1</sup>), i.e. the tunnel current,  $I$ .

### 5.3 Tunnel current and the scanning tunnelling microscope

For electrons tunnelling through an energy barrier, there is an exponential dependence of the tunnel current (i.e. the number of electrons crossing the barrier per unit time) on the width,  $d$ , of the barrier:

$$I \propto e^{-2\kappa d} \quad (5.1)$$

<sup>1</sup>It is, however, important to realise that tunnelling is of key importance not only in nanoscience but throughout physics. See Knight for various examples of tunnelling in nuclear fusion, radioactivity etc...



**Figure 5.3** – Tunnelling through a barrier. Note both the exponential drop in the amplitude of the wavefunction in the barrier region and the conservation of the total energy of the electron (the wavelength is the same on both sides of the barrier). Taken from the Hyperphysics website.

where  $\kappa$ , called the inverse decay length (a measure of how quickly the wavefunction decays in the barrier region), is given by

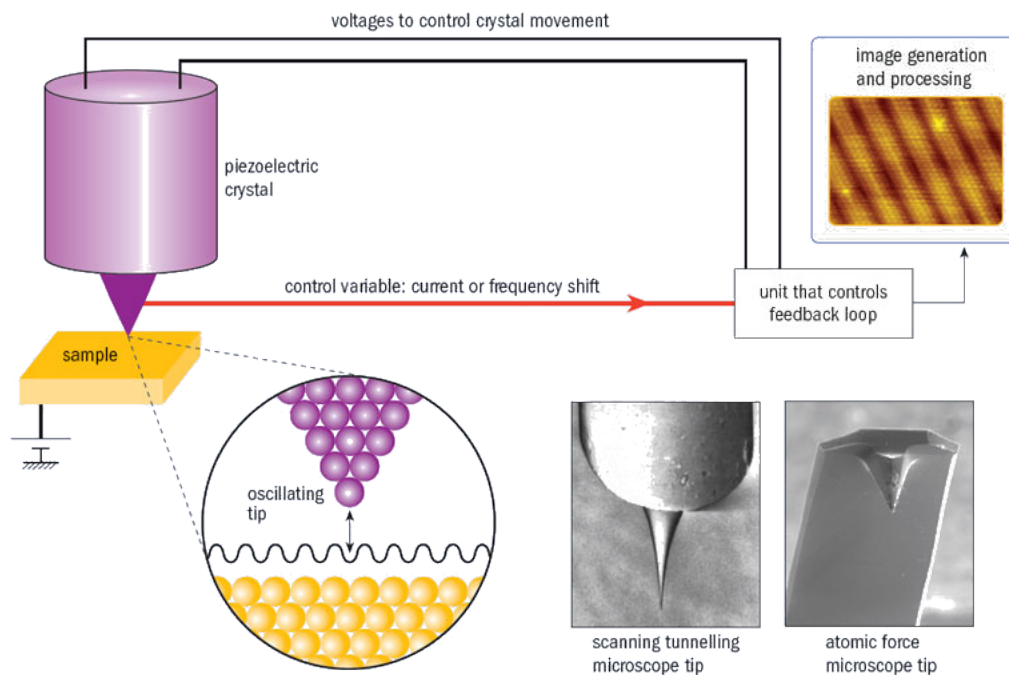
$$\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} \quad (5.2)$$

and  $U_0 - E$  (the difference between the height of the barrier and the energy of the electron) is called the apparent barrier height.

You may have noticed that the expression for  $\kappa$  involves the  $\frac{2m}{\hbar^2}$  constant that appears in the Schrödinger equation discussed in Chapter 4. This is not a coincidence! The formulae for  $I$  and  $\kappa$  given above are derived by solving the Schrödinger equation for a potential energy function of the type shown in Figs. 5.2 and 5.3.

The scanning tunnelling microscope (STM) exploits quantum mechanical tunnelling to produce images of surfaces at the atomic level: individual atoms - or, more accurately, their associated electron probability density - can be “seen” (and, indeed, moved). A simple illustration of the principle of operation of the STM is shown in Fig. 5.4. A sharp - preferably atomically sharp (we’ll come back to this point) - metal tip is brought to within a nanometre of the surface of a conducting sample with a voltage of anything from a few tens of millivolts to a few volts between tip and sample. Even though the tip and sample aren’t in electrical contact, i.e. there is a vacuum gap between them, a current can still flow due to electrons quantum mechanically tunnelling across the vacuum gap. In the STM, the barrier width,  $d$  in Equation 5.1 above, is the separation between the tip

and the sample. This separation is typically less than 1 nm and can be controlled with an accuracy of down to the picometre level (i.e.  $\sim 1\%$  of an atomic diameter).



**Figure 5.4** – A simple schematic diagram of the operation of a scanning probe microscope. Both an STM and an atomic force microscope (AFM) tip are shown. (AFM is covered in detail later in this chapter). Figure taken from *Resolution Frontiers*, Physics World 2010. This article is available online [here](#).

## 5.4 STM imaging modes

To apply electron tunnelling to the generation of atomically resolved images of surfaces, the tip must be rastered or scanned back and forth across the surface (hence, the *scanning* tunnelling microscope). There are two modes of STM operation: constant current and constant height. These are sketched schematically in Fig. 5.5.

In the constant height mode, the tip is scanned back and forth across the surface (i.e. in the x-y plane) while its z-position (its height) is kept constant. As the tip is scanned, the tunnel current (typically  $\sim 1$  nA, although, depending on the sample, STM images may be acquired with tunnel currents ranging from less than 1 pA up to 100 nA) is measured. A computer converts the tunnel current signal into either a line plot as shown in the illustrations in Fig. 5.5 or into a grey scale or false colour plot where small currents are represented by dark shades and higher currents by brighter shades.

In the constant current mode, the  $z$ -position of the tip is varied as the tip moves across the surface so that the tunnel current is kept constant. A topographic map of the surface is generated from the variation of the tip position which, again, is computer controlled. Hopefully you can see that unless the substrate is particularly flat, constant current mode is essential to prevent the tip crashing into the surface!

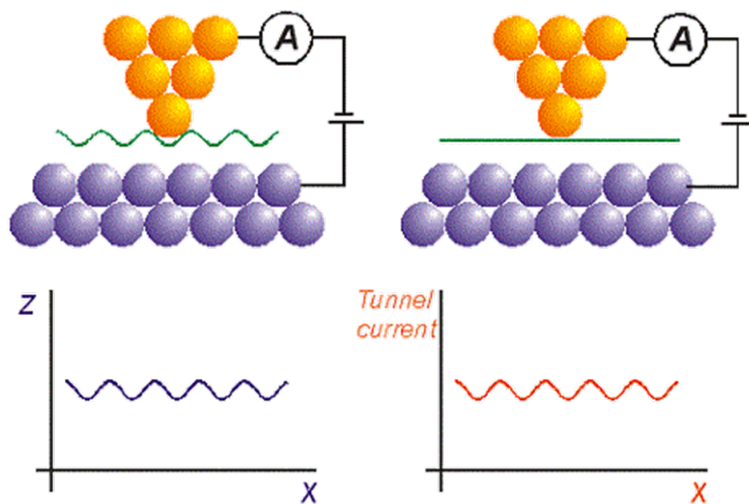
In both scanning modes note that the tunnel current variations depend on the variation of the distribution of electrons (the charge density distribution) at the surface. Thus, although it is tempting to associate each "bump" in an STM image directly with a surface atom, this can sometimes (usually) be a dangerous assumption. The key point to realise is that an STM image is a map of the spatial variation of the distribution of electronic states at the surface. This is not necessarily simply related to the positions of surface atoms<sup>2</sup>.

## 5.5 STM instrumentation

We have thus far discussed the basic concept behind STM, and indeed all scanning probe, imaging: a sharp tip is scanned back and forth across a conducting surface<sup>3</sup>. The tunnel

<sup>2</sup>The interpretation of scanning probe microscope images is far from straight-forward and has led to some rather heated debates. See, for example, [this blog post](#).

<sup>3</sup>The STM is just one of a family of instruments called scanning probe microscopes (SPMs). In each case the imaging process involves the measurement and mapping of a tip-sample interaction. Later in this chapter I'll focus on the atomic force microscope (AFM) but there is a rapidly expanding set of probe microscopies available including electric force microscopy (EFM), magnetic force microscopy (MFM), magnetic resonance force microscopy (MRFM), and scanning capacitance microscopy.

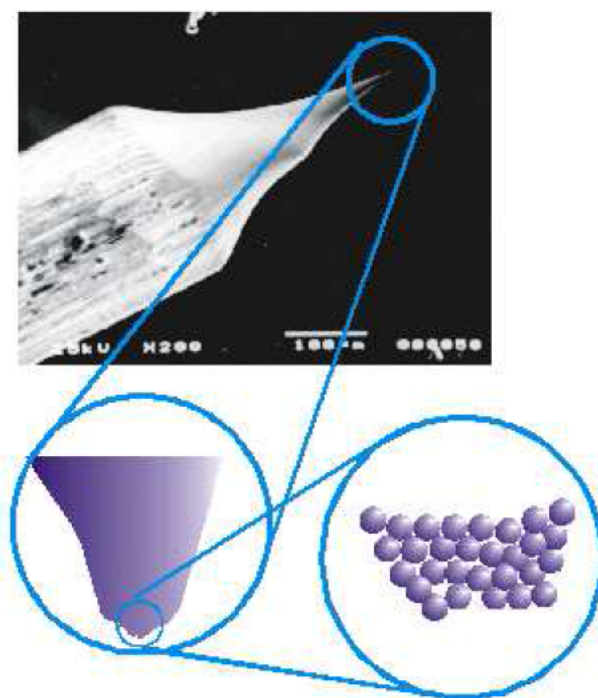


**Figure 5.5** – STM imaging modes. Left: constant current. Right: constant height

current flowing between the tip and sample is measured and, in constant current mode, used to adjust the tip-sample separation to maintain the current at a pre-set setpoint level. Atomic scale imaging involves a lateral resolution of  $\sim 0.1$  nm and vertical resolution in the 1 pm to 10 pm range, coupled with the measurement of nA level currents. These factors place particularly stringent requirements on the design of an STM system. There are four key design elements of an STM that must be considered:

### 5.5.1 Tip preparation

Sharp metallic tips are generally prepared by electrochemical etching. Fig. 5.6 shows a scanning electron microscope (SEM) image of a typical tip produced in the Nottingham Nanoscience group's labs. It is important to realise that due to the exponential relationship between tunnel current and tip-sample separation, all that is required for atomic resolution imaging is that one atom at the end of the tip protrudes slightly more than its neighbours. Thus, although the scanning electron microscope image shown in Fig. 5.6 indicates that the tip has a radius of curvature far in excess of that expected for a single atom termination, this tip produced atomic resolution STM images because, as shown in the schematic "zoom" of the tip, tunnelling occurred from a sharp asperity at the end of the tip.



**Figure 5.6** – A scanning electron microscope image of an STM tip and schematic illustrations of atomic arrangements at the end of the tip.

As the tunnel current falls by approximately an order of magnitude for an increase in tip-sample separation of 0.1 nm, other tip atoms that are more than approximately 0.2 nm distant from the surface than the "primary" tip atom will make a very small contribution to the tunnel current. However, on occasion it is possible that two (or more) tip atoms have very similar distances to the surface resulting in the formation of double-tip image artifacts. In addition, as the tunnel current fundamentally arises from the overlap of the tip and surface electronic wavefunctions, the exact *chemical* structure of the tip can play an important role in atomic resolution STM imaging. Thus, following electrochemical preparation of a tip, it is usually treated in ultrahigh vacuum (by heating or bombardment by ions) to remove contaminants such as oxide and hydrocarbons.

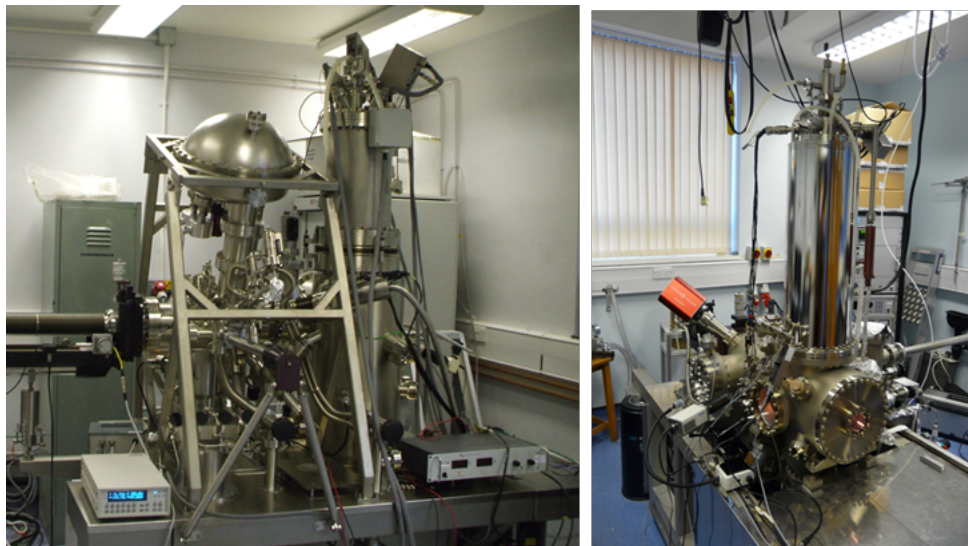
## 5.5.2 Vibration isolation

A vertical resolution of order 1 pm is not uncommon in STM measurements. Achieving this resolution necessitates that the tip-sample spacing is stable to better than the 1 pm level. Typically, floor vibrations have amplitudes of the order of 0.1 to 1 micron - six to seven orders of magnitude greater than the vibration levels we require for STM imaging. To reduce the vibrations at the tip-sample junction to the levels required, a vibration isolation system is used. A number of quite different systems have been used to decouple the STM from external vibrations - in their original design Binnig and Rohrer used magnetic levitation above a superconducting bowl of lead. Much simpler forms of vibration isolation are now used - we will focus on perhaps the most common: spring suspension.

Most modern ultrahigh vacuum (UHV) scanning probe microscopes (see Fig. 5.7 for photos of two of the UHV SPM systems used by the [Nottingham Nanoscience group](#)) use some form of spring suspension system for vibration isolation. A key point to realise is that at or below the resonant frequency of the springs, vibrations will be enhanced instead of being attenuated. Therefore, the resonant frequency of the vibration isolation system should be as low as possible.

The resonant frequency of a spring depends only on the stretched length of the spring - the longer the spring extension the lower the resonant frequency. An appropriate choice of spring constant allows resonant frequencies in the 1 to 5 Hz range to be easily attained. In addition to suspending the STM from springs, it is important to provide a mechanism to damp the vibrations. This generally involves eddy current damping via a combination of Cu plates and strong permanent magnets. Finally, to minimise the degree to which the residual low frequency vibrations from the spring suspension system couple to the STM, the STM unit itself should have as high a resonant frequency as possible. This means that the STM head should be small and rigid. It is also common for a combination of spring suspension and pneumatic feet to be used, with the entire UHV system supported on the pneumatic feet. (This is the case for the systems shown in Fig. 5.7.)





**Figure 5.7** – Photographs of two of the commercial ultrahigh vacuum and low temperature (5 K) scanning probe microscope systems used at the University of Nottingham by the research group of which the author is a member.

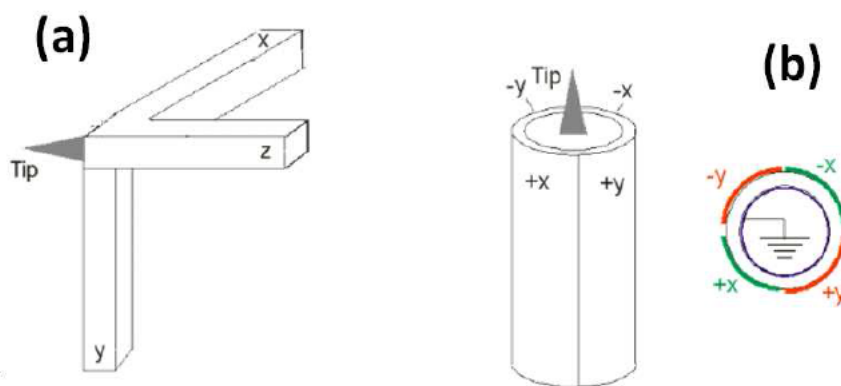
### 5.5.3 Piezoelectric elements

Piezoelectricity arises from the displacement of ionic charges within a crystal. If, when a crystal is strained, a net dipole moment, and therefore electric field, is produced the crystal is piezoelectric. Very small stresses applied to piezoelectrics can generate very large electric fields. Conversely, application of an electric field to a piezoelectric will lead to a deformation of the material. This effect is used in STMs to control the tip position with subnanometre accuracy. The tip is mounted on either a piezoelectric tripod or piezoelectric tube as shown in Fig. 5.8(a) and (b) respectively (although the tripod was common in early designs, the tube scanner is now almost exclusively used in UHV scanning probe microscopes).

### 5.5.4 Feedback loop and computer-based data collection

STM scanning is carried out under computer control. The computer is programmed to carry out the following functions (constant current mode assumed):

- generate the voltage ramps that are applied to the X and Y piezoelectric elements to move the tip in the x and y directions;
- at each point in the scan compute the difference between the measured tunnel current (which may be the result of a number of averages to reduce noise) and the



**Figure 5.8** – Piezoelectric actuators used for tip positioning and scanning in scanning probe microscopes. **(a)** A tripod piezoelectric scanner; **(b)** a tube scanner.

set-point tunnel current and adjust the z-position of the tip accordingly (see below) by applying the appropriate voltage to the z-piezoelectric element.

- represent the voltage applied to the z-piezo (which corresponds to the z-position of the tip) as a shade of grey and plot this on the computer monitor;

## 5.6 Do we *really* see atoms?

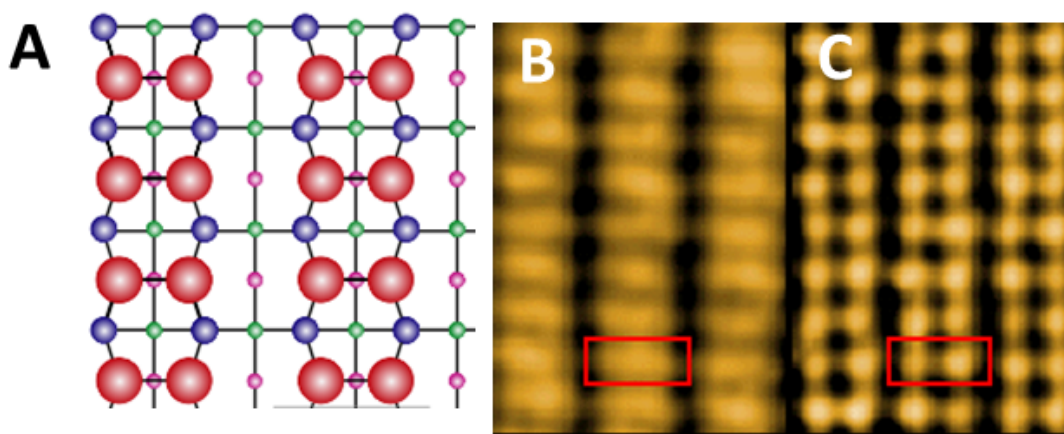
As alluded to above, an important question to address is the relationship between the maxima seen in an atomic resolution STM image and the atomic positions at the surface. Although it is tempting to associate each "bump" in an STM image with the position of a surface atom, this can be a dangerous assumption to make.

An STM image represents the spatial variation in the distribution of electrons at a surface. The distribution of electrons will depend sensitively on the chemistry of the surface and will be determined by the bonding (ionic, covalent, van der Waals, see Chapter 2) of the surface atoms and molecules. In a semiconductor such as silicon, the bonds holding the crystal together are highly directional (and give rise to the regular crystal lattice formed by silicon). When one "cuts through" the crystal to expose a surface, the atoms at the surface will have exposed (dangling) bonds pointing out into the vacuum above the surface (because they no longer have the neighbouring atoms they had in the bulk crystal). This directionality means that the spatial positions of maxima in the electron distribution may not coincide exactly with atomic positions or, depending on the energy of the particular orbital (dangling bond) through which tunnelling occurs, *an atom may not be visible at all in an STM image!*



Importantly, a flow of electrons from the tip to the sample may well involve entirely different orbitals than for the case when electrons flow from the sample to the tip. We can reverse the direction of current flow simply by changing the polarity of the voltage applied to the sample or the tip. Fig. 5.9 shows an example of this type of voltage-dependent STM imaging for a silicon surface<sup>4</sup>. The images shown in Fig. 5.9 are of a small (few nanometres square) region of a particular silicon surface where the atoms at the surface have paired up to form what are termed dimers. In the negative sample voltage image shown on the left the dimers appear as “bean-like” features whereas in the positive sample voltage image on the right the individual atoms of the dimers are apparently visible. (The rectangle on each image highlights an individual dimer). It is importantly to realise that both of the images were acquired in parallel with the same tip so the apparently higher resolution in the image on the right-hand side of Fig. 5.9 is not due to a change in the tip structure. Instead, electrons tunnel from the tip into dangling bonds (electron orbitals) when the sample is positively biased and tunnel from *different* electron orbitals when the

<sup>4</sup>Although you do not need to know this for the *Frontiers* module, or in order to understand the point being made regarding the contrast observed in STM images, this particular surface is designated as Si(100). The (100) notation is known as the Miller index representation of the crystal plane and defines a ‘cut’ in a particular direction through the silicon crystal.



**Figure 5.9** – (A) Section from a schematic ‘ball-and-stick’ model of the arrangement of atoms at a silicon surface. Note how the surface atoms (shaded in red) are paired up into two-atom units. These are called silicon dimers. The dimers are organised in rows (running vertically in this case). Taken from A. Sweetman et al., J. Phys. Cond. Matt. 24 084009 (2012). (B) STM image of silicon dimer rows taken with a negative voltage on the sample. Note how the dimers appear as “bean-like” protrusions. (C) STM image of same dimers as shown in (B) but with a positive sample voltage. Note how a node in the middle of each of the dimers is now visible. This is because the STM is imaging a different probability density distribution in (B) and (C) respectively. Images (B) and (C) are taken from [the website of the Hamers Research Group](#).

sample is negatively biased.

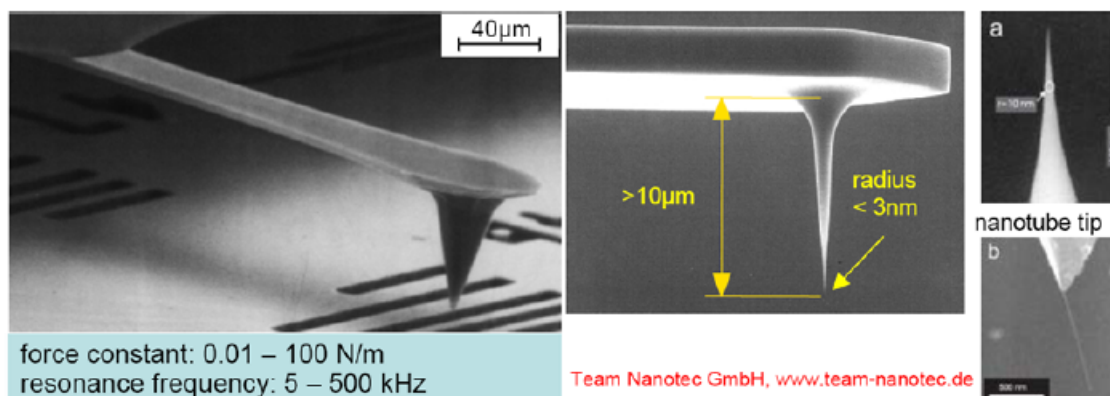
## 5.7 Bonding and anti-bonding orbitals

The previous section asserts that the STM can image different types of orbital but doesn't explain how those orbitals arise. Luckily, however, the key quantum physics (and chemistry!) underpinning the origin of molecular orbitals – and, in particular, the concept of bonding vs anti-bonding orbitals – can be explained on the basis of the finite potential well models we've touched on in Chapter 4 and which you've covered in some detail in “*From Newton to Einstein*”.

Knight's description of the origin of bonding and anti-bonding orbitals is particularly clear. Instead of repeating the discussion in Knight, I urge you to read “The covalent bond” section in the chapter entitled “One-dimensional quantum mechanics” (**p.1347** of “Physics for Scientists and Engineers”). However, I have also put together the following video which adds a little more detail to Knight's description<sup>5</sup>.

Bonding and anti-bonding orbitals.

<sup>5</sup>It's worth noting that one aspect that both Knight and I neglect in our discussion of covalent bonding is the importance of the electron's kinetic energy, i.e. the curvature of the wavefunction. (Remember that the kinetic energy term in the 1D time-independent Schrödinger equation is  $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ ). There's an important comment under the YouTube video linked to above which highlights the importance of wavefunction curvature in bonding.



**Figure 5.10** – Scanning electron microscope (SEM - NB *not* STM!) images of AFM cantilevers and tips. Taken from *Scanning Probe Microscopy: The lab on a tip*, E. Meyer, HJ Hug, and R. Bennewitz, ©Springer (2004).

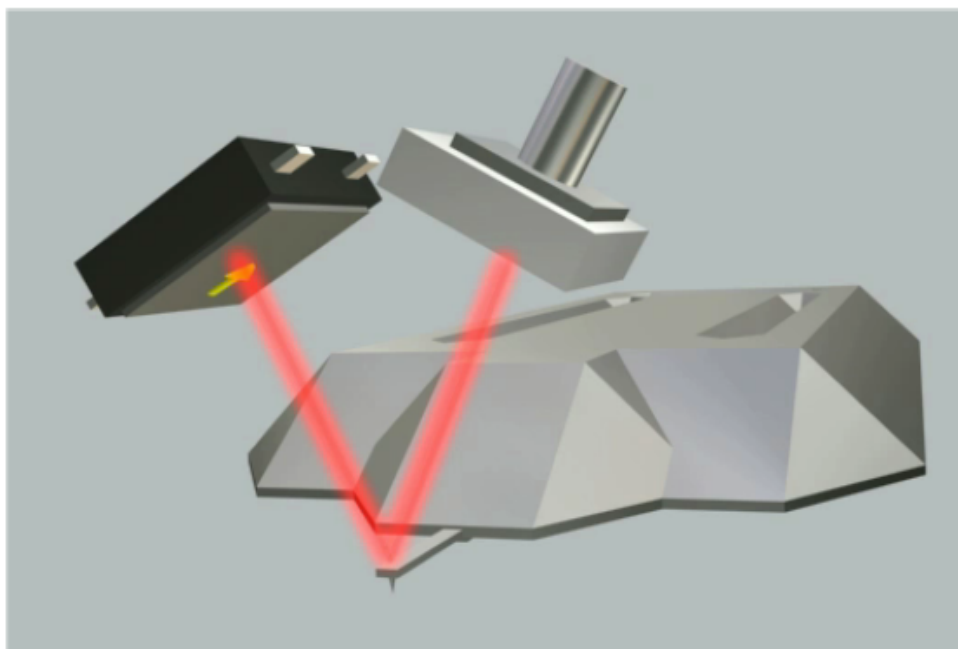
As we’ll discuss in the next section, STM is not the only scanning probe technique capable of atomic resolution. Atomic force microscopy now not only enables atoms to be resolved but, since 2009, is capable of resolving single chemical bonds. Unlike STM, AFM does not rely on a flow of tunnelling electrons.

## 5.8 Atomic force microscopy

The concepts underlying atomic force microscopy (AFM) were developed by Gerd Binnig and co-workers shortly following their invention of the STM at the IBM Zurich research labs (see [this article](#)). Their key motivation was the development of a technique that would enable atomic-scale imaging of *insulating* surfaces. (STM, which relies on the flow of a small electrical current, cannot generally image insulating samples). Instead of using variations in tunnelling current as a probe of tip-sample separation, a tip, mounted on a cantilever (Fig. 5.10), is brought into contact with the sample surface (in the original *contact mode* variant of AFM). The force on the cantilever is related to its deflection via Hooke’s law:  $F = -kx$ , where  $k$  is the spring constant of the cantilever and  $x$  is its deflection. Spring constants for contact mode AFM cantilevers range from a few tens of N/m down to 0.01 N/m. The latter are required for very soft (e.g. biological) samples. (As discussed below, however, there are better methods of probing delicate samples than simply using low spring constant cantilevers for contact mode AFM).

AFM relies on very many of the same advances in instrumentation that underlie the operation of the STM (and which are discussed in Section 5.5 above). The tip and cantilever are scanned across the surface using piezoelectric elements, a feedback loop updates the position of the tip with respect to the sample surface, and the instrument is “shielded” from external vibrations via isolation and damping mechanisms. Where STM and AFM

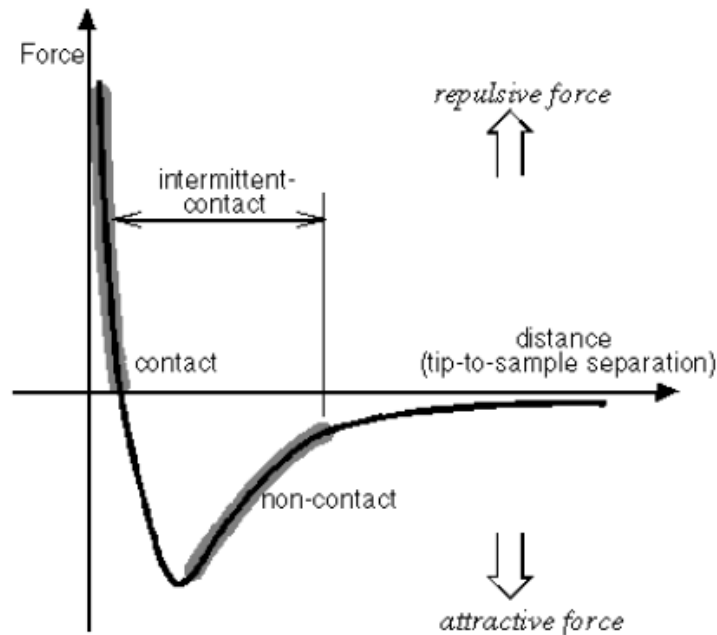
instruments differ lies in the detection of the movement of the tip (and, of course, the fundamental physics giving rise to the tip-sample interaction!). The majority of atomic force microscopes (which operate in air, rather than under (ultrahigh) vacuum conditions) use a laser beam deflection method (see Fig. 5.11) to determine the tip position. There are then two modes of operation: constant force and constant height and these are analogous to the constant current and constant height modes used in STM.



**Figure 5.11** – Illustration of laser beam deflection method. (Taken from <http://virlab.virginia.edu/VL/home.htm>).

## 5.9 Non-contact AFM (aka dynamic force microscopy)

A very important extension of AFM that significantly extends the range of samples and forces that may be studied is non-contact atomic force microscopy. In contact mode AFM, it is the repulsive interatomic forces that are probed via a measurement of the deflection of the cantilever as it is “dragged” across the surface. If, however, we increase the tip-sample separation then we move out of the repulsive interaction regime and the interaction of the tip and sample arises from (weaker) attractive interactions. This is much the same physics as that underpinning the Lennard-Jones (L-J) potential discussed in Chapter 2: at large tip-sample separations (analogous to large interatomic or intermolecular separations for the L-J potential), the tip interacts weakly with the surface due to the van der Waals forces. As the tip-sample separation decreases, the attractive force increases. The tip



**Figure 5.12** – Variation in force as a function of tip-sample separation. Taken from <http://www.mechmat.caltech.edu/index.html>

and sample ultimately reach an equilibrium separation where there is no net force (i.e. the attractive and repulsive forces balance). At tip-sample separations smaller than this equilibrium separation there is a net repulsive force (e.g. in contact mode). Instead of plotting potential, as we have done for the L-J interaction, Fig. 5.12 shows the variation in force (i.e.  $-\frac{\partial U}{\partial z}$ , where  $U$  is the potential) as a function of tip-sample separation.

Imaging via long-range attractive forces - including van der Waals interactions, electrostatic and magnetic forces - significantly reduces the possibility of damaging the surface (and tip) (a substantial problem with contact mode imaging of fragile samples). However, these long range forces are substantially smaller than the short range interactions exploited in contact mode AFM and a different measurement mode is required. To increase the sensitivity to weak attractive forces, the cantilever is vibrated at its resonant frequency. This resonant excitation of the cantilever is at the core of non-contact (also called dynamic) AFM. In the “*From Newton to Einstein*” module you have studied the physics of simple harmonic oscillators and resonant systems, while in your Maths module you have studied the solution of second order differential equations. Both of these modules cover important aspects of the behaviour of damped, driven oscillators such as the cantilever at the heart of every AFM instrument and you should make sure that you understand these underpinning concepts.

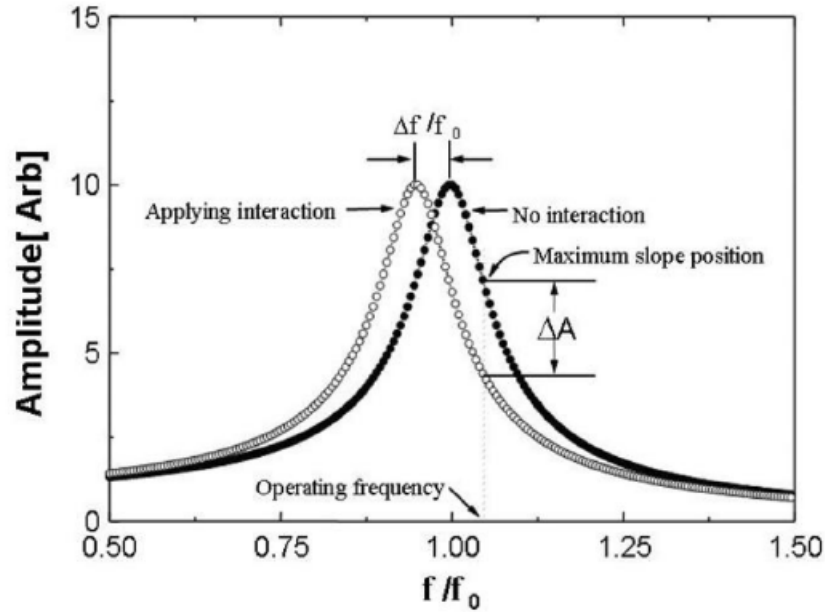
A brief outline of the basic operating principles of the non-contact mode is as follows.

First, the cantilever (with the tip at its end) is vibrated at its resonant frequency ( $\omega_0$ ) using a piezoelectric element while far from the surface (assuming no interaction). As the tip is moved towards the surface, the presence of a force gradient,  $F' = \frac{\partial F}{\partial z}$ , effectively modifies the spring constant of the cantilever so that  $k_{eff} = k - F'$ , where  $k$  is the spring constant of the cantilever in the absence of a tip-sample interaction. The key point is that, as shown in Fig. 5.13, this modification of the spring constant will produce a shift of the resonant frequency of the cantilever to a new value,  $\omega$ , given by:

$$\begin{aligned}\omega &= \sqrt{\frac{k_{eff}}{m}} = \sqrt{\frac{k - F'}{m}} \\ \Rightarrow \omega &= \sqrt{\frac{k}{m}} \sqrt{1 - \frac{F'}{k}}\end{aligned}\tag{5.3}$$

$$\Rightarrow \omega = \omega_0 \sqrt{1 - \frac{F'}{k}}\tag{5.4}$$

where  $\omega$  is the new resonant frequency of the cantilever due to its interaction with the surface and  $\omega_0$  is the original resonant frequency of the cantilever (before the tip



**Figure 5.13** – Shift of resonance curve due to the interaction of the AFM tip with a surface. An attractive interaction leads to a lower value of resonant frequency as compared to the free resonance (i.e. where the tip does not interact with the surface). Compare to the data you may have obtained in the First Year laboratory for the “macroscopic AFM” experiment. Figure ©Park Systems.

interacts with the surface). The majority of you will have carried out the experiment in the 1st year laboratory involving a "macroscopic" demo of an AFM and seen this shift in resonant frequency for yourselves.

In practice, the user first selects an operating resonant frequency,  $\omega_{sp}$ . As the tip moves towards the surface both the shift in resonance frequency and the damping of the cantilevers oscillation due to tip-surface interactions will produce a corresponding change in the amplitude of oscillation measured at  $\omega_{sp}$ . To generate a NC-AFM image using the most common technique adopted in air-based AFMs, the user chooses a setpoint amplitude,  $A_{sp}$ . As the tip is scanned across the surface the feedback loop controls the tip-sample separation so as to maintain the oscillation amplitude constant at  $A_{sp}$ . A NC-AFM image therefore represents a map of a constant force gradient (defined by  $A_{sp}$ ) due to the tip-sample interaction.

### 5.9.1 Quality factor, damping, and the vagaries of vacuum

In ultrahigh vacuum conditions (an environment which is a prerequisite for atomic resolution imaging of a wide variety of samples, due to their reactivity in air), the strategy for NC-AFM imaging described above doesn't work so well. This is because air acts to damp the oscillations of the cantilever. In vacuum, there is insufficient air available for effective damping. This means that the quality of the resonance will be much higher – in other words, the oscillations of the cantilever will take a lot longer to 'die out'.

The effective of higher damping on the resonance curve for a (simulated) cantilever is shown in Fig.5.14. Note how in the lightly damped situation, where it takes of order 500 milliseconds for the oscillations of the cantilever to decay away (after it is excited with a pulse - think of 'twanging' a ruler on the edge of a table), the resonance curve is quite narrow. When the damping is increased (as in Fig. 5.14(B)), the cantilever oscillations in this case fade away about an order of magnitude more quickly ( $\sim 50$  ms) and the resonance curve is much broader<sup>6</sup>

We quantify the quality of the resonance by the width of the resonance curve using a very simple unitless number,  $Q$ .

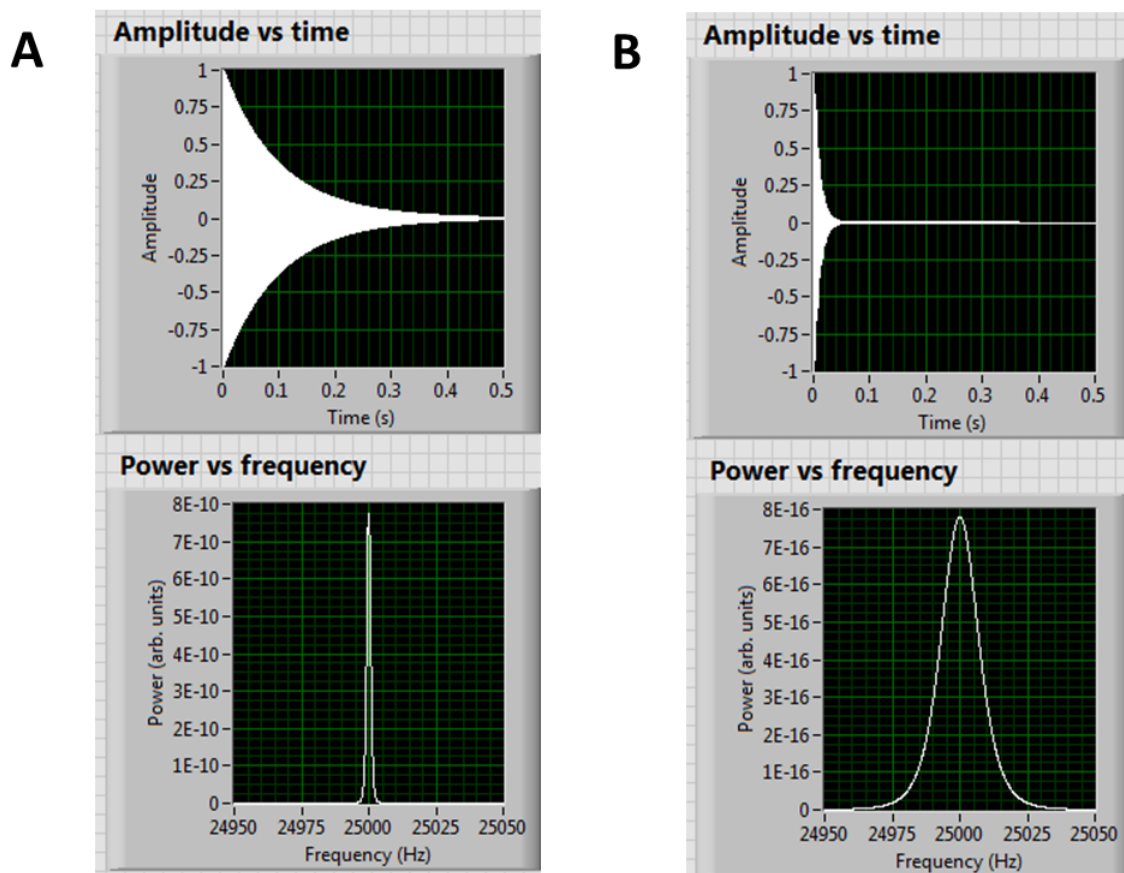
$$Q = \frac{\omega_0}{\Delta\omega} \quad (5.5)$$

where  $\omega_0$  is the resonant frequency of the cantilever (or, indeed, any resonant system) and  $\Delta\omega$  is the full-width-at-half-maximum of the resonance curve. Thus, a broader resonance curve leads to a smaller value of  $Q$ .

---

<sup>6</sup>It is worth highlighting that the reciprocal nature of the cantilever's response in time as compared to its frequency response - i.e. broader in time, narrower in frequency (and vice versa) - is yet another example of the basic mathematics underpinning the uncertainty principle. See [here](#). Note how damping the guitar string in that case similarly broadens the frequency response curve.

Due to the very high quality factor that can be present in vacuum, a different mode of tracking the resonant frequency shift is used. You don't need to worry about the details of this (it's covered in detail in the 3rd year nanoscience modules) - suffice it to say that the frequency itself is directly measured and tracked in vacuum (instead of using a measurement of the amplitude of the cantilever as a "proxy" for tracking the frequency, as described in the previous section and as used for the vast majority of air-based AFMs).



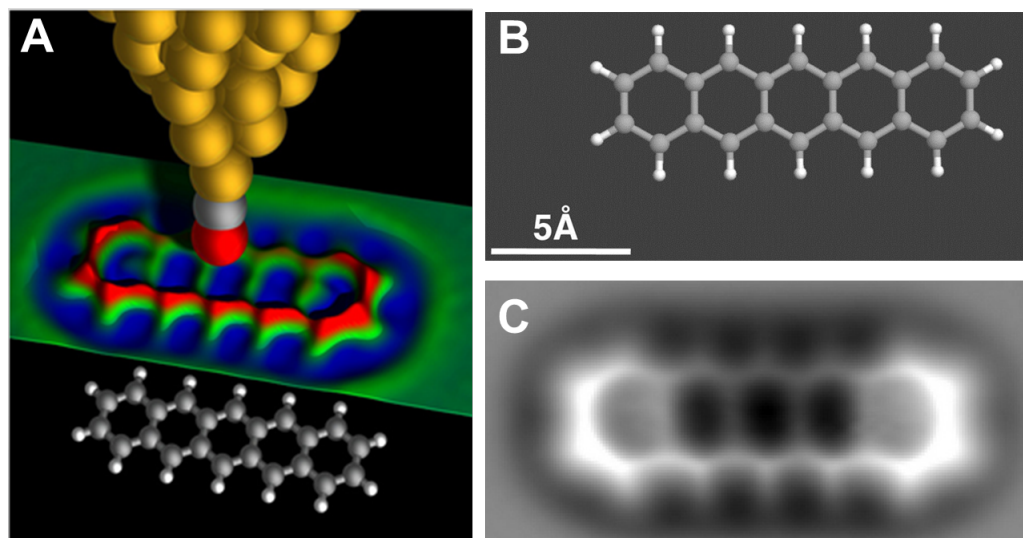
**Figure 5.14** – Comparison of the quality of the resonance for two different levels of damping: (A) low damping, (B) high damping. Note that when the oscillations of the cantilever extend for an appreciable period of time (upper graphs) under conditions of little damping, the resonance curve is narrow (i.e. it spans a smaller range of frequencies). When the damping is high, the oscillations of the cantilever die out much more quickly and the resonance curve is correspondingly wider. (Only the 'envelope' of the cantilever's oscillations are shown; the individual sinusoidal periods of the cantilever motion cannot be resolved in the figure. In addition, the height of the resonance peak reduces significantly in the case of higher damping. I have scaled both peaks in Fig. 5.14 to the same height for better comparison of their widths but it is important to note that that y-axis scaling is significantly different for each).



## 5.10 Resolving single chemical bonds: From nanoscience to picoscience

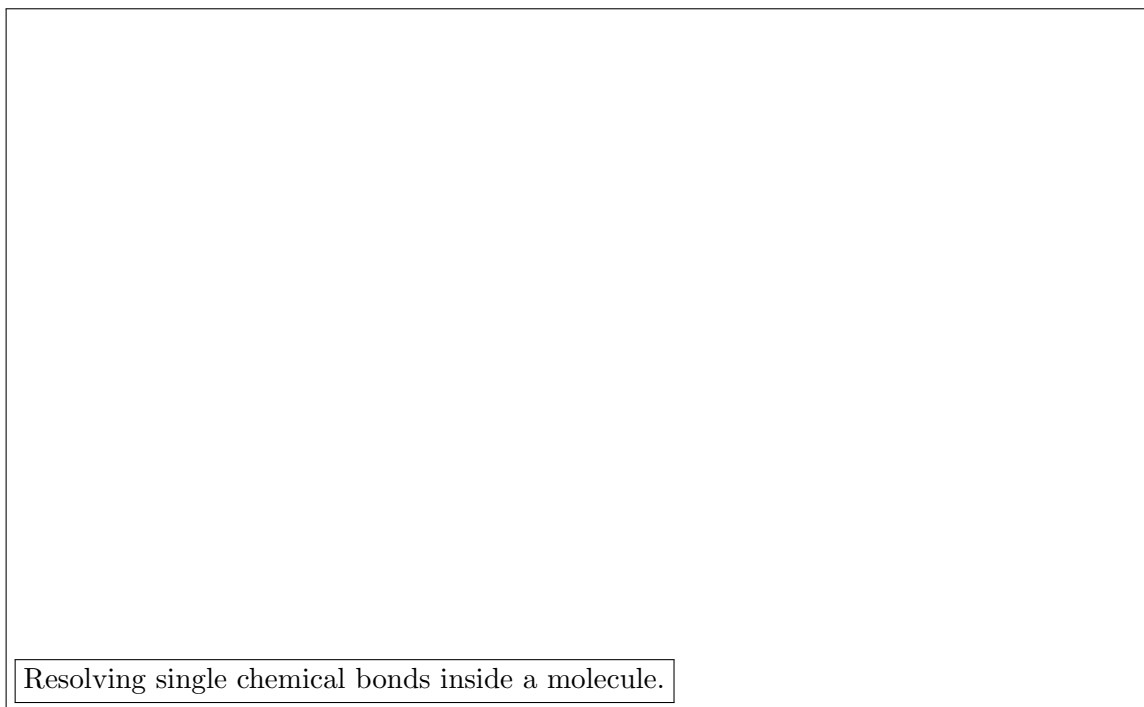
Leo Gross and his colleagues at the IBM research labs in Rüschlikon, Switzerland have pioneered a mode of operation of the dynamic force microscope where not only can single atoms be observed, but individual *bonds* can be resolved. A seminal image resulting from their approach is shown in Fig. 5.15. Note the close, and rather remarkable, similarity of the AFM image to the simple ball-and-stick models of molecules beloved of chemists (and physicists!).

To attain this type of resolution, which has at the time of writing (April 2014) been reproduced by a small, but growing, number of scanning probe groups across the world (including our group at Nottingham), Gross *et al.* had to adopt three key experimental protocols: (i) use of high spring constant cantilevers made of quartz rather than silicon; (ii) rendering the apex of the tip used for imaging chemically unreactive by picking up a molecule (in their case, CO); (iii) reduce the tip-sample separation to the point where the repulsive (Pauli exclusion) component of potential plays a strong role in the interaction.



**Figure 5.15 – Imaging chemical bonds.** (A) The experimental set-up used by Gross *et al.* to image the chemical structure of a pentacene molecule. The tip of an atomic force microscope was deliberately terminated by a CO molecule to render it chemically unreactive and so enable the probe to move extremely close to the molecule without disturbing it. (B) Ball and stick model of the pentacene molecule. Grey circles represent carbon atoms; white circles represent hydrogen atoms. (C) Dynamic force microscope image of a pentacene molecule. Note similarity to (B). Taken from L. Gross *et al.*, *Science* **325** 1110 (2009); ©American Association for the Advancement of Science (2009).

In the following video clip, the researchers themselves explain how they carried out this pioneering experiment.



## 5.11 Atomic manipulation with scanning probes

If you cast your mind back to Chapter 1, right at the outset of this book I discussed K. Eric Drexler's concepts for 'nanofactories' and 'nanobots', incorporating an animation in Section 1.1 of how a nanofactory was perceived to work. I was at pains to stress that the nanofactory concept put forward by Drexler and colleagues was, and remains, science fiction.

But if Drexler's vision of nanotech and atomtech is currently pure science fiction, what is the state-of-the-art in the manipulation of matter at the atomic scale? Scanning probe microscopes enable astoundingly fine control of matter and elsewhere in Chapter 1 I described a few of the key examples, including the work of Don Eigler and his group at IBM (this time in California, rather than Switzerland) on forming quantum corrals and the like.

Just how can STMs and AFMs be exploited to manipulate matter on an atom-by-atom or molecule-by-molecule basis? In principle, it's a straightforward concept and protocol. In practice, it's fiendishly difficult. To push or pull an atom/molecule across a surface one moves from the imaging mode of the instrument, where the interactions with

the sample are weak, to the manipulation mode simply by moving the tip closer to the surface. That's it!

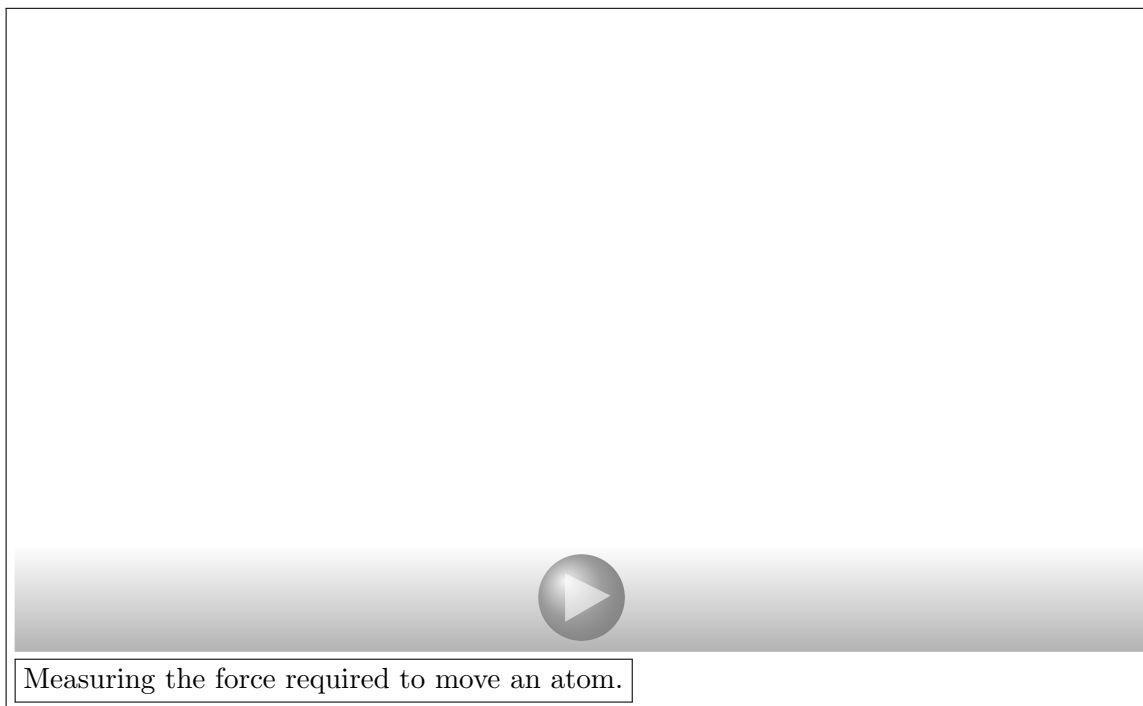
In the imaging mode, the tip is relatively far from the surface. The operator first acquires an STM or AFM image in this mode and identifies an atom or molecule she would like to manipulate. She then zooms in on this atom/molecule and pushes the tip closer to the surface by, for example, increasing the setpoint tunnel current (in STM mode) or the setpoint frequency shift (in AFM mode). The tip is then moved from one position to another on the sample under this higher tunnel current/frequency shift, with the hope that the adsorbed atom or molecule follows the tip trajectory due to the stronger interaction (because the tip is closer to the surface). After the tip has been moved, the tunnel current/setpoint frequency is restored to the original value used for imaging, and another image is taken to check whether the manipulation attempt has been successful.

This process is repeated, with the tip pushed closer to the surface in small increments, until the manipulation event occurs (or until the tip fails and picks up the atom/molecule or otherwise changes its structure).

It is also possible to carry out the manipulation events in constant height mode, pushing the tip closer to the surface by directly changing the tip height until an adsorbed atom or molecule is moved. Indeed, at low temperatures (where thermal drift is less of an issue) and on atomically flat samples this is the preferred procedure.

A variety of different nanostructures, including the Pd particle-in-a-box (i.e. quantum well) structures discussed in Chapter 5, have been fabricated using this type of approach. It is an exceptionally elegant method of manipulating single atoms but, like all scanning probe techniques, the tip is crucial: without a stable tip apex (and this can take days of time to generate) controlled manipulation is exceptionally difficult, if not impossible.

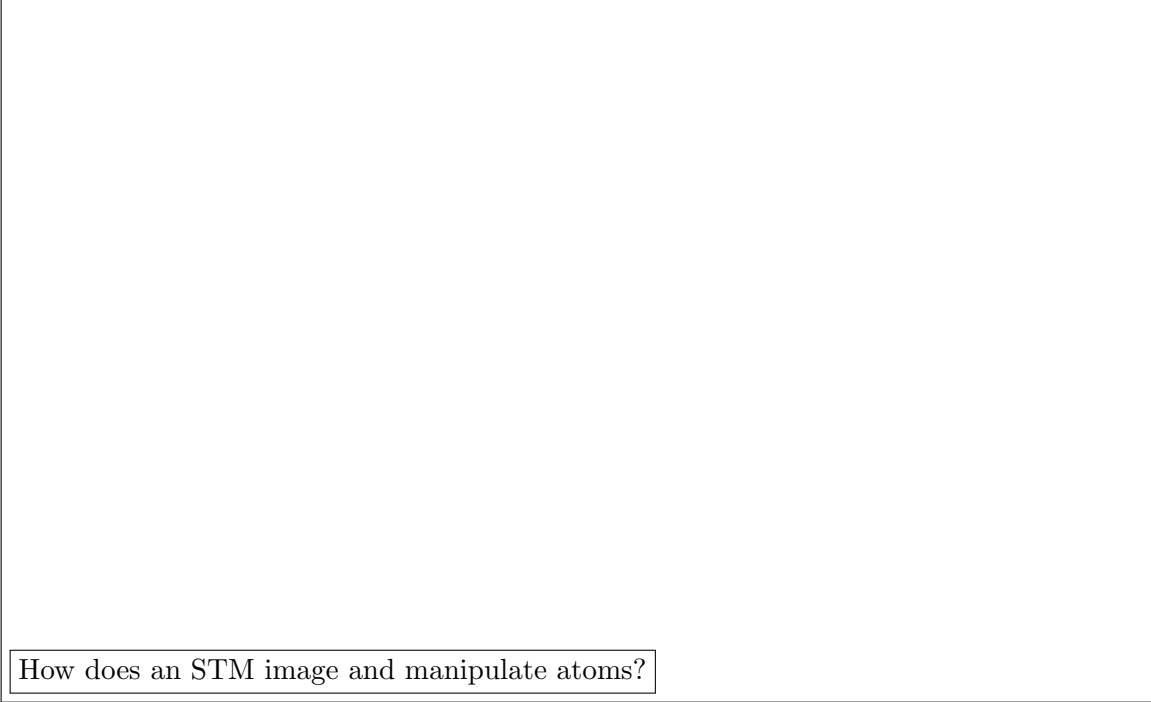
The short video below describes how the force required to move an atom across a surface was determined via atomic manipulation with a dynamic force microscope.



As well as pushing or pulling adsorbates across a surface, scanning probe microscopes can also be used to manipulate single atoms by, for example, picking them up; exchanging atoms between the tip and the surface; and by modifying bond angles. The latter is something that our group here at Nottingham carried out back in 2011 on a silicon surface...



## 5.12 Tutorial video: How does an STM image and manipulate atoms?

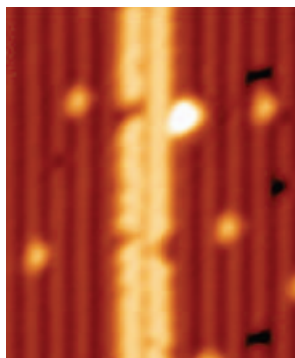


How does an STM image and manipulate atoms?

## 5.13 Problems

**P5.1.** [Taken from the 2011-2012 *Frontiers in Physics* exam paper]. Early in 2012 it was shown that Ohms law applies all the way down to the atomic limit for silicon nanowires [B. Weber et al., *Science* **335** 64 (2012)]. The wires, see Fig. 5.16, were fabricated and imaged using a scanning tunnelling microscope (STM).

- i The wire shown in Fig. 5.16 was created by removing H atoms from the surface of a silicon sample terminated in a single layer of hydrogen. Given that atoms were removed, why does the wire appear bright, rather than dark, in Fig. 1? **{2}**
- (ii) The H atoms were desorbed by an increased flow of electrons tunnelling from the tip into the surface. It was found that a current of 10 nA applied for 100 ms was necessary to desorb a hydrogen atom. Determine the number of atoms removed per electron incident on the surface. **{3}**
- (iii) [NB Note that this part of the question is not part of the examinable syllabus for 2013-2014]. The energy barrier for diffusion of an hydrogen atom along a nanowire is 1.80 eV. Calculate the maximum temperature at which the structure shown in Fig. 5.16 is thermally stable, where stable is defined as a rate of one hop in a ten year period. (Assume that the characteristic vibrational time of a hydrogen atom on the surface is  $10^{-12}$  seconds). [7]



**Figure 5.16** – Atomic wire formed by removal of hydrogen atoms from a H-terminated silicon surface. B. Weber et al., *Science* **335** 64 (2012)

**P5.2** In a scanning tunnelling microscope (STM) experiment on a silicon sample, the tunnel current decreased from 1 nA to 0.1 nA when the tip-sample separation was changed by 0.1 nm.

- (i) Was the tip moved closer to, or further away from, the sample surface? **{2}**

- (ii) Show that the apparent barrier height,  $\phi$ , for the electrons can be written as follows,

$$\phi = \frac{\hbar^2}{8m} \left( \frac{d \ln I}{dz} \right)^2$$

where  $I$  is the tunnel current and  $z$  is the tip-sample separation) {6}.

- (iii) Calculate the value of the apparent barrier height for the electrons tunnelling to the silicon surface {3}.

**P5.3** [Taken from the 2008-2009 *Frontiers in Physics* exam paper.] The tunnel current,  $I$ , flowing between the tip and sample in an STM can be written as:  $I \propto \exp(-2\kappa d)$

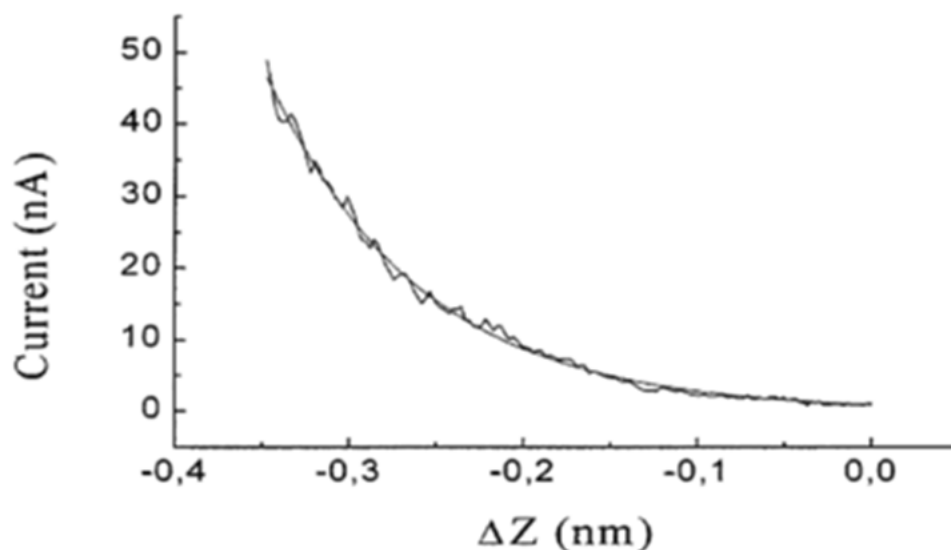
- (i) What quantities do the variables  $\kappa$  and  $d$  represent? {2}
- (ii) Assuming that  $\kappa$  is  $0.1 \text{ nm}^{-1}$ , by what percentage will the tunnel current change for a change in  $d$  of  $0.1 \text{ nm}$ ? {3}
- (iii) The barrier height,  $\phi$ , that a tunnelling electron “sees” in an STM measurement can be determined from the following formula:

$$\phi = \frac{\hbar^2}{8m} \left( \frac{d \ln I}{dz} \right)^2$$

where  $I$  is the measured tunnel current and  $z$  is the tip-sample separation.

Figure 5.17 is a graph of the variation in tunnel current observed as the tip of an STM was moved towards a metal surface. From this graph, estimate the barrier height,  $\phi$ , for the electrons. {7}





**Figure 5.17** – Graph of the variation in tunnel current measured as a function of the change in separation between an STM tip and a metal surface. Data taken from B. Grandier *et al.*, *Appl. Phys. A* **66** S977 (1998), ©Springer-Verlag 1998.

**P5.4** [Taken from the 2008-2009 *Frontiers in Physics* exam paper.] An iconic nanoscience image is that of the IBM logo generated by manipulating individual Xe atoms on a nickel surface using a scanning probe microscope. In 2008, almost two decades following the IBM logo demonstration, the force required to move an individual atom on a surface was measured using a non-contact atomic force microscope (NC-AFM). A resonance curve for an NC-AFM cantilever is shown in Fig. 5.18.

- (i) What is the resonant frequency and quality factor ( $Q$ ) of the cantilever whose resonance curve is shown in Fig. 5.18? **{2}**
- (ii) The Lennard-Jones potential is commonly used to model the pair potential for atoms interacting via van der Waals forces. It is thus particularly suited to inert gases such as the Xe atoms used in the IBM experiment. A simple expression for the Lennard-Jones potential as a function of separation  $r$ ,  $U(r)$ , is as follows:

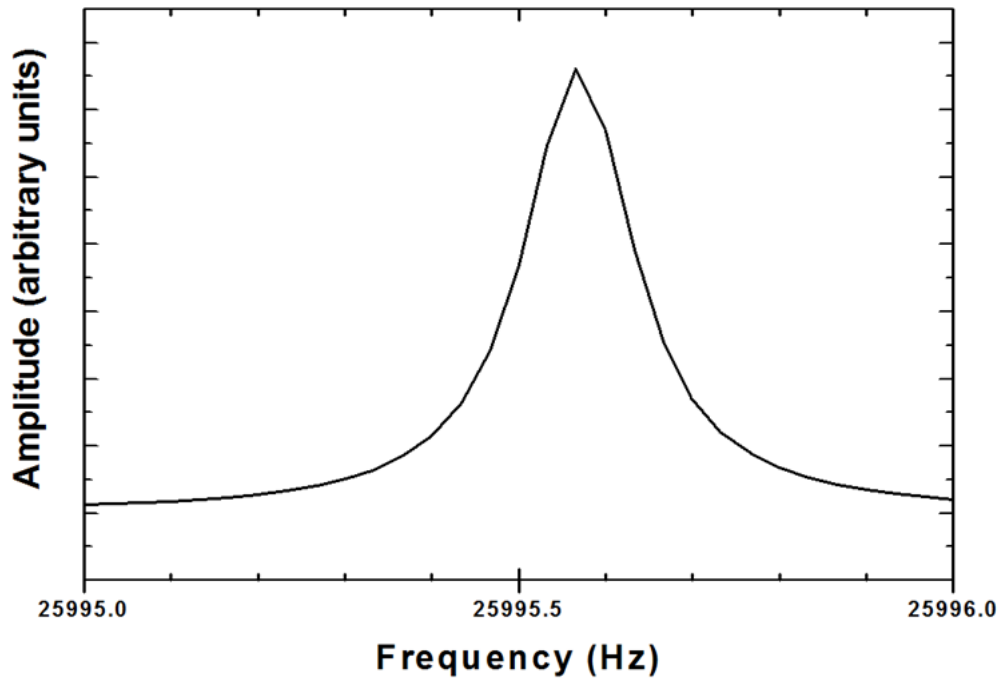
$$U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

The Lennard-Jones potential parameters for Xe are  $\epsilon = 3.05 \times 10^{-21}$  J and  $\sigma = 3.96 \times 10^{-10}$  m. Show that the equilibrium separation and binding energy of the two Xe atoms are  $4.45 \times 10^{-10}$  m and 19 meV respectively. **{6}**

- (iii) The effective spring constant (or stiffness) of the Xe-Xe interaction can be estimated (for small displacements from equilibrium) from the following formula:

$$k = 72 \frac{E_B}{r_0^2} \quad (5.6)$$

where  $E_B$  is the binding energy and  $r_0$  is the equilibrium separation. The reduced mass of the  $\text{Xe}_2$  molecule is  $1.09 \times 10^{-25}$  kg. What is the resonant frequency of the  $\text{Xe}_2$  molecule?**{2}**. Explain whether you would expect the resonant frequency for covalently bonded atoms (such as Si-Si) to be higher or lower than that for the  $\text{Xe}_2$  molecule.**{1}**



**Figure 5.18** – Resonance curve for an AFM cantilever.

**P5.5** In 2012, Joachim Welker and Franz Giessibl at the University of Regensburg reported the measurement of the chemical bond formed between an atom at the end of a dynamic force microscope tip and a CO molecule adsorbed on a copper surface (see Fig. 5.19 for an illustration of the experimental configuration)<sup>7</sup>.

Welker and Giessibl fitted their experimental force microscopy data to a Morse potential,  $V_M$ , of the following form:

$$V_M(z) = E_{bond} \left[ -2 \exp \left( -\frac{(z - \sigma)}{\lambda} \right) + \exp \left( -\frac{2(z - \sigma)}{\lambda} \right) \right] \quad (5.7)$$

where  $z$  is the atom-molecule separation and  $\lambda$  is the decay length of the interaction. Take  $E_{bond}$  to be 37 meV.

- (a) For  $z$  values ranging from 100 pm to 800 pm, and with  $\sigma=220$  pm, use MATLAB to plot<sup>8</sup>  $V_M(z)$  for  $\lambda=100$  pm. **{5}**. What does  $\sigma$  in the expression for  $V_M(z)$  physically represent? **{1}**
- (b) How does the decay of the interaction with separation for the repulsive component of the potential compare to that for the attractive component? **{2}**
  - (i) Starting from the expression for  $V_M(z)$  above, analytically determine an expression for the tip-sample force as a function of  $z$  **{4}**. Graph this function in MATLAB (in a new plot window) for the same range of  $z$  and value of  $\lambda$  as used for P5.5(a) **{2}**.
  - (ii) Use the gradient function in MATLAB (check the Help files<sup>9</sup>) to numerically differentiate  $V_M(z)$ . Graph the function  $dV_M/dz$  on the same MATLAB plot (i.e. on the same graph axes) as for the graph for P5.5(b)(i). **{4}**
  - (iii) Use the MATLAB graph to find the maximum attractive force (in nanoNewtons). **{2}**
- (c) A dynamic force microscope does not provide a direct measurement of interatomic forces. Instead, the frequency shift of the cantilever is measured, which, under the appropriate operating conditions (as was the case for the study of Welker and Giessibl), is linearly proportional to the force gradient between the atom terminating the tip and the underlying atom(s).

The frequency shift is related to the force gradient as follows:

$$\Delta f = -\frac{f_0}{2k} \frac{dF}{dz}$$

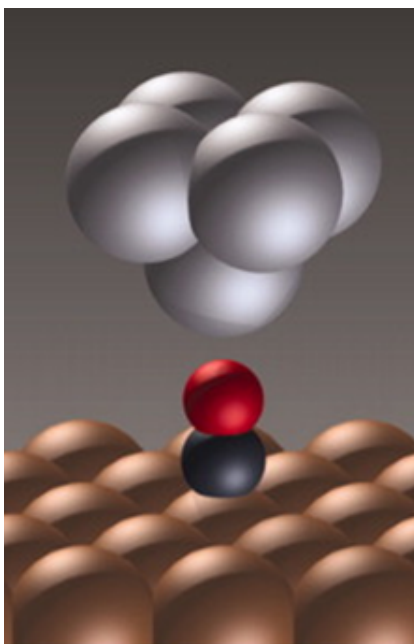
---

<sup>7</sup>This question currently forms part of the coursework for the *Frontiers* module and thus numerical solutions are not given at the end of the book

<sup>8</sup>You should ensure that the values of  $z$  are equally spaced. Use at least 200 points.

<sup>9</sup>You will need to use syntax of the following form: `gradient(F, delta_z)` where  $F$  is the vector you wish to differentiate and  $delta\_z$  is the separation of the  $z$  values.

where  $f_0$  and  $k$  are the resonant frequency of the cantilever in the absence of any interaction with the surface, and the cantilever spring constant, respectively. Assuming that the frequency shift in the experiment arises only from the Morse interaction potential, and taking  $f_0 = 25$  kHz and  $k = 1800$  N/m, use MATLAB to plot the frequency shift vs tip-sample separation curve{3}. What is the value of the frequency shift measured when the tip-sample separation is  $\sigma$  (i.e. 220 pm)?{2}



**Figure 5.19** – Illustration of the experimental configuration used to measure the symmetry of a chemical bond. [From J. Welker and FJ Giessibl, *Science* **336** 444 (2012); ©American Association for the Advancement of Science (2012)]

# Chapter 6

## Atoms and molecules in motion

*Every body continues in its state of rest or uniform motion in a straight line,  
except insofar as it doesn't.*

Arthur Stanley Eddington (1882-1944)

### 6.1 The nanofactory revisited: Brute force vs self-assembly

All the way back in Chapter 1 we discussed and dissected the concept of the nanofactory/molecular assembler. Now that we've covered scanning probe-based imaging and manipulation of matter at the atomic level in some depth (in Chapter 5), it's worth doing a simple back-of-the-envelope estimate of just how long it would take a scanning probe to make a macroscopic (or, indeed, microscopic) object.

Let's say that we can carry out a given atomic manipulation event (i.e. pick, push, pull, place, or otherwise move a single atom) in 1 second. This is an extremely optimistic estimate given current technology but let's use it as a baseline order of magnitude figure. An illuminating question to ask is just how long it would take to 'build' a single atomic layer of atoms, 1 cm x 1 cm in area. Given that a typical surface atom number density is  $10^{15} \text{ cm}^{-2}$  then it's clear that it would take of the order of  $10^{15}$  seconds to fabricate a monolayer via 'brute force' atom-by-atom manipulation. For comparison, the age of the universe is  $\sim 10^{17}$  seconds. (And, remember, that 1-second-per-operation estimate was wildly optimistic...)

Of course, the nanofactory doesn't rely on just one tip – the fabrication speed is improved dramatically (at least in principle and in the computer simulations – remember

---

PowerPoint slides associated with this chapter are available [here](#).

that a nanofactory doesn't exist!) via the parallel operation of very many tips or molecular tools. Nature can generate an atomic layer in times much, much smaller than  $10^{15}$  seconds using a similar type of "parallelisation" but without any need to direct the trajectories of the atoms – a flux of atoms 'raining' down on a surface will very often spontaneously *self-assemble* into a complete layer on a time scale of seconds, rather than billions of years. In this chapter we'll cover some of the basic principles underpinning self-assembly, with a particular focus on atomic and molecular diffusion.

## 6.2 The crystal maze

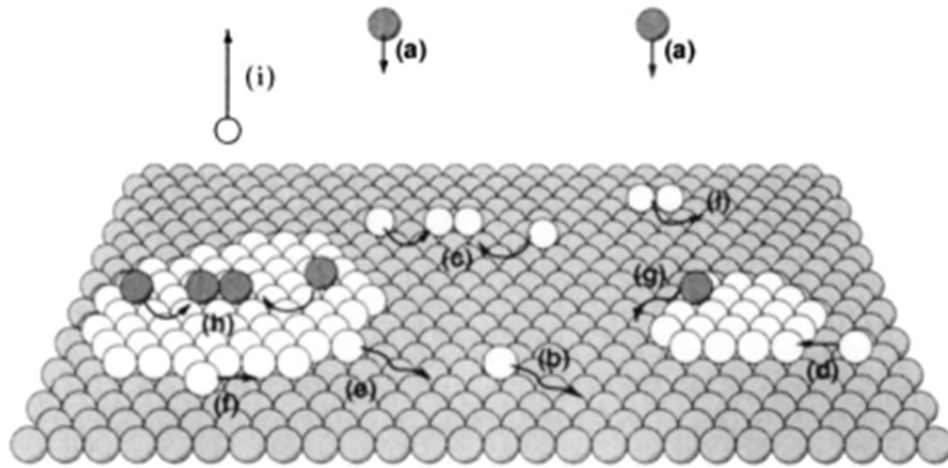
There are very many ways of 'growing' crystals. We'll focus on just one method: epitaxial<sup>1</sup> growth in vacuum using a beam of atoms or molecules incident on a surface. Fig. 6.1 below (taken from Ratsch and Venables, J. Vac. Sci. Tech. A 21 S96 (2003)) depicts the essential processes underpinning this type of crystal growth, *viz.*

- (a) Deposition and **adsorption**<sup>2</sup> of an atom/molecule. Note that the interatomic/intermolecular potential energy curves we discussed at length in Chapter 2 are of key importance in adsorption processes.
- (b) **Diffusion** across the surface, where an atom hops from site to site. We will consider this process in detail later in this chapter.
- (c) **Nucleation**. This is where a diffusing atom binds to another atom at the surface, often forming a stable 'nucleus' or 'seed'. This nucleation process is the first step in the growth of an island and, subsequently, a layer of atoms. Many nucleation events of this type can happen across the surface.
- (d) **Attachment**. Atoms attach to a 'seed' and an island grows. Generally, atoms want to form bonds – this lowers the energy of the system. (Again, consider the interatomic/intermolecular potential energy curves discussed in Chapter 2). An atom in an island (particularly in the centre of an island!) is much more highly coordinated (i.e. has a greater number of neighbouring atoms) than an isolated atom at the surface, or, indeed, an atom at the edge of an island.
- (e) **Detachment**. Statistics plays an essential role in crystal growth. Although there is a strong energetic preference for the attachment of an atom to a growing island, there is also a finite – and, at relatively high temperatures, rather large – probability for an atom to detach. It is the balance of atomic fluxes onto, and away from, an island which determines not only the growth rate but the degree of order of the island. In the

---

<sup>1</sup>Epitaxy is the growth of a crystalline layer on top of a crystalline surface

<sup>2</sup>Adsorption refers to the binding of atoms and/or molecules to a surface. It is a distinct process from *absorption*, which involves interaction with the bulk volume, rather than surface, of a material/substance.

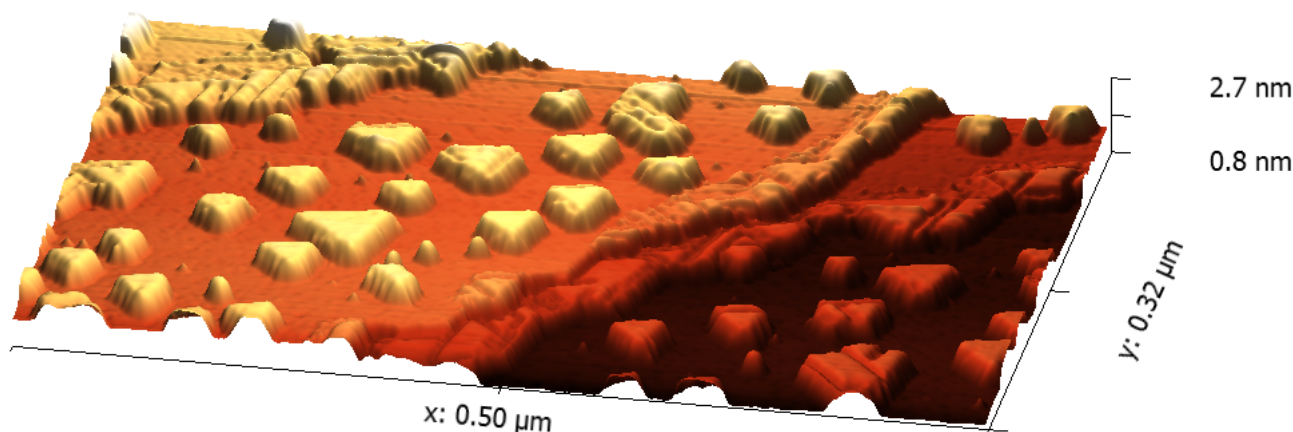


**Figure 6.1** – Key processes in the growth of a crystalline layer (or thin film) from an atomic or molecular beam. Each of the processes shown schematically as (a) - (i) is described in the main text. Figure taken from Ratsch and Venables, *J. Vac. Sci. Tech. A* 21 S96 (2003). ©American Institute of Physics (2003).

following section we'll see a particularly fascinating example of what happens when the detachment rate is effectively zero – i.e. when an atom binds to a neighbour, it is locked in place and cannot detach. This is called the “hit and stick” mechanism of growth.

- (f) **Edge diffusion.** An atom does not have to detach entirely from an island (as in process (e) above). Instead, it can diffuse around the edge of an island.
- (g) **Diffusion across a step** An atom can diffuse across the top surface of an atomic island and, when it reaches the edge, can diffuse onto the lower terrace. There is an additional energy barrier associated with this process because the atom has fewer neighbours as it crosses the step, as compared to when it diffuses across a flat surface.
- (h) **Second layer nucleation.** Atoms can also nucleate on the top of an island, leading to three-dimensional growth.
- (i) **Desorption.** Just as atoms can both attach and detach to/from a growing island, they can adsorb (as in process (a)) and desorb. The rate of desorption depends critically on the balance of the atomic binding energy and the temperature.

Scanning probe microscopy is an extremely powerful technique for the analysis of crystal growth as it can not only provide atomic-level detail on the structure of a sample but, under well-controlled conditions, track individual diffusing atoms and molecules. Fig. 6.2 is an STM image from the Nottingham Nanoscience group (courtesy of Dr. Philipp



**Figure 6.2** – Scanning tunnelling microscope image of calcium fluoride islands on a Si(111) surface which have epitaxially grown via the processes sketched in Fig. 6.1. Image courtesy of, and ©Dr. Philipp Rahe, University of Nottingham (2015).

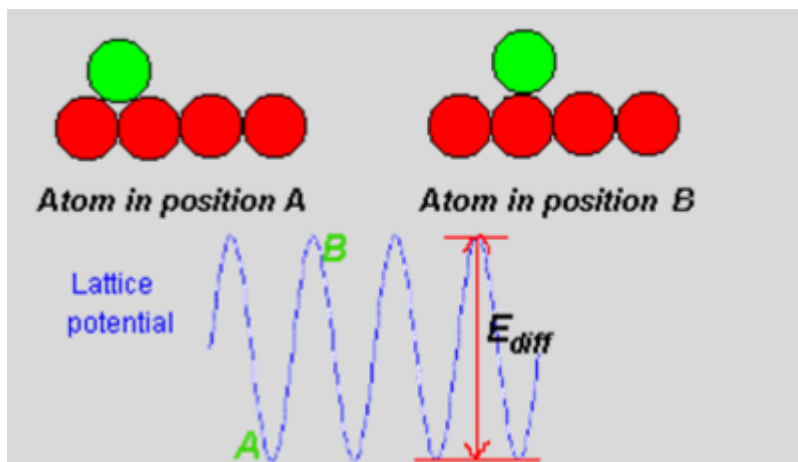
Rahe) which shows the nucleation and growth of islands of calcium fluoride on a silicon surface. All of the processes depicted in Fig. 6.1 have worked in concert to produce the island shapes and overall morphology of the calcium fluoride film.

### 6.3 Crossing the barrier: atomic and molecular diffusion

Atomic diffusion (i.e. process (b) in Fig. 6.1) is exceptionally important throughout not just nanoscience but in practically all science. We’ve already discussed diffusion in Chapter 3 (Section 3.4). Here, however, we’ll look at the atomistic detail in rather more depth, with a particular focus on the question of the diffusion barrier and its relationship to the rate at which adsorbates diffuse across a surface. The very simple diagram shown in Fig. 6.3 captures the key mechanism underpinning atomic (or molecular) diffusion on a surface. In this case we consider only a 1D variation of potential energy, but the concept is just as valid in two or three dimensions.

In Position A, the adsorbed atom interacts with its two nearest neighbours – which, depending on the system, could be via van der Waals, ionic, and/or covalent bonds, for example – and is associated with a relatively high binding energy. If the adsorbed atom moves either left or right it would experience exactly the same binding configuration (and this would have precisely the same binding energy). However, there is an energy barrier to surmount in order for the adsorbed atom to move between those equivalent binding positions. This barrier arises because the diffusing atom must move through a





**Figure 6.3** – Simple schematic diagram of the origin of the diffusion barrier. When in Position A, the diffusing atom is in a lower energy state. It needs to surmount an energy barrier to move from one site to another. This involves passing through position B where the atom is in a higher energy (i.e. less preferred) state.

configuration where it is much less favourably bonded. This means that its binding energy is lower and so there is a barrier it must surmount (the difference in energy for positions A and B) in order to diffuse.

Where does the atom get the energy to surmount the barrier? That energy comes from the thermal vibrations of its environment (and of the atom itself). There is thus a strong dependence of the diffusion coefficient of the atom – or, in more atomistic terms, the hopping rate of the atom (i.e. the rate at which it hops from atomic site to atomic site) – on not just the size of the energy barrier but the temperature. Indeed, the hopping rate,  $\nu$ , depends exponentially on the ratio of the energy barrier ( $\Delta E$  or  $E_{diff}$ ) and the temperature, i.e.

$$\nu \propto \exp(-\Delta E/kT) \quad (6.1)$$

where  $k$  is Boltzmann’s constant (which ‘converts’ between temperature and energy and thus must be included so that the exponent in Eqn 6.1 above is dimensionless). It is very important to note that Eqn 6.1 is not restricted to the case of atoms or molecules diffusing on a surface. It is a key result in statistical mechanics which stems from an analysis due to Boltzmann. As such, the  $\exp(-\Delta E/kT)$  term is known as a *Boltzmann factor* and this type of exponential dependence crops up repeatedly in a wide variety of diverse and (apparently) disparate systems. (You’ll see *much* more on the statistical physics underpinning Boltzmann factors and diffusion next year).

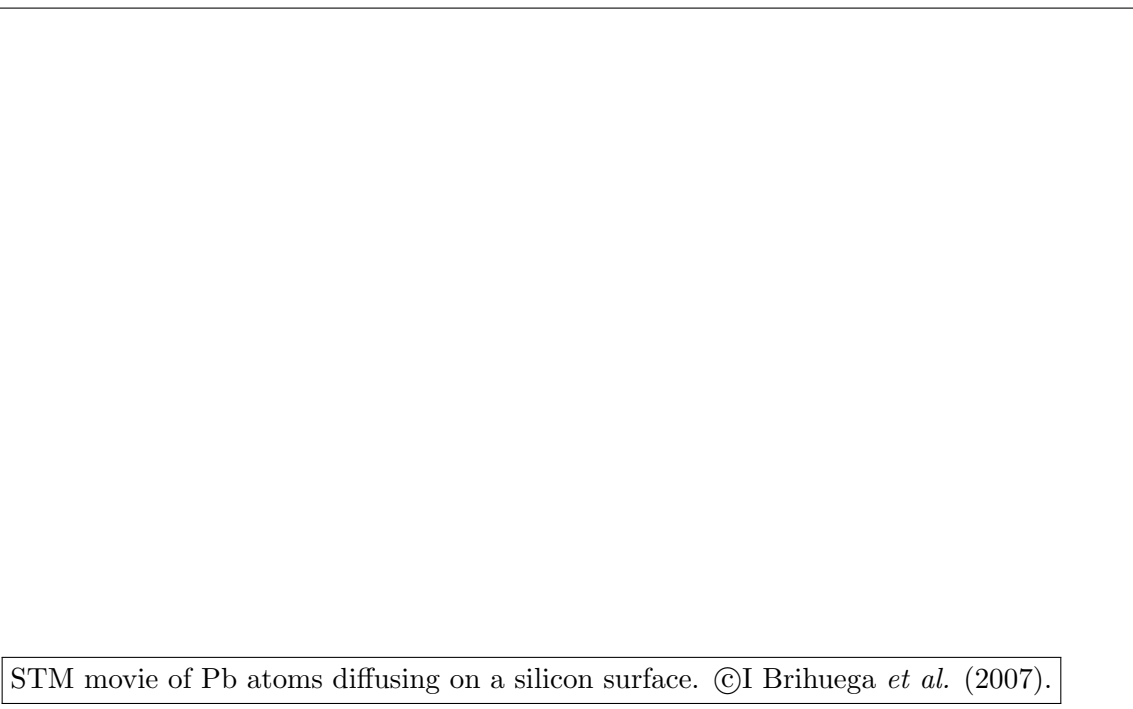
The constant of proportionality for Eqn 6.1 is known as the diffusion pre-factor or the attempt frequency and is related to the vibrational frequency of the atom within the

potential well<sup>3</sup> The prefactor is written as  $\nu_0$  and so Eqn 6.1 becomes:

$$\nu = \nu_0 \exp(-\Delta E/kT) \quad (6.2)$$

The energy barrier (i.e. the diffusion barrier),  $\Delta E$  is also often written as  $E_{\text{Diff}}$  or  $E_{\text{D}}$ . This exponential dependence of the hopping rate on both the energy barrier and temperature is known as *Arrhenius behaviour*.

The movie below shows a series of STM images of Pb atoms diffusing on a silicon surface<sup>4</sup>. The STM can directly measure the hopping rate per second (when the hopping rate is sufficiently slow) and from this, and knowledge of the sample temperature, the diffusion barrier can be determined.



---

<sup>3</sup>Remember that the uncertainty principle means that even at 0 K – *if* we could ever reach 0 K (which we can't) – there is atomic and molecular vibration. This is known as the zero point energy.

<sup>4</sup>Taken from I. Brihuega et al., *Phys. Rev. Lett.* **98**, 156102 (2007)

## 6.4 Worked Problem: Tracking Diffusion

One issue with tracking the motion of atoms and molecules by doing complete scans of a surface area with an STM is that this strategy is very slow; the microscopist spends a great deal of time scanning other features of the surface instead of following the diffusing atom/molecule of interest. A clever method of circumventing this problem to follow diffusion events directly with the STM (or any scanning probe microscope) was developed by Brian Swartzentruber at Sandia National Laboratories in the US in 1996 [BS. Swartzentruber, *Phys. Rev. Lett.* **76**, 459 (1996)].

In addition to conventional STM feedback, which controls the  $z$  position of the tip, lateral  $(x, y)$  feedback was used to ‘lock onto’ (i.e. hold the tip above) an individual diffusing atom. By monitoring the position of the tip as a function of time, the trajectory of the diffusing adsorbate can be obtained. The key advantage of this atom-tracking technique is that it increases the measurement bandwidth (i.e. the rate at which measurements can be taken) by up to three orders of magnitude.

**P6.1** The following data were extracted from atom tracking measurements of the diffusion of a silicon molecule ( $\text{Si}_2$ , i.e. a silicon dimer) on a silicon surface [BS Swartzentruber, *Phys. Rev. Lett.* 76, 459 (1996)].

Temperature (C)	Hopping rate
22	0.001
45	0.003
65	0.07
125	10

Plot an appropriate graph **{6}** and thus determine the diffusion barrier **{2}** and diffusion prefactor **{2}** for  $\text{Si}_2$  on the surface.

We know that the hopping rate is related to the temperature as follows (i.e. Eqn 6.1),

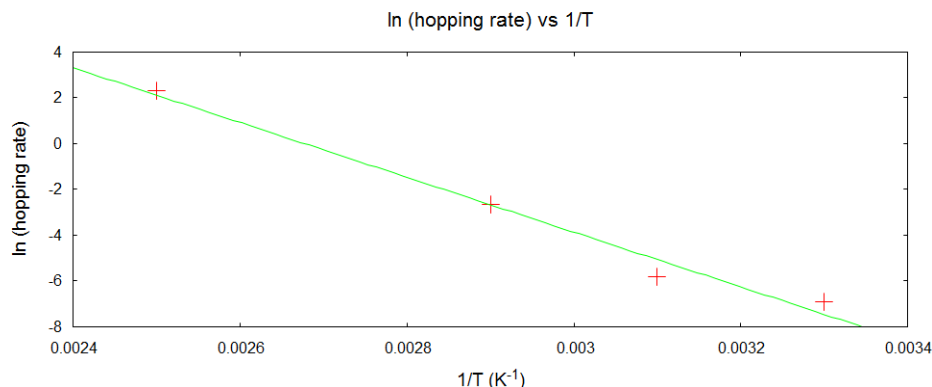
$$\nu = \nu_0 \exp(-\Delta E/kT)$$

We can linearise this equation by taking logs of both sides, which gives us:

$$\ln \nu = -\Delta E/kT + \ln \nu_0 \quad (6.3)$$

So a graph of  $\ln \nu$  vs  $1/T$  (Fig. 6.4) has a slope of  $-\Delta E/k$  and an intercept of  $\ln \nu_0$ .

The fit to the data points yields a value for  $\Delta E$  of 1.03 eV and a prefactor of  $8.4 \times 10^{13}$  Hz.



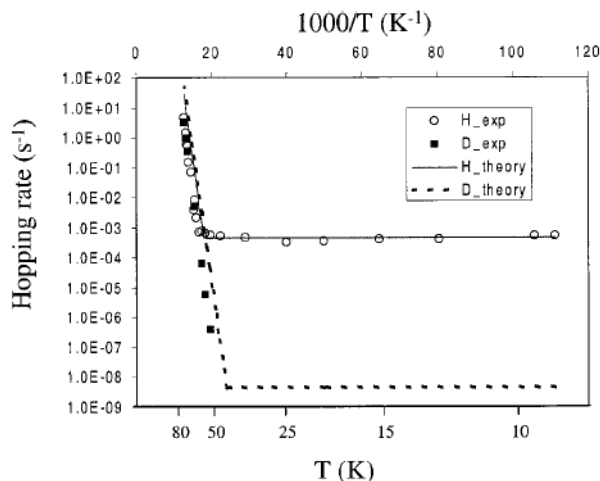
**Figure 6.4** – A graph of the log of the hopping rate of  $\text{Si}_2$  on a silicon surface vs inverse temperature. The slope and intercept of this graph can be used to find the diffusion barrier and prefactor, respectively.

## 6.5 Tunnelling rather than hopping?

Thus far, we have considered that an adsorbate diffuses (‘hops’) from site to site by acquiring enough thermal energy to surmount the diffusion barrier. In Chapter 5, however, we covered the process of quantum mechanical tunnelling *through* a barrier. A fascinating question arises: can diffusing atoms tunnel? Importantly, even the smallest atom, hydrogen, has a mass which is nearly 2,000 times larger than that of an electron. Equation 5.2 in Chapter 5 shows that the inverse decay length,  $\kappa$ , of the wavefunction depends on the square root of the mass. As the probability for tunnelling depends exponentially on  $\kappa$ , it is clear that even small changes in mass will have a very strong influence on the ability of a particle to tunnel. Compared to an electron, it is *much* more unlikely that an atom will tunnel<sup>5</sup>.

Nonetheless, in a landmark and very elegant STM experiment in 2000, Lauhon and Ho measured the hopping rates for hydrogen (H) and deuterium (D) on a copper surface [Phys. Rev. Lett. **85** 4566 (2000)]. The results are shown in Fig. 6.5. Note the very strong deviation from the behaviour predicted by Eqn. 6.2 for hydrogen (the experimental data are the open circles in the graph). Below approximately 50 K, there is no dependence of the hopping rate on temperature. The hydrogen atom is not being thermally activated below 50 K, i.e. it is not diffusing by acquiring enough thermal energy to cross the diffusion barrier; *it is directly tunnelling through the barrier!* Deuterium does not show the same behaviour in the experiment due to its higher mass (twice that of hydrogen) and thus lower tunnelling probability. (Note that the hopping rate of  $\sim 5 \times 10^{-9}$  Hz in the tunnelling

<sup>5</sup>It is important to note, however, that the simple 1D model of tunnelling described in Chapter 5 is exactly that – a highly simplified model. It can provide insights into the tunnelling process but cannot be expected to provide precise quantitative agreement for a ‘real world’ tunnelling process.



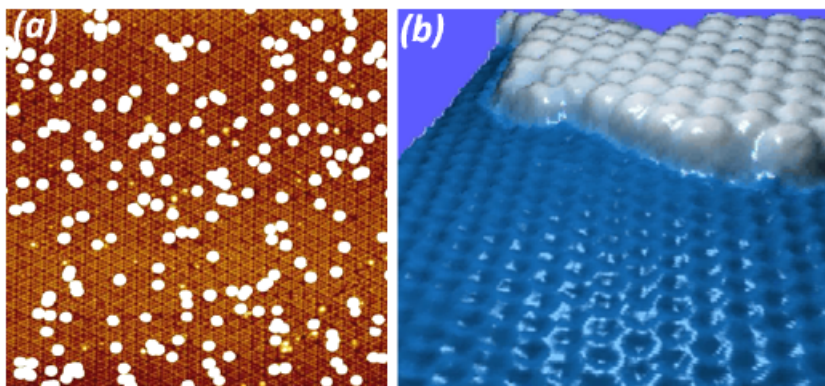
**Figure 6.5** – Hopping rate vs temperature for H and D on a copper surface. Note the very strong deviation from linear behaviour (the y-axis is a log scale) for H below a temperature of  $\sim 50$  K. This is the signature of quantum mechanical tunnelling of H atoms. Taken from Kua et al., *J. Chem. Phys.* **115** 5620 (2001). ©American Institute of Physics

regime for deuterium corresponds to one hop on average every 83 months – not an easy experiment to do!)

## 6.6 Self-assembly: A question of balance

When we deposit atoms (or molecules) onto a surface the assemblies that are formed depend critically on the energy balance, i.e. the balance of the thermal energy, the energy of the bond between the deposited atom and the surface, the diffusion barrier, and the energies for attachment/detachment of an atom from other atoms or clusters of atoms on the surface (i.e. processes (d) and (e) in Fig. 6.1).

A good example of “tipping” the energy balance to control the arrangement of molecules at a surface is shown in Fig. 6.6. When  $C_{60}$  molecules are deposited onto a clean silicon surface, they form strong Si-C bonds. This bonding means that there is a very large diffusion barrier for the molecules - so large that they are pinned in place at room temperature (Fig. 6.6(a)). If, however, we treat the silicon surface by covering it with a very small amount of silver (approximately an atomic layer), the energy of the  $C_{60}$ -surface bond is dramatically reduced. This in turn leads to a smaller diffusion barrier so that at room temperature the  $C_{60}$  molecules can diffuse across the surface, meet other molecules, and form large well-ordered assemblies (Fig. 6.6(b)).



**Figure 6.6** –  $C_{60}$  molecules deposited on (a) a clean silicon surface, and (b) a silicon surface treated to reduce the  $C_{60}$ -surface bond energy. Note the strong difference in the distribution of the molecules in each case. In (a) the molecules are pinned in place because the surface-molecule bond energy and the diffusion barrier are much, much greater than the average thermal energy,  $kT$ . In (b), the molecule-surface interaction energy and diffusion barrier are much lower, meaning that the molecules can diffuse to form well-ordered assemblies. (The atoms of the silicon substrate are seen in blue in the ‘foreground’ of the image).

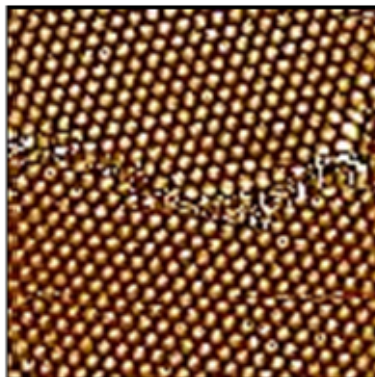
## 6.7 From “hit-and-stick” to close-packing

In addition to the adsorbate-surface bond energy and the diffusion barrier, the bonding between the adsorbates at the surface plays a central role in determining the type of structures formed during self-assembly. At one limit we have the case shown in Fig. 6.6(b) and in Fig. 6.7 where the  $C_{60}$  molecules are bonded weakly to the surface, and due to a low diffusion barrier can diffuse long distances until they “collide” with another molecule or a growing island of molecules. If the intermolecular interaction is also relatively weak then the molecules can diffuse along the edge of an island until they find a low energy bonding site. For  $C_{60}$ , this is a site for which the molecule has as many neighbours as possible<sup>6</sup>.

If the interaction of the adsorbates is strong, however, then a “hit-and-stick” situation can develop where an adsorbate diffusing across a surface meets a growing island but cannot diffuse to a lower energy bonding site because the interaction with the edge of the island pins it in place. This type of process is known as diffusion limited aggregation (DLA), is exceptionally important in many processes in nature, and leads to the formation of striking branching patterns. Fig. 6.8 shows a series of screenshots from an

---

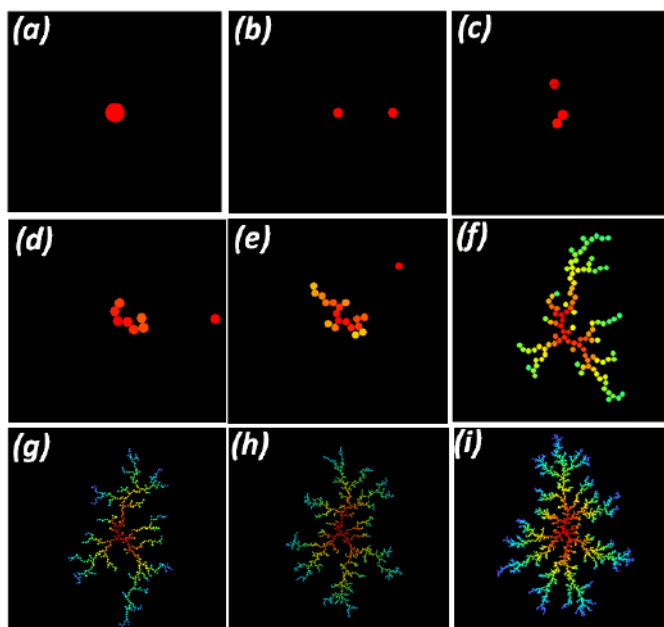
<sup>6</sup> $C_{60}$  interacts with other  $C_{60}$  molecules purely via attractive van der Waals, and repulsive Pauli exclusion-derived, forces. It is thus well-described by intermolecular potentials similar to the Lennard-Jones curves described in Chapter 2.



**Figure 6.7** – An STM image of the type of highly ordered molecular assembly formed by  $C_{60}$  molecules. There is a domain boundary visible approximately half-way up the image. This type of boundary arises when two molecular islands that have nucleated at different positions on the surface (c.f. the islands in Fig. 6.1) “grow into” each other

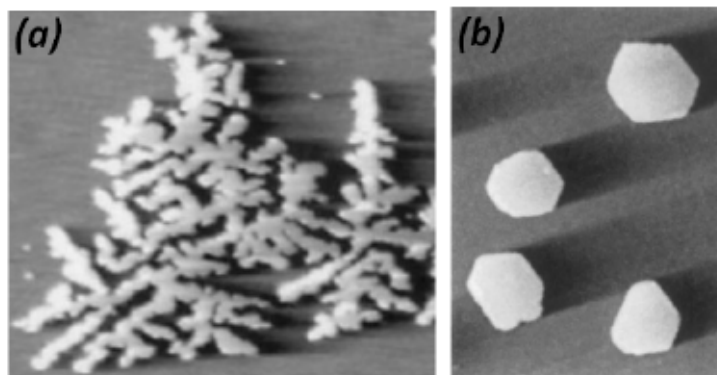
excellent website by Chi-Hang Lam, Hong Kong Polytechnic University on DLA which includes an online simulation of the growth process. (I strongly recommend that you visit [Dr. Lam’s website](#)). Note how a complex branched structure - a fractal - forms due to the diffusion-limited aggregation of the atoms. As atoms are not free to diffuse around the edge of the aggregate they remain locked in place. This type of structure generally occurs at intermediate temperatures where the atoms have sufficient thermal energy to hop freely across the surface but when they interact with another atom they do not have sufficient energy to break the bond (at least on a reasonable time scale). Thus, the atoms are prohibited from reaching their preferred bonding state.

If, however, the fractal structure is warmed up, the atoms gain enough energy to diffuse away from their neighbours and to form a close-packed assembly. This significantly increases the number of neighbours each atom has and thus each atom’s potential energy is lowered considerably. A striking example of the difference that a simple increase in sample temperature can make to the self-assembly process is shown in Fig. 6.9. Fig. 6.9(a) shows how Ag atoms deposited on a platinum surface form a branched DLA-type aggregate for a sample temperature of 130 K. If, however, metal atoms are deposited on a Pt surface at 455 K, close-packed islands form because the atoms can diffuse to their preferred bonding site (Fig. 6.9(b)). By heating up the system we can move it from a far-from-equilibrium state (Fig. 6.9(a)) to a close-to-equilibrium state (Fig. 6.9(b)).



**Figure 6.8** – A series of screenshots from [an online DLA simulation](#) (©Chi-Hang Lam, Hong Kong Polytechnic University). In (a) a single adsorbed atom acts as a nucleation site; (b) Another adsorbate diffuses towards the nucleation site; (c) The second adsorbate hits and sticks. A third atom is diffusing towards the pair of atoms; (d) - (i) As more and more atoms hit and stick to the growing aggregate, a complex branched structure (a fractal) forms.





**Figure 6.9** – (a) Atoms adsorbed on a platinum surface held at 130 K form branched DLA aggregates because there is insufficient thermal energy to enable the atoms to break bonds with their neighbours so diffusing atoms “hit and stick”; (b) If the atoms are deposited on a platinum surface held at 450K, large islands form because the adsorbates can diffuse to find a lower energy configuration. (From Brune, Surf. Sci. Rep. 31 125 (1998)).

## 6.8 Problems

**P6.1** Ganz et al. [Phys. Rev. Lett. **68** 1567 (1992)] found that at 24°C the hopping rate of Pb atoms on a germanium surface was  $2 \times 10^{-4}$  Hz, whereas at 79°C it was  $4.5 \times 10^{-3}$  Hz. Assuming Arrhenius behaviour, calculate the energy barrier for Pb adatom diffusion on the germanium surface. {5}

# Appendix

## Why do some problems related to the uncertainty principle apparently assume that $\Delta p = p$ ?

This is a great question. Often the uncertainty principle is used in a rather “back of the envelope” fashion to get estimates of length scales, momentum, energy scales, or, indeed, time scales. There’s nothing wrong with doing this as long as we remember that the values we determine in this way are indeed *estimates*. Nonetheless, there is a reasonably sound mathematical argument for using the uncertainty in momentum to make an estimate of the energy of, for example, a particle in an infinite potential well. It appears as if we are equating  $\Delta p$  and  $p$  but, as shown below, the important point is that we use  $\Delta p^2$  and not  $\Delta p$  (or  $p$ ) for the estimate.

Consider a potential well which is fixed at a certain position in space. The well is not moving so the *mean* momentum<sup>7</sup> of the trapped particle,  $\langle p \rangle$ , must be zero.

$$\langle p \rangle = 0 \tag{A1}$$

However, the uncertainty in momentum is given by the root mean square deviation from the mean, i.e.

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{A2}$$

$$\implies (\Delta p)^2 = \langle p^2 \rangle \tag{A3}$$

The key point is that when we want to make estimates of kinetic energy on the basis of uncertainty in the momentum, it is  $\langle p^2 \rangle$  (and not  $\langle p \rangle$  itself) which is used. This is because  $E = p^2/2m$  and so

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{\Delta p^2}{2m} \tag{A4}$$

---

<sup>7</sup>As you’ll see in your quantum physics course next year, this is also called the expectation value for the momentum.

# Numerical answers to problems

## Chapter 2

**P2.1(a):** Equilibrium separation,  $r_0=3.01$  nm;

**P2.1(b):** Maximum attractive force is 4.28 pN; occurs at a separation of 3.33 nm;

**P2.1(c):** Effective spring constant is 37.7 mN/m.

## Chapter 3

**P3.1(a)(i)** Scales as  $L^{-1}$ ; **(ii)** Scales as  $L$ ; **(iii)** Scales as  $L$ ; **(iv)** Scales as  $L^{-1}$

**P3.1(b)(i), (ii), (iii)** All scale as  $L$

## Chapter 4

**P4.1(ii)** 0; **P4.1(iii)**  $3.6 \mu\text{m}$ .

**P4.2(i)** 4.7 pm; **P4.2(ii)**  $47 \mu\text{radians}$ ; Yes.

## Chapter 5

**P5.1(ii)**  $1.6 \times 10^{-10}$  atoms/electron; **P5.1(iii)** 440 K;

**P5.2(iii)** 5.06 eV

**P5.3(ii)** Tunnel current changes by a factor of  $e^2$ ; **P5.3(iii)** 1.18 eV

**P5.4(iii)** 0.5 THz;

## Chapter 6

**P6.1** 0.45 eV

## Video tutorials on worked solutions to exam papers

### Exam Paper 2010-2011

Worked solutions to *Frontiers* exam paper 2010-2011.

**Exam Paper 2011-2012**

Worked solutions to *Frontiers* exam paper 2011-2012.

# Bibliography

- [1] DM Eigler and EK Schweizer, *Nature* **344** 524 (1990)
- [2] *Single Bond Formation and Characterization with a Scanning Tunneling Microscope*, H.J. Lee and W. Ho, *Science* **286**, 1719-1722 (1999)
- [3] *Inducing All Steps of a Chemical Reaction with the Scanning Tunneling Microscope Tip: Towards Single Molecule Engineering*, Saw-Wai Hla, Ludwig Bartels, Gerhard Meyer, and Karl-Heinz Rieder, *Phys. Rev. Lett.* **85**, 2777 (2000)
- [4] Markus Ternes, Christopher P. Lutz, Cyrus F. Hirjibehedin, Franz J. Giessibl, and Andreas J. Heinrich *Science*, 1066 (2008)
- [5] *7 × 7 Reconstruction on Si(111) Resolved in Real Space*, G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Phys. Rev. Lett.* **50**, 120 (1983)
- [6] *Engines of Creation*, K Eric Drexler, Anchor Books (1990)
- [7] *Nanosystems: Molecular Machinery, Manufacturing, and Computation*, K. Eric Drexler, Chichester: Wiley Interscience (1992)
- [8] *Nanoscience and Nanotechnologies: Opportunities and Uncertainties*, The Royal Society and The Royal Academy of Engineering; <http://www.nanotec.org.uk/finalReport.htm> (2004) [Accessed April 03 2014]
- [9] *The quantum bridge of asses*, <http://www.softmachines.org/wordpress/index.php?p=117> (2005) [Accessed April 04 2014]
- [10] C. Toumey, *Nature Nanotech.* **2** 9 (2007)
- [11] MF Crommie, CP Lutz, and DM Eigler, *Science* **262** 218 (1993)
- [12] S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, *Phys. Rev. Lett.* **92** 056803 (2004)
- [13] K. Eric Drexler and R.E. Smalley, *Chem. Engng. News* **81** 37 (2003); Available online at <http://pubs.acs.org/cen/coverstory/8148/8148counterpoint.html> [Accessed April 04 2014]

- [14] C. Phoenix and P. Moriarty, <http://www.softmachines.org/wordpress/index.php?p=70>;  
R. Jones, <http://www.softmachines.org/wordpress/?p=130>; [Accessed April 03 2014]
- [15] R. Jones, <http://www.softmachines.org/wordpress/index.php?p=80> [Accessed April 03 2014]
- [16] [www.softmachines.org](http://www.softmachines.org) [Accessed April 03 2014]
- [17] *Soft Machines: Nanotechnology and Life*, RAL Jones, Oxford: University Press (2004).