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Mathematical Modelling for Metrology at the Nanoscale

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Mathematical Modelling for Metrology at the Nanoscale

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ABSTRACT

This report for the Software Support for Metrology programme considers mathematical modelling at the nanoscale and its application to problems in metrology. The motivation for the report arises from the recognition that modelling at the molecular scale is becoming more important for metrologists working on programmes funded by the National Measurement System Directorate (NMSD). It has been drafted with metrologists from other NMSD programmes in mind. It aims to set out the most important mathematical modelling issues that metrologists who need to tackle nanoscale problems should take into account. Its purpose is both to provide metrologists with advice on how to assess the potential contribution that nanoscale modelling techniques may be able to make and to assist them in identifying sources of help with modelling problems. It describes some of the software available and suggests ways in which non-commercial software can be used to gain experience in modelling at the nanoscale.

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1 Introduction

This report has been produced for the National Measurement System Directorate as part of 2004-2007 Software Support for Metrology programme. It considers *mathematical modelling at the nanoscale* and its application to problems in metrology. It arises from the recognition that modelling at the molecular scale is becoming more important for metrologists working on programmes funded by the National Measurement System Directorate. A major focus of current DTI support for innovation is nanotechnology, so it is appropriate that the Software Support for Metrology (SS*f*M) programme should particularly support innovation through use of nanotechnology. The need for work to support nanoscale modelling was identified clearly in the *New Directions* study on *Future directions in mathematics and scientific computing* [33] that was prepared during the previous SS*f*M programme. Nanotechnology applications are becoming increasingly common in metrology, owing to the development of new measurement devices and the need to understand materials and their properties at the nanoscale. There is a growing need for mathematical modelling at this scale to investigate new measurement techniques, quantify the associated uncertainties, and to predict the behaviour of materials. Methods that can be applied at this scale have been the subject of much research in universities, and software (free, shareware, and commercial) is available to tackle a range of nanoscale problems. However, such techniques are relatively new to metrology. There is a need for guidance to metrologists on the choice of methodology and software to solve a problem of interest and the present report aims to fill this gap. Visualisation is also employed to demonstrate the interactions of atoms and molecules with each other and with surfaces, and it is essential to ensure that good practice in visualisation is also adopted in nanoscale applications. *Good Practice Guide no. 13 Data Visualisation*, which is being revised in the current Software Support for Metrology Programme, is relevant here [39].

An important area of nanoscale modelling applications is biotechnology. Many biological processes occur at the nanoscale and the key to effective measurement in biology often lies in understanding how molecules such as proteins attach themselves to surfaces, and in identifying the sites of reaction on a molecular chain. Such measurements can help in designing treatments. At present NPL mathematicians and statisticians provide support to NPL biologists in statistics and in model solving. Despite that, there is currently no demand from biologists for assistance in computational biology or in validating software that solves problems of molecular interactions. It is likely that this type of modelling at the molecular scale will be required for future NPL biotechnology work.

A number of National Measurement System (NMS) programmes, particularly VAM Physical, Engineering Measurement (for pressure & vacuum), the various Materials programmes and the new Measurement for Emerging Technologies programme, in addition to NPL's own Strategic Research Programme, have identified problems to which nanoscale modelling may be able to make a contribution. However, before such techniques can become more widely adopted in the context of metrology, it will be necessary to ensure that metrologists can have confidence in the results of modelling and of software, and that they understand the limitations of models. This report sets out the results of an initial review and study that will be a first step towards building the required understanding and which can provide a foundation for future work both within the Software Support for Metrology programme and within other NMSD programmes.

1.1 Nature of this report

NPL is new to a number of aspects of modelling at the nanoscale, and this is the case for molecular modelling. However, recent developments at NPL will help to ensure that NPL begins to develop its own expertise in molecular modelling. A Strategic Research Fellow in molecular modelling has been appointed and began work at NPL in the autumn of 2005. The responsibilities of the new post include carrying out specific molecular modelling tasks for a number of projects in NPL's scientific divisions, supporting and training NPL scientists in molecular modelling, developing modelling software resources at NPL and building links with academic modellers who are part of the Collaborative Computational Projects community of the UK's Council for the Central Laboratory of the Research Councils.

The process by which NPL came to identify the need for this new post and how the initial research topics for the post were decided forms a major part of chapter 5 of this report. The existence of the new post will also help in identifying potential activities to support modelling at the nanoscale in the fourth Software Support for Metrology programme that begins in April 2007.

This report has been drafted with metrologists from other NMSD programmes in mind. It aims to set out the most important mathematical modelling issues that metrologists who need to tackle nanoscale problems should take into account. Its purpose is both to provide metrologists with advice on how to assess the potential contribution that nanoscale modelling techniques may be able to make and to assist them in identifying sources of help with modelling problems. It describes some of the software available and suggests ways in which non-commercial software can be used to gain experience in modelling at the nanoscale. In this way one can begin to appreciate the specific problems that arise in nanoscale modelling and to understand the kinds of questions that one should put to software providers and academic collaborators when one is considering using nanoscale modelling methods in the context of specific research projects.

It is hoped that this report will be of use to a wide range of metrologists, including those who would regard themselves primarily as experimentalists, rather than theoreticians. In addition, it aims to present the topic at an accessible level that does not require extensive prior theoretical or mathematical knowledge. Nanoscale modelling can contribute to improved understanding in more traditional areas of metrology as well as in developing fields such as biotechnology. Of course, biological applications bring their own special problems, such as the need to recognise the natural variability inherent in biological processes, the need to consider specific effects such as transport through cell walls, and the vital part that environment plays in determining biological behaviour.

1.2 Multi-scale modelling

The *New Directions* study [33] identified a number of issues that nanoscale modelling poses for metrologists. The report emphasised that one of the key issues facing metrologists, particularly those working in nanotechnology, biotechnology and in materials science, is the problem of validating and testing mathematical models which describe phenomena that manifest themselves over several length scales and time scales. The understanding of multi-scale phenomena, and especially of those properties of matter which are sensitive to structure, poses a significant challenge to physicists and mathematicians. Chapter 7 of this report is specifically devoted to considering multi-scale modelling issues.

1.3 Limitations of quantum mechanical modelling

Quantum mechanics, as Wright and Chorin point out [111], is not always able to deal effectively with some of the most useful and interesting characteristics of materials, especially where these properties are structure-sensitive, that is, they are affected by the microstructure of the material in question. These authors list a number of examples of such structure-sensitive properties: strength, plasticity, magnetic hysteresis, dielectric constant, optical properties of liquid crystals, and superconductivity, among others. They also emphasise the wide range of time scales over which processes of interest to materials metrologists occur.

This report gives a flavour of a range techniques that can be applied in nanoscale modelling and for the reasons identified in the previous paragraph does not simply concentrate on modelling at the quantum mechanical scale.

1.4 Why NMS metrologists need to develop molecular modelling resources

It is sometimes the case in research carried out for DTI NMS programmes that one comes across scientific challenges that cannot be addressed directly because of a lack of fundamental understanding of the processes involved at the microscopic level. Often the limitations are closely linked with the determination of *Type B uncertainties*, i.e. sources of systematic uncertainty. These may involve the way atoms and molecules interact with surfaces or the way materials behave in the presence of boundaries.

To take an example from the apparently mature area of pressure metrology, in the case of gas flows in pressure balance standards, we currently have no way of evaluating the uncertainties resulting from transition flow (the regime that links hydrodynamic and kinetic descriptions of the flows and surface texture effects), so simple continuum models and perfect surfaces are assumed world-wide. This lack of scientific understanding is a fundamental limitation to the metrology, making the continually challenging industrial demands on the accuracy of standards increasingly difficult, if not impossible, to achieve. Similar challenges exist in the newer areas of metrology. For instance, the need to know and understand the orientation of biological molecules on surfaces is crucial to a range of techniques from atomic force microscopy to methods of monitoring biological molecules through macroscopic measurement. In general, predicting the properties of materials at the nanoscale where boundaries influence performance presents substantial challenges.

Molecular or atomistic modelling has been recognised as having the potential to provide the foundations for addressing and solving existing metrological problems as well as supplying essential knowledge in some of the newer metrological areas such as nanotechnology, biometrology, and functional materials. In recent years enormous progress in molecular modelling has been made, both in methodology and range of applications, but it is not necessarily clear to scientists working with the practicalities of maintaining and developing measurement standards that the scientific challenges posed in NPL's metrology work can be answered by the current molecular modelling capability and knowledge base. One of the purposes of this report is provide some assistance in deciding whether nanoscale modelling methods may be able to assist in tackling a particular metrology problem.

1.5 Software Support for Metrology and modelling at the nanoscale

As nanoscale modelling develops at NPL, mathematicians in NPL's Mathematics and Scientific Computing Group are likely to be called on to provide support in this area to scientists working on NMS programmes. Until recently we had little expertise in nanoscale modelling, especially modelling at the quantum and atomic scales. However, NPL has recently employed a specialist molecular modeller to work with scientists from the Performance Materials and Process Materials groups of NPL's Engineering and Process Control Division and from the Applied Electrical and Quantum Detection groups of the Enabling Metrology Division. We plan to build on his experience to develop within NPL's Mathematical and Scientific Computing Group the specific mathematical skills needed to be able to support scientists working at the nanoscale.

It is, of course, the case that the general methodology applied to mathematical and statistical work funded by the SS*f*M programme is also appropriate for modelling at the nanoscale, that is, we aim to provide a comprehensive approach to the solution of a problem that encompasses all stages of the modelling process from writing down the equations that embody the physical model to testing and validating of the software that solves the model. In addition, we ensure that best practice in algorithm development, numerical analysis, the calculation of uncertainties, and in software development, is followed at all times. These requirements are no different for modelling at the nanoscale.

In addition, we are developing new skills and resources within the current Software Support for Metrology programme that are likely to be of direct benefit to modellersb tackling nanoscale problems.

- Grid computing systems of the kind that exist at NPL and the Rutherford Appleton Laboratory [80] provide an efficient and cost-effective resource for large-scale computations. The current SS*f*M programme has produced a guide to good practice in the development and implementation of algorithms for parallel and distributed processing [34].
- Monte Carlo methods are a popular technique for the solution of atomic and molecular scale problems. When these are applied in the context of grid and parallel processing, it is necessary to ensure that the period of any random number generator that is employed is large enough to avoid the risk of repetition of sequences and also to be confident that the random number sequences used or generated on specific processors in the grid are independent. The improved Wichmann-Hill random number generator, which NPL's Mathematics and Scientific Computing Group advocates, meets both these requirements. See `http://www.npl.co.uk/ssfm/ssfm3/theme1/modelling_techniques/project1_2/wichman_hill_rng/` for more information.

1.6 Nanoscale modelling in a traditional metrology area

To set the scene for the rest of this report, this introductory chapter ends with a short introduction to a mechanical metrology problem that cannot be solved using traditional methods and which requires molecular modelling for its solution. This is the pressure-balance problem that was introduced in section 1.4.

In mechanical metrology piston-cylinder pressure balances are used to generate accurately-known static pressures in the pressure range from 0.1 MPa to

1 GPa. Pressure balances consist of a piston located within a closely fitting cylinder. The radius of the piston is typically a few mm and the external radius of the cylinder may be several times that of the piston. The clearance between the piston and cylinder is of the order of one micrometre or less. The gap between the piston and cylinder is filled with fluid, which flows along the gap under the influence of a pressure gradient. This pressure gradient arises because the lower end of the piston and cylinder assembly is connected to a pressurised reservoir of fluid (in practice this may be another pressure balance) and the top of the assembly is exposed either to atmospheric pressure or to a vacuum. The force on the piston generated by the application of the pressurised fluid is balanced by weights applied to the top of the piston. The calculation of the pressure generated by a piston-cylinder pressure balance or deadweight tester, as it is sometimes called, requires one to know both the forces applied to the piston and the area over which they act. However, the piston and cylinder assembly is itself distorted by the pressure generated in the pressure balance fluid, and accurate determination of the generated pressure requires this distortion to be taken into account. In other words, it is necessary to know the effective area over which the force is applied in practice. Traditionally, finite element methods, in which materials are modelled as continua, have been used to study both the flow of fluid along the gap and the manner in which the balance distorts under pressure.

At the low pressure range of operation, gas-operated balances are used to generate static pressures from approximately 0.1 MPa to 20 MPa. It has been observed by many National Metrology Institutions that there are differences in nominally identical devices of the order of several parts per million per MPa. Furthermore, different devices exhibit different degrees of non-linearity. This is becoming increasingly unacceptable to primary standards laboratories and to end-users, as the uncertainties associated with these non-linearities are virtually of the same magnitude as the claimed accuracy of the primary standards. It is believed that this arises from nanometric flow effects in the annular gap between the piston and cylinder, which can be in the range 50 nm to 2 micrometres when the balance is in operation. Existing finite element methods are unable to tackle such a problem and there are no existing theories of pressure balance behaviour that can be used to calculate the frictional drag forces on the piston and cylinder and the local pressures along the gap, and which cover the range from the high pressure end of the piston-cylinder gap where continuum/viscous flow predominates, through to the low pressure end where the molecular flow regime predominates. Furthermore, there is no existing method of accounting for differences in surface texture. There is a need for new mathematical models that can address this problem of modelling over several length scales, from nano flow to macroscopic continuum flow, and which can also model the effect of surface irregularities. It is also important to note that conventional pressure balances use rotating pistons and cylinders, hence there is potential for rubbing and therefore changing the surface texture. Understanding flow at the nanoscale along channels with realistic surfaces will become increasingly important in achieving further improvements in primary pressure standards.

To attempt to answer some of the questions posed above, NPL has been collaborating with the researchers from the Department of Chemistry at Imperial College London and a case study on the application of molecular modelling to understanding piston-cylinder pressure balances is described in chapter 8 of this report.

1.7 Structure of this report

The structure of this report is as follows. Chapter 2 discusses the difficulty of defining precisely what the nanoscale is and also gives a brief introduction to a number of aspects of NPL's experimental work that can be regarded as nanoscale.

Chapter 3 identifies sources of information and advice about modelling at the nanoscale. Several of the resources that have been identified are World-Wide-Web-based. As a result there is a risk that they rapidly become out of date or are superseded by more up-to-date resources. Nevertheless, at the time of writing this report all the cited pages are accessible. The next two chapters review a report from the USA on the future of computational chemistry and consider the new mathematical challenges that confront the the various National Measurement System programmes. A review of the issues involved in modelling polymers is set out in chapter 6 and chapter 7 discusses multi-scale modelling. The case study on the application of molecular modelling to understanding gas flows in piston-cylinder pressure balances is presented in chapter 8. Chapter 9 describes a case study on the usability of the *Materials Studio* molecular modelling software that is marketed by Accelrys. Finally, chapter 10 makes some recommendations for the mathematical support that will be needed in future for metrologists who are tackling metrology problems at the nanoscale.

2 What is nanotechnology?

This chapter of the report reviews some existing definitions of nanotechnology and the nanoscale to demonstrate that these are concepts that have ambiguous meanings. As a consequence, it is not possible to give a clear definition of what constitutes mathematical modelling at the nanoscale. In addition, the chapter provides a brief account of the main areas of current research at NPL that are relevant to nanotechnology. This gives an idea of the range of modern metrology topics that can be regarded as nanotechnology and indicates where mathematical modelling at this scale might make a contribution.

There is no general agreement as to what constitutes *nanotechnology*, nor is there agreement on what *nanoscale* means. An Internet search to find definitions of nanotechnology, using the search term *define nanotechnology* within a popular search engine, came up with a wide range of answers. These included:

- In recent general usage, any technology related to features of nanometre scale: thin films, fine particles, chemical synthesis, advanced microlithography, and so forth . . . a technology based on the ability to build structures to complex, atomic specifications by means of mechanosynthesis; this can be termed molecular nanotechnology.
- Nanotechnology is a new technology for creating MEMS structures in the Nano range which is three orders of magnitude, or 1000 times smaller than the current generation of MEMS devices. Refers to devices ranging in size from a nanometre to a micron.
- a manufacturing technology able to inexpensively fabricate most structures consistent with natural law, and to do so with molecular precision.
- The application of science to developing new materials and processes by manipulating molecular and atomic particles.
- Research and technology development at the atomic, molecular or macromolecular levels in the length scale of approximately one to several hundred nanometres.
- an experimental technology which uses individual atoms or molecules as the components of minute machines, measured by the nanometre, or a millionth of a millimetre
- nanotechnology is synonymous with molecular systems engineering. An interdisciplinary field where devices are constructed at the molecular scale and function at this scale. This technology is expected to allow the construction of very compact and high performance computing devices.
- Atomic engineering: the ability to devise self-replicating machines, robots, and computers that are molecular sized.
- the branch of engineering that deals with things smaller than 100 nanometres (especially with the manipulation of individual molecules).

What is clear from the above is the relatively wide dimensional range to which the term *nanotechnology* is applied, with sizes up to several hundred nanometres being regarded as “nanoscale”. In fact, it can be difficult to distinguish between the microscale and the nanoscale. NPL itself often brackets the two terms together. For example, in a description of its work in the field of nanobiotechnology, NPL specifically states that:

> *Nanobiotechnology applies the tools and measurement techniques of micro and nanoscale physics and chemistry to study biosystems (www.npl.co.uk/nanotech/nanobio.html).*

In relation to dimensional metrology at the nanoscale NPL once again combines the micro and the nanoscale:

> *NPL has developed instrumentation for measurement of surface features and surface texture in the micro- to nano-dimensional range with direct traceability to the national length standard. . . . NPL is developing co-ordinate measurement technology to deliver accuracy in the nanometre regime over micrometre to millimetre measuring volumes (www.npl.co.uk/nanotech/nanodim.html).*

An example of a specific NPL definition of the nanoscale is that of nano-structured materials, which are defined as:

> *Nanomaterials is (sic) essentially an enabling technology for most nanotechnology applications. They are defined here as materials with at least one phase having one dimension lower than 100 nanometres, which profoundly changes the materials (sic) behaviour.* (www.npl.co.uk/nanotech/nanostruc.html)

The Department of Trade and Industry combines the micro- and nanoscale into its Micro and Nanotechnology Manufacturing Initiative (www.microandnanotech.info/).

The DTI-commissioned study by the Royal Society and Royal Academy of Engineering entitled *Nanoscience and nanotechnologies : opportunities and uncertainties* published in July 2004 is more precise in its definition (www.nanotec.org.uk/finalReport.htm). It distinguishes nanoscience from nanotechnologies in the following manner:

- **nanoscience**: the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale.
- **nanotechnologies**: the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanoscale.

The size range that is important for nanotechnologies was defined in the same report in the following way:

> *The size range that holds so much interest is typically from 100 nm down to the atomic level (approximately 0.2 nm), because it is in this range (particularly at the lower end) that materials can have different or enhanced properties compared with the same materials at a larger size. The two main reasons for this change in behaviour are an increased relative surface area, and the dominance of quantum effects. An increase in surface area (per unit mass) will result in a corresponding increase in chemical reactivity, making some nanomaterials useful as catalysts to improve the efficiency of fuel cells and batteries. As the size of matter is reduced to tens of nanometres or less, quantum effects can begin to play a role, and these can significantly change a material's optical, magnetic or electrical properties.*

Other words that are often used to describe the small scale are *mesoscale* and *mesoscopic*. This presents even more problems than *nanoscale*. In meteorology, mesoscale is used specifically to refer to features of weather systems that range from 10s to 100s of kilometres in size. However, within the discipline of non-destructive testing of materials, the USA's Lawrence Livermore Laboratory has defined mesoscale objects as those that have millimetre extent with micrometre features [46]. *Meso* simply means *middle* and only has meaning when comparing smaller and larger entities. The Oxford English Dictionary defines *mesoscopic* as:

> *large enough for examination with the naked eye but small enough for examination as a single entity;*

whereas the McGraw-Hill Dictionary of Scientific and Technical Terms, 6th edition, 2003 defines *mesoscopic* as:

> *pertaining to a size regime, intermediate between the microscopic and the macroscopic, that is characteristic of a region where a large number of particles can interact in a quantum-mechanically correlated fashion.*

McGraw-Hill then defines *mesoscopic physics* as:

> *a subdiscipline of condensed-matter physics that focuses on the properties of solids in a size range intermediate between bulk matter and individual atoms or molecules.*

This last definition seems also to cover most of the nanoscale. This confusion makes understanding of much that is written about the nanoscale and the mesoscale difficult. Perhaps the most useful distinction that has practical value for mathematical modelling purposes is between representing a material as a continuum, or representing it as a collection of discrete entities. However, this latter approach is by no means new and encompasses many traditional ways of modelling materials (molecular mechanics and dynamics, lattice Boltzmann methods, cellular automata) that were in use before the term *nanotechnology* became commonplace. The problem is further complicated by the fact that mathematical models that represent materials as continua are often discretised when one solves them. Both finite element and finite difference models are solved on grids, in which the structure or field being modelled is discretised.

2.1 Nanoscale properties v. bulk properties: the issues

As the Royal Society/Royal Academy of Engineering report argues, nanoscience and nanotechnology are not new and "many chemicals and chemical processes have nanoscale features", as do biological processes. However, it is the development of tools "to investigate and manipulate matter at the nanoscale, which have greatly affected our understanding of the nanoscale world." Nanoscience and nanotechnology are inter-disciplinary activities that cover a wide range of scientific activities, tools, materials and methods. As a result, apart from the question of scale, there is no guarantee that different *nanotechnologies* possess common aspects. The consequence of this for mathematical modelling is that there is no single approach or set of techniques that can be considered to be appropriate to all nanoscale problems.

In spite of the warning in the previous paragraph, it is possible to lay down one or two principles that demonstrate why methods that have been applied to bulk materials might not be appropriate at the nanoscale, and to indicate why many input parameters to mathematical models that use properties of bulk materials have to be amended to cope with nanoscale behaviour.

Firstly it is important to take into account the dimensionality of the model. For example, coatings and thin films may be large in two dimensions (the surface which they cover) and may be small, perhaps only a few atoms or molecules thick, in the other dimension. Systems of this geometry can present problems for modelling techniques that rely on meshes to represent a domain, such as finite element methods, as the need to avoid extreme aspect ratios for elements may lead to the production of very dense meshes, lengthy run times and large memory requirements. A typical case in which these problems arise is in the modelling of engineering components that consist of volumes that are joined by thin adhesive layers. Even when the layers have micrometre- rather than nanometre-range thicknesses, their representation in finite element models can be problematic. The Software Support for Metrology Programme has published reports and good practice guides that contain guidance on meshing and testing meshes for finite element and finite difference models, including cases where one dimension of the mesh is much smaller than other dimensions [35, 36, 37].

Examples of structures that have nanoscale features in one dimension and extended features in the remaining dimensions are nanotubes and nanowires. Carbon nanotubes, for example, have a range of diameters and lengths. Depending on the manner in which they are prepared, the length of tubes may vary from hundreds of nanometres to several micrometres or even millimetres and diameters may range from 1 to 20 nanometres. Nanowires are one-dimensional nanometre-scale objects that are grown from a variety of materials such as silicon, germanium, gallium nitride, metals and oxides, up to several micrometres in length. Three-dimensional nanoscale materials are typically particles. One example is the quantum dot where a dot may be between 2 and 10 nm (10 and 50 atoms) in diameter.

It is the smallness of at least one of the dimensions of a material that leads properties at the nanoscale to differ from bulk properties. This is because the smallness of at least one dimension increases the surface area of a material in relation to its volume, so that, as the volume decreases, a greater proportion of atoms find themselves located at the surface of the material rather than in its interior. As the Royal Society/Royal Academy of Engineering report emphasises, a particle 30 nm in diameter has 5% of its atoms at the surface, whereas a 10 nm diameter particle has 20% of atoms at the surface and a 3 nm particle has 50 % of its atoms at the surface. It is at the surface that chemical reactions occur and also where additional atoms adhere, so that the smaller the volume, the more reactive the material will be. At this small scale quantum effects must also be taken into account. These arise from the confinement of electrons, so that the electrical, optical and magnetic behaviour at the nanoscale differs from that of bulk materials.

The mathematical challenges for metrologists working on NMS programmes that have nanotechnology components can best be understood by reviewing briefly the main measurement issues in nanometrology.

2.2 Traditional metrology at the nanoscale

The traditional metrology disciplines are, of course, also required at the nanoscale, including length and size measurement, force, mass, amount of substance, electrical properties, and so on. Many measurement problems encountered at the nanoscale are similar to those that are encountered at the macroscale. For example, environmental instabilities must be monitored and minimised, as in macroscale metrology. The difference is that at the nanoscale environmental effects can have relatively large consequences.

A second concern is that while it may often be possible to obtain good repeatability of nanoscale measurements within one laboratory, much work needs to be done to establish measurement standards that are widely accepted and which allow absolute measurements and transferability of measurement results from one laboratory to another.

An example of the problems that must be overcome is provided by a comparison of scanning probe microscope measurements that was reported by Breil and his colleagues [10]. Thirteen laboratories from several European countries took part in a comparison of measurements of three measurement standards - a flatness standard, a step height standard (240 nm step) and a lateral standard with a one micrometre pitch. Some observations from the paper reporting the results are of interest.

- The instruments used were of very different metrological quality and for most of them uncertainty statements had not been made.
- Standards and directives are not yet available for the field of nanometrology and the evaluation software of the individual devices can neither be influenced nor completely understood by the user.
- Most of the partners were not in a position to state uncertainties for the measurements. . . . Instead, the scatter of the measured values from the repeated measurements were used to state a standard deviation, together with the mean value.
- As far as roughness measurements were concerned values from different instruments were not comparable . . . part of the problem is related to the software programs used.
- Roughness values measured by different instruments can hardly be compared. The state-of-the-art in roughness measurements is insufficient and it is absolutely necessary to standardize the measurement conditions.

2.3 NPL's work at the nanoscale

Much of the nanoscale metrology work of laboratories such as NPL is concerned with devising measurement methods that can demonstrate traceability at the nanoscale.

NPL currently has significant activity in nanotechnology and nanobiotechnology. Some examples of the work are described below. The wide range of work once again reflects the fact that nanotechnology and the nanoscale are broad terms.

2.3.1 Single molecule detection

Detecting and characterising chemical and biological entities on the nanoscale is becoming increasingly important in analytical science. The ultimate challenge in this field is the detection, identification and characterisation of single molecules. The detection of single molecules has several advantages, most notably removal of ensemble averaging phenomena to provide detail about the environment and properties of individual molecules and observation of the innate variability of, in particular, biological molecules. Single Molecule Detection (SMD) is currently one of the most exciting, challenging and wide-ranging areas of physico-chemical study available to researchers. An NPL Report [13] provides a useful review of techniques for single molecule detection for biological applications.

The report summarises a range of technologies under the main headings of microscopy and spectroscopy. Under the microscopy rubric the report includes atomic force microscopy, magnetic resonance force microscopy, scanning electrochemical microscopy and scanning tunnelling microscopy. As the report points out, scanning probe microscopies are used in a wide variety of disciplines. These include fundamental surface science, routine surface roughness analysis, and three-dimensional imaging - from atoms to micrometre-sized protrusions on the surface of a living cell. Scanning probe microscopes may also be used to measure physical properties such as surface conductivity, static charge distribution, localized friction, magnetic fields, and elastic moduli.

In the case of spectroscopic measurements, the report reviews fluorescence correlation spectroscopy, evanescent wave induced fluorescence spectroscopy, scanning near-field optical microscopy, surface enhanced Raman and surface enhanced resonant Raman spectroscopy and surface plasmon resonance.

The report emphasises that many of the initial applications of single molecule spectroscopy in biotechnology have been in the realm of extremely sensitive imaging and analyte detection. More recently a number of studies have emerged that are truly aimed at studying the spectroscopy and dynamics of single molecules and their reactions and interactions with the molecules and complexes that surround them.

At this stage it is not clear what contribution to these technologies can be made by techniques such as molecular modelling. It is necessary to validate the measurement methodologies employed and to establish the reliability of measurements. In addition, visualisation of processes at the cellular level will become more and more important. However, these problems are likely to require more traditional mathematical and statistical methods for their solution.

2.3.2 Measurement at the nanoscale

Summarised below are some of NPL's main activities in measurement at the nanoscale.

- NPL's surface and nano-analysis team uses a number of methodologies for the study of surfaces. These include Auger electron spectroscopy, x-ray photoelectron spectroscopy, secondary ion mass spectroscopy, time of flight secondary ion mass spectroscopy, and atomic force microscopy.
- Dimensional metrology: measurement of surface features and surface texture at the micro and nanoscales (stylus profilometry, scanning probe microscopy, scanning electron microscopy, and super resolved optical microscopy). In addition, NPL has pioneered traceable nanometric and subnanometric displacement measurement using optical interferometry and X-ray interferometry. NPL provides the home for the Combined Optical X-ray Interferometer that was developed by a European consortium for measuring displacement. NPL is also establishing systems for traceably measuring force from sub nano- to millinewtons, such as the force exerted by an AFM tip on a surface or the thrust from an ion engine.
- In nanoelectronics NPL is studying the fabrication of atomic wires, single electron tunnelling devices and attofarad structures. NPL is also working on an ultra-small Superconducting Quantum Interference Device (SQUID) for use in single particle detection.

- NPL designs and simulates nanoscale devices. NPL has pioneered the manufacture of microfabricated lens arrays and nanoscale Josephson junctions for use as voltage standards.
- Atomic force microscopy is used to measure mechanical properties with sub 10 nm resolution. Stiffness and viscous damping of a material can be imaged qualitatively at NPL with 2 nm resolution. Adhesion can also be mapped. Quantitatively Young's modulus of a polymer blend can be identified using AFM in force spectroscopy mode or combining atomic force microscopy with a nanoindenting unit. NPL is also developing analytical and finite element models of nanomechanical measurements.
- A system has been designed and manufactured at NPL to characterize the dynamical mechanical properties of nanomaterials such as thin films, multi-layered coatings, nanowires and nanostructured polymers. This unique facility measures both nanoscale displacements and forces in three orthogonal directions, independently from each other.

A general overview of metrology challenges at the nanoscale from an NPL perspective can be found in an article by Sheridan and colleagues [82]. This article concentrates on experimental developments and does not discuss mathematical modelling questions, other than to make passing mention of some difficulties in quantifying uncertainties at the nanoscale. Nevertheless, validation of the many measurement methods that are discussed will rely on mathematical modelling to support claims about their performance.

3 Sources of information about nanoscale modelling

This chapter identifies some important resources on modelling at the nanoscale, and molecular modelling in particular, that have been employed in writing this report and which the reader may find useful to supplement and develop the ideas expressed here. They also provide background information that documents the growing recognition among NPL scientists that modelling at the nanoscale will take on greater importance in their work. In addition, this chapter gives links to a wide range of resources on nanoscale modelling, including text books, journals and web pages, that may be of use to readers investigating the potential contribution that nanoscale modelling may be able to make to tackling particular metrology problems.

3.1 NPL and Software Support for Metrology background

3.1.1 NPL's mathematical modelling review

In recent years NPL has begun to recognise the importance of developing expertise in mathematical modelling at the nanoscale. The first formal record that set out what developments were needed at NPL was an internal NPL report on future mathematical modelling requirements prepared with the help of Strategic Research funding by a committee of NPL senior scientists chaired by Neil McCartney of NPL's Materials Centre (now part of the Division of Engineering and Process Control) [59]. The committee submitted a report to NPL's Science Director that made a series of recommendations for the future of mathematical modelling at NPL. It argued that mathematical modelling is the derivation of mathematical relationships that quantify the observed behaviour of physical, chemical or biological systems, and that mathematical modelling pervades quantitative science. The quality of that science depends both on the quality of the measurements and the quality of mathematical models. The report illustrated how mathematical modelling contributes to the development of good quality science, metrology and standards. Figure 1 demonstrates how it is the interaction of measurement methods, physical models and mathematical methods that produces the best science. The uses of mathematical models in metrology are typically:

- explaining a physical process that is the basis of a measurement method,
- analysing the results of measurements, especially uncertainty estimation,
- interpreting the results of measurements in order to extract properties that cannot be measured directly,
- simulating measurement processes enabling better design,
- visualising results of experiments and simulations,
- extrapolating measurements in a reliable way to conditions that are not possible experimentally at reasonable cost,
- enabling developments in software to contribute to the tasks listed above.

It is worth quoting in full two paragraphs from the introduction to the report as they help emphasise the growing recognition of the importance to metrology of modelling at the nanoscale.

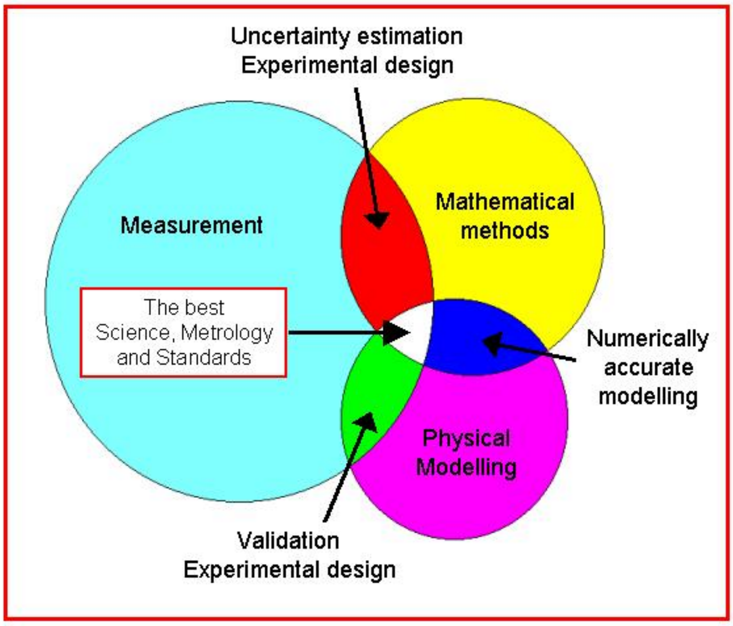

Figure 1: Interaction between measurement, physical modelling and mathematics

> *The planned growth at NPL in measurement activities associated with nanotechnology, biometrology and functional materials is expected to lead to new requirements for mathematical modelling. These will often be similar to existing activities, but new challenges will also appear. Modelling at the nano-level is possible by techniques that range from quantum mechanics, through molecular dynamics, to continuum approaches. One key challenge will be to produce models that are valid for more than one length scale, and spectral range, and for different types of excitation or perturbation: seamless modelling from atoms to structures. NPL is uniquely placed to contribute to the validation of nanoscale models and software in some areas.*
>
> *The proliferation of scientific software, though very useful to metrology, has been a major challenge to NPL scientists over the last decade. In addition to their experimental strengths they have developed an understanding of the many complex models embodied in these software packages. Sharing knowledge and experience of such issues across all scientific centres will promote greater efficiency and increased levels of technical awareness, and will identify specific needs for staff training.*

3.1.2 New Directions study

Within the previous Software Support for Metrology programme the *New Directions* theme studied the changing mathematics, statistics and software requirements of NMS programmes to ensure that the SS*f*M programme was well-placed to be able to respond to the rapid pace of change in other science programmes. One of the studies [33] focused on the new developments in mathematical and software engineering research that would be needed to meet the future challenges of the NMS. It considered, for example, what had been learned from the Smith Institute study of industrial requirements for mathematics and computing.

The Smith Institute roadmap [45] identified simulation as an essential component of modern science and engineering, particularly given the development of cheaper and more powerful computers, so that simulation is used not only to support but often to replace experimentation. This has consequences for modelling at the nanoscale. The traditional manner in which scientists and engineers have attempted to validate theories and the results of model predictions has been the comparison of theoretical predictions with experimental results. When no experiment exists or when the modelling and simulation is done to replace experimental work, this practical approach to validation is no longer available. However, the Institute argued that many simulations are insufficiently realistic because good models do not exist, or because input data are uncertain or incomplete. Modelling at the nanoscale may be able to provide the missing data or may be able to extend the applicability of models to smaller length and time scales. The report's authors also point out that improving the realism of a simulation usually leads to a longer time being needed to carry it out. Expensive models on fine scales often need to be replaced with effective coarse-scale descriptions when computation on the fine scale is not feasible. Thus, hierarchical methods may be employed so that a small, fine-scale simulation may be used to verify a much larger coarse-scale model.

The *New Directions* study also identified some key questions for modelling at the nanoscale.

- How many atoms can be handled using the proposed method?
- How many different properties and material types can be handled simultaneously?
- How well do the various nanoscale modelling approaches overlap - if at all?
- How is it possible for nanoscale models to be validated and benchmarked?
- Are the approximations used in a particular technique reasonable for the problem of interest?
- Are current computing resources adequate to tackle large calculations or is there a need to move to parallel processing, Grid or distributed computing techniques to speed up computation times?

The topic of multi-physics and multi-scale modelling was also addressed by the Shercliff report [81] whose main conclusions were summarised in the *New Directions* study. The report, which reviewed UK activity and requirements in the modelling of materials and processes, made a number of observations relevant to the problems of multi-scale modelling. These are summarised below.

- Centres of excellence in each industrial sector are needed to offer advice and training in modelling, to transfer expertise to industry (particularly SMEs), and for benchmarking software.
- Industrial modelling problems are no less demanding academically than purely scientific research.
- Increased computer power is absorbed far too readily in added complexity, rather than in the more thorough use of an existing model.

- Choosing the appropriate level of complexity is an essential element of all model building.
- Finite element methods are largely mature. Much more can be achieved by integrating microstructural and damage modelling with FE.
- The data needs of a modelling activity, both for input and to validate the output, should be considered (and costed) from the start.
- Interface properties, friction and heat transfer in particular, are critical in all materials process modelling. There is a need for research on micro-modelling of interfacial conditions, and the coupling of these models to macroscopic FE computations and to experiment.

In setting out these conclusions, Shercliff made a number of important comments. He argues that multi-physics models and modelling over several length scales required the development of numerical methods to tackle the solution of problems with many coupled boundary conditions. Shercliff believes that micro-level models are not actually connected to a macro-model for much commercial work, but that a micro-level model is used to generate a higher-level approximation to the phenomenon of interest and that this approximation is then passed on to the next higher-level model.

Occasionally, limitations in macro-modelling generate work in associated micro-modelling. Shercliff's example is of current research on friction and heat transfer, where average values used in macro-models are accepted as inadequate. A combined programme of micro-modelling and experiment is needed. Similar requirements exist in the modelling of piezoelectric materials, where the use of average properties (which are themselves often the subject of large uncertainties), means that the real behaviour of piezoelectric components is not captured by finite element models, for example.

3.2 Prof Quirke's study of molecular modelling opportunities at NPL

Nick Quirke, who is Professor of Physical Chemistry and Head of the Computational and Structural Chemistry Group at Imperial College London, was also a visiting fellow at NPL during the period 2003 to 2005 with responsibility for advising NPL scientists on how best to take advantage of molecular modelling in their research.

In December 2004 Prof Quirke submitted a short internal report to NPL's Director of Science entitled *A Strategy for Molecular Modelling at NPL*. He argued that the motivation for the report was the need to ensure that NPL could achieve a leadership position in metrology for nanotechnology, bioscience and photonics. Molecular modelling plays a key role in ensuring success for industrial and university research laboratories engaged in developing these technologies and there was a range of examples of projects and activities within DTI-funded programmes that required molecular modelling to achieve a leadership position.

He defined molecular modelling as:

> *A set of techniques which enable predictions to be made of molecular and materials properties by using computers to solve the underlying equations governing chemical behaviour. In this sense it is similar to more familiar mathematical modelling work in computational fluid dynamics, acoustics, optics and finite elements: the key difference is that the modelling starts at the level of atoms and electrons not continuous*

> *material elements. It allows materials properties to be predicted and therefore provides inputs to continuum models as well as allowing the molecular or electronic nature of underlying processes to be elucidated.*

He pointed out that many major UK and overseas companies have been employing molecular modelling techniques since the mid 1980s and quoted a recent US report that put the return on investment in modelling for materials science at $3 to $9 for every $1 invested.

During the preparation of the report Prof Quirke identified at least £4m of research work at NPL in the area of nanotechnology that could benefit from molecular modelling. Many of these projects are concerned with the interaction between tips and surfaces which is fundamental to the development of nanoprobe devices for nanoscale characterisation and metrology.

In addition, Prof Quirke commented that molecular modelling can enhance and support continuum modelling of the type routinely required for NMS programme work and could exploit NPL's distributed computing system, and contribute to related SS*f*M work, for example, in visualisation.

3.3 USA study on computational chemistry

In 1999 the USA's Council for Chemical Research (CCR) published a report on the future of computational chemistry in which it attempted to forecast the challenges that would need to be overcome in the field of molecular modelling in the first 20 years of the 21st century (www.ccrhq.org/vision/index/roadmaps/complete.html). The report reviewed the start of the art at the quantum scale, the atomistic scale and the mesoscale and also considered the problems that exist in trying to bridge these length scales. The authors identified a number of computational issues that are relevant to the subject of this report. At the quantum scale they argued, amongst other things, that there was a need for accessible benchmark calculations for selected "gold standard" reference molecules and that more usable robust software was needed. Another major barrier to the development of molecular modelling at this scale was lack of validation of results, and of inadequate methods for predicting uncertainties in calculations. They were also critical of modelling capability at the mesoscale and they argue that there was a need to develop methods for applying statistical and stochastic methods to mesoscale phenomena.

In a discussion of bridging techniques for joining together the various spatial and temporal scales involved in molecular modelling, they argued for the increased use of seamless data interfaces which permit interactions between calculations performed at different size scales. They also considered coarse-graining techniques, which allow knowledge gained from calculations at a small scale to be usefully applied at a larger scale. Lack of good statistical techniques was seen as a critical computational limit for the development of bridging techniques. More research was needed on stochastic methods, including Monte Carlo methods, which are regarded as being able to provide a basis for the techniques needed for moving from scale to scale.

Finally, at all length scales they saw the need for increased computing power, including parallel and distributed computing systems. Distributed and parallel computing could itself assist in bridging length scales simply by allowing very large scale calculations to be carried out.

This report is considered in more detail in chapter 4.

3.4 Textbooks

In preparing this report a number of textbooks have proved useful, both for describing the background to particular methods and for providing software that can be used to test out some of the key mathematical ideas and techniques in modelling at the nanoscale.

The list is not exhaustive and readers are likely to be able to find equivalent texts by other authors. Equally, if a book does not appear in the list, this does not mean that it is not recommended.

3.4.1 Allen and Tildesley, 1987

A book that is now nearly twenty years old but is worth reading as an introduction to computer simulation of materials is *Computer simulation of liquids* by Allen and Tildesley [1]. This book concentrates on atomic and molecular liquids using Monte Carlo and molecular dynamics methods and aims to guide readers through the stages needed to develop software that can be used for modelling liquids. The book contains listings of code in FORTRAN77. In addition, it is possible to download the programs the book discusses from the web server at the Council for the Central Laboratory of the Research Councils' Daresbury Laboratory (www.ccp5.ac.uk/). The book includes chapters on statistical mechanics, molecular dynamics, Monte Carlo methods, advanced simulation techniques, non-equilibrium molecular dynamics, Brownian dynamics and quantum simulations, as well as specific advice on efficient programming techniques and how to analyse the results of modelling.

3.4.2 Frenkel and Smit, 2001

Frenkel and Smit's textbook *Understanding Molecular Simulation: from algorithms to applications* [31] concentrates on molecular dynamics and Monte Carlo methods. It provides a basic introduction to these areas and includes extensive examples, including computer algorithms, data, test case analyses, appropriate references and methodological comparisons. To obtain a flavour of the work consult the authors' web site at molsim.chem.uva.nl/frenkel_smit/ This site also provides links to the FORTRAN software for the case studies and exercises in the book.

3.4.3 Garcia, 1994

Like Vesely's book (described below in section 3.4.9), this text, *Numerical Methods for Physics* [38], covers a wide range for mathematics for computational physics, using Matlab and FORTRAN as the languages for the computing examples. The chapter on stochastic methods, which concentrates on Monte Carlo methods, probably has most relevance for modelling at the nanoscale. The book includes examples in Matlab for some specific problems such as the use of the direct simulation Monte Carlo method for rarefied gas dynamics. The software for this problem and other examples can be downloaded from www.algarcia.org/nummeth/Programs2E.html.

3.4.4 Gubbins and Quirke, 1996

Molecular Simulation and Industrial Applications: methods, examples and prospects by Nick Quirke and Keith Gubbins [40] is a collection of papers, some of them very long, on applications of molecular modelling in industry and in universities. The aim of the book is to present a sample of industrially important applications of molecular modelling. Of course, the selection reflects the position at the time the book was published (1996). However, it is nevertheless an important collection that provides a useful introduction to molecular simulation.

Section one of the book gives an introduction to molecular simulation in industry. The second section concentrates on potentials and the derivation of intermolecular potentials for modelling. Section three discusses the simulation methods most relevant to industry. The fourth section concentrates on simulating the physical properties of fluids. Section five's topic is simulation for biochemistry and pharmacology, and the final section deals with research on polymers, zeolites, carbons, superconducting materials and metals.

3.4.5 Haile, 1997

J.M. Haile's textbook *Molecular Dynamics Simulation: Elementary Methods* [41] concentrates on methods of devising models for specific molecules. The book has useful end-of-chapter exercises to test the reader's understanding and there are FORTRAN listings of molecular dynamics code for hard and soft sphere problems.

3.4.6 Leach, 2001

The text by Leach [54] *Molecular Modelling: principles and applications* gives a detailed account of the mathematical techniques employed in molecular modelling and computational chemistry. The book's range of topics includes an introduction to computational quantum mechanics, advanced *ab initio* methods, empirical force field models, energy minimisation methods, molecular dynamics simulations, Monte Carlo simulations, conformational analysis, and protein structure prediction, sequence analysis and protein folding. Although the book tackles many of these topics in depth it always begins its discussion at a basic level so that it is possible for the non-expert reader to follow the argument. The book contains example calculations together with examples from the scientific literature. There is a companion web site www.booksites.net/leach2/molecular/molecular_modelling_2.html There are also extensive lists of references in the text.

3.4.7 Rapaport, 2004

Denis Rapaport's textbook *The Art of Molecular Dynamics Simulation* is an introduction to molecular dynamics [73]. In the author's own words:

> *This book is a blend of tutorial and recipe collection, providing both an introduction to the subject for beginners and a reference manual for more experienced practitioners. It is organized as a series of case studies that take the reader through*

> *each of the steps from formulating the problem, developing the necessary software, and then using the programs to make actual measurements.*

The software described in the book can be downloaded from the author's web site at www.ph.biu.ac.il/rapaport/mdbook/index.html.

3.4.8 Schlick, 2002

Tamar Schlick's book [76] *Molecular Modeling and Simulation: an interdisciplinary guide* is based on a course in molecular modelling that Prof Schlick taught at New York University in the late 1990s. The book concentrates mainly on biological applications and is designed to act as a framework for teaching graduate students about molecular modelling. It contains chapters on biomolecular structure and modelling from an historical perspective and concentrates on problems and applications, protein structure and protein structure hierarchy, nucleic acid structure, force fields, multivariate minimisation in computational chemistry, Monte Carlo methods, and molecular dynamics. There is much useful mathematical advice in the later chapters of the book. For example, the chapter on minimisation in computation chemistry reviews the fundamentals of optimisation methods, giving suggested algorithms for minimisation and recommendations for ensuring confidence in the result of a geometry optimisation process. These include:

- Use many starting points. Schlick points out that for the minimisation of phenol from a planar geometry, many minimisers produce a planar structure, but this corresponds to a maximum rather than a minimum. The correct non-planar structure can be obtained from the use of different starting points.
- Compare results from different algorithms. Schlick's example here is the minimisation of DNA. In a vacuum system different algorithms are likely to produce very different results because in such a case the DNA strands may separate. To obtain a physically and chemically correct result it is necessary to include water and ions in the system. Modelling the water alone keeps the DNA strands in close proximity but untwists them.
- Compare results from different force fields where possible.
- Check eigenvalues of the solution when possible. At a minimum, for example, the eigenvalues should be positive or zero.
- Beware of artificial minima caused by nonbonded cut-offs or improper physical models. Such models may lead to numerical artefacts such as large gradient values near the cut-off region. A good algorithm will find these minima although they are not physically correct.

The above list is typical of the practical advice given in the book, which will be of use to those developing their own software or using software that offers a range of modelling and solution methods where the user has to chose the most appropriate method for the problem in question.

The author also includes advice on the choice of random number generators for Monte Carlo problems, including the need to appreciate that a particular random number generator may in some cases interact with the problem algorithm in subtle but unpredictable ways.

Prof. Schlick's web pages are at monod.biomath.nyu.edu/.

3.4.9 Vesely, 2001

This book, *Computational Physics: an introduction*, is based on courses that the author, Prof Vesely, teaches at the University of Vienna [105]. It covers basic mathematical techniques that are needed for all computational physics, such as finite difference methods, linear algebra, stochastics, ordinary differential equations and partial differential equations but also topics that are directly relevant to modelling at the nanoscale: simulation for statistical mechanics, including Monte Carlo methods, quantum mechanical simulation, and modelling hydrodynamics problems. The style is very much that of a tutorial in these topics with suggested algorithms, including advice on how to circumvent potential computational problems, and some end-of-chapter exercises. To obtain the most benefit from the book it is probably best to use it together with the author's web site, which also includes teaching material from his university courses (www.ap.univie.ac.at/users/Franz.Vesely/).

3.5 Journals

Some key journals for mathematical modelling at the nanoscale that are published by the UK's Institute of Physics are:

- *Journal of Physics: Condensed Matter* reports on studies of the structural, thermal, mechanical, electrical, magnetic, optic and surface properties of condensed matter and covers surface, interface and atomic-scale science including theory, experiment and simulations, and liquids, soft matter and biological physics.
- *Nanotechnology* concentrates on nanoscale science and technology with a particular emphasis on interdisciplinary papers. Its definition of nanotechnology is wide:

  > *. . . nanotechnology is taken to include the ability to individually address, control, modify and fabricate materials, structures and devices with nanometre precision, and the synthesis of such structures into systems of micro- and macroscopic dimensions such as MEMS based devices. It encompasses the understanding of the fundamental physics, chemistry, biology and technology of nanometre-scale objects and how such objects can be used in the areas of computation, sensors, nanostructured materials and nano-biotechnology.*

- *Modelling and Simulation in Materials Science and Engineering* covers a wide range of topics from *ab initio* and semi-empirical methods for electronic structure and properties of materials, microstructural level phenomena, continuum modelling, macrosopic process models and also publishes papers on simulation to aid the interpretation of experimental data.
- *Journal of Micromechanics and Microengineering* deals with micromechanical structures, devices and systems, including fabrictaion technologies. The journal also publishes papers on computer aided design of MEMS devices, metrology aspects of MEMS, and on modelling to predict the performance of MEMS devices.

Molecular Simulation is published by Taylor and Francis and concentrates on applications of simulation methods, and original contributions to the development of simulation methodology in the fields of biology and biochemistry, chemistry, chemical engineering, materials and nanomaterials, medicine, physics and information science. The journal seeks to encourage cross-fertilization between application areas, methodologies, disciplines, and between academic and industrial researchers.

3.6 Web resources

The Internet contains substantial resources on nanotechnology and mathematical modelling. A search on the Google search engine during the period when this report was being written produced nearly 300,000 responses to the words “nanotechnology mathematical modelling”. Other extensive resources can be obtained using “computational chemistry” and “molecular modelling” as search terms.

Some suggested sites for those who are not experts in this field and who wish to learn more about what is possible are set out below. This list is not meant to be exhaustive but to be indicative of the kinds of nanoscale modelling resources that can be found on the Internet.

- The USA’s National Centre for Supercomputing Applications has *ChemViz* which aims to help high school students learn quantum chemical concepts and is an interactive chemistry program which incorporates computational chemistry simulations and visualizations for use in the classroom chemviz.ncsa.uiuc.edu/. Their Resources page chemviz.ncsa.uiuc.edu/content/doc-resources.html has a range of useful links, especially if one is interested in learning the basics of computational chemistry. A good place to begin is with their Overview of Computational Chemistry page www.shodor.org/chemviz/overview/ccbasics.html.
- The Virtual Library of molecular modelling and simulation resources is at www.liv.ac.uk/Chemistry/Links/refmodl.html and is maintained by *Links for Chemists (University of Liverpool)* (www.liv.ac.uk/Chemistry/Links/links.html), which is an index of chemistry resources on the web. It is in fact the chemistry section of the WWW Virtual Library vlib.org/.
- *The EMSL Ab Initio Methods Benchmark Report : A Measure of Hardware and Software Performance in the Area of Electronic Structure Methods* (www.emsl.pnl.gov/docs/tms/abinitio/cover.html) provides information on the computational performance of various *ab initio* codes. Although the work is nearly a decade old it is still a useful starting point. The aims of the report are stated by the authors to be:

  > *Assist scientists who are performing ab initio calculations to make decisions about which hardware/software combinations will run their problem most efficiently. When changes in hardware are not under consideration, these findings should help users determine the best software for a particular type of calculation.*
  >
  > *Assist individuals who are attempting to track the rapidly changing hardware scene by providing a measure of the relative speed of some of the major hardware platforms in the area of electronic structure methods.*
  >
  > *Assist developers of new codes for both conventional microprocessors and advanced architectures by providing a meaningful yardstick for performance measurements on the new hardware and software.*
  >
  > *Assist developers of graphical user interfaces for ab initio applications who wish to provide built-in assistance to the users as they choose programs and/or machines on which to run.*

- *A Tour of the Foundations of Computational Chemistry And Material Science*, Computational Chemistry and Materials Science pages, USA Army Research Laboratory Major Shared Resource Center (www.osc.edu/PET/CCM/skeleton/training/courses/foundations/foundations.html).
- *Workshop on Applications of Molecular and Materials Modelling: Preliminary Findings of the International Comparative Study* (the "Westmoreland report", produced under the chairmanship of Phillip Westmoreland, University of Massachusetts) (www.wtec.org/loyola/molmodel/views/welcome.htm).
- The *NetLaboratory* is an Internet-based community for researchers and engineers. One of its functions is to provide users with the opportunity to find tools that will make high quality research easier to perform and to provide links for computational chemists and materials scientists that are found to be particularly relevant. These cover software, meeting announcements and general research tools (such as journals and search engines) (venus.netlaboratory.com/cae/fecit/fecit1.html). It contains an extensive list of available software, including much freeware and shareware.
- Molecular Graphics and Modelling Society(MGMS) www.mgms.org/. The MGMS was set up in 1981 as a society dedicated solely to the interests of molecular modelling and related aspects of computational chemistry. It publishes the *Journal of Molecular Graphics and Modelling* (www.sciencedirect.com/jmgm).
- The software holdings of the UK Computational Chemistry Facility lists current software recommended by the UK Computational Chemistry Working Party (www.nsccs.ac.uk/software.php). Although this site is for academics who will be running software on EPSRC computing resources at the Rutherford Appleton Laboratory, it contains detailed information on a wide range of computational chemistry software and links to websites associated with the software it describes.
- The Center for Molecular Modelling, National Institutes of Health, USA (cmm.cit.nih.gov/modeling/) is part of the Division of Computational Bioscience of the USA's National Institutes of Health. Its research concentrates on the development and application of theoretical and computational methodologies, from *ab initio* quantum mechanics calculations of small organic molecules to molecular mechanics simulations of macromolecular systems.
- The European Science Foundation programme "Challenges in Molecular Simulations: Bridging the time-scale and length-scale gap" (SIMU) aims to build cooperation across Europe in the field of computational physics and chemistry of condensed matter, with emphasis on the development of tools to perform multiscale molecular simulations. Its web site can be found at www.esf.org/.

3.6.1 Collaborative Computational Projects

The Collaborative Computational Projects (CCPs) assist universities in developing, maintaining and distributing computer programs and promoting the best computational methods. They are funded by the UK's Engineering and Physical Sciences Research Council, the Particle Physics and Astronomy Research Council and the Biotechnology and Biological Sciences Research Council (www.ccp.ac.uk/). Each focuses on a specific area of research and those that are most relevant to modelling at the nanoscale are:

- CCP1 (www.ccp1.ac.uk/) concentrates on software for studies of the electronic structure of molecules.
- CCP2 (www.ccp2.ac.uk/index.shtml) has the aim of developing theoretical techniques and computer programs to describe collisions between projectiles such as electrons, positrons or photons and atomic or molecular targets. Topics of current interest include atoms and molecules in strong laser fields, chaos, Bose-Einstein condensates and atom-optics.
- CCP3 (www.ccp3.ac.uk/) concentrates on the computer simulation of surface structure and properties. It seeks to provide high quality, accurate and up-to-date computer codes for the analysis of a wide range of surface science experiments.
- CCP5 (www.ccp5.ac.uk/) is dedicated to the computer simulation of the condensed phases of matter. It has an extensive library of software on molecular dynamics, Monte Carlo methods, Lattice Statics and Lattice Dynamics. Software from *Computer Simulation of Liquids* by Allen and Tildesley [1] is available from this site.
- CCP9 (www.ccp9.ac.uk/) is the Collaborative Computational Project for the study of the electronic structure of condensed matter. Their work includes the study of metals, semiconductors, magnets, and superconductors from microscopic quantum mechanical calculations. Their activities also include magneto-electronics, photonics, nano-technology, high-temperature superconductors, and novel wide band gap semiconductors.

3.7 Software

This section of the report identifies some sources of public domain software that are useful in learning the basics of molecular modelling and in giving users experience of modelling at this scale.

3.7.1 Tinker

The Jay Ponder Laboratory in the Department of Biochemistry and Molecular Biophysics at the Washington University School of Medicine in Saint Louis, Missouri, distributes a range of software that is useful for modelling at the nanoscale. Their home page is at dasher.wustl.edu/. Perhaps the most important package that can be downloaded from their site for free is the TINKER molecular modelling package. The home page for the software is at dasher.wustl.edu/tinker/. A users' manual of more than 200 pages can also be downloaded.

To quote from the introduction to the users' guide to the software:

> *TINKER is designed to be an easily used and flexible system of programs and routines for molecular mechanics and dynamics as well as other energy-based and structural manipulation calculations. It is intended to be modular enough to enable development of new computational methods and efficient enough to meet most production calculation needs. Rather than incorporating all the functionality in one monolithic program, TINKER provides a set of relatively small programs that interoperate to perform complex computations. New programs can be easily added by modellers with only limited programming experience. The series of major programs included in the distribution system perform the following core tasks:*

> 1. *building protein and nucleic acid models from sequence*
> 2. *energy minimization and structural optimization*
> 3. *analysis of energy distribution within a structure*
> 4. *molecular dynamics and stochastic dynamics*
> 5. *simulated annealing with a choice of cooling schedules*
> 6. *normal modes and vibrational frequencies*
> 7. *conformational search and global optimization*
> 8. *transition state location and conformational pathways*
> 9. *fitting of energy parameters to crystal data*
> 10. *distance geometry with pairwise metrization*
> 11. *molecular volumes and surface areas*
> 12. *free energy changes for structural mutations*
> 13. *advanced algorithms based on potential smoothing*
>
> *Many of the various energy minimization and molecular dynamics computations can be performed on full or partial structures, over Cartesian, internal or rigid body coordinates, and including a variety of boundary conditions and crystal cell types. Other programs are available to generate timing data and allow checking of potential function derivatives for coding errors. Special features are available to facilitate input and output of protein and nucleic acid structures. However, the basic core routines have no knowledge of biopolymer structure and can be used for general molecular systems.*
>
> *Due to its emphasis on ease of modification, TINKER differs from many other currently available molecular modeling packages in that the user is expected to be willing to write simple front-end programs and make some alterations at the source code level. The main programs provided should be considered as templates for the users to change according to their wishes. All subroutines are internally documented and structured programming practices are adhered to throughout. The result, it is hoped, will be a calculational system which can be tailored to local needs and desires.*

Associated with TINKER is the FORCE FIELD EXPLORER software (dasher.wustl.edu/ffe/) which is a graphical user interface to the TINKER suite of programs. This allows one to set up TINKER routines through a menu system, to visualise results and play back the trajectory of a particular simulation.

The software also comes with a suite of examples that can be used to gain some familiarity with the system and which demonstrate among other things energy minimisation, determination of molecular volume and surface area, and determination of the lowest frequency normal mode of an amino acid sequence.

This package, which can run on Windows machines, is useful for those who wish to investigate what can be achieved with molecular modelling software. The user can also modify the code to tackle new problems.

3.7.2 Molecular Modelling Toolkit

For those with experience of Python or who are willing to learn Python it may be worth considering the open source Molecular Modelling Toolkit (MMTK) starship.python.net/crew/hinsen/MMTK/ which is a program library for molecular simulation applications. In addition to providing ready-to-use implementations of standard algorithms, MMTK serves as a code basis that can be easily extended and modified to deal with standard and non-standard problems in molecular simulations. It was developed by Konrad Hinsen at the Laboratoire Léon Brillouin and is described in a paper by him in the Journal of Computational Chemistry [44].

On the website given above Hinsen describes the software in the following way:

> *MMTK is based on an object-oriented model of molecular systems. A system is made up of atoms, molecules, and complexes, all of which are defined in MMTK's chemical database. A molecule, for example, is defined in terms of atoms, functional groups, bonds, force field parameters, etc. It is possible to introduce specialized versions of these objects; for example, MMTK has special support for proteins, which are basically chemical complexes, but can be handled in terms of peptide chains, residues, sidechains etc.*
>
> *MMTK's functionality includes:*
>
> - *construction of molecular systems, with special support for proteins and nucleic acids*
> - *infinite systems or periodic boundary conditions (orthorhombic elementary cells)*
> - *common geometrical operations on coordinates*
> - *rigid-body fits*
> - *visualization using external PDB and VRML viewers; animation of dynamics trajectories and normal modes*
> - *the AMBER 94 force field, with several options for handling electrostatic interactions*
> - *a deformation force field for fast normal mode calculations on proteins*
> - *energy minimization (steepest descent and conjugate gradient)*
> - *molecular dynamics (with optional thermostat, barostat, and distance constraints)*
> - *normal mode analysis*
> - *trajectory operations*
> - *point charge fits*
> - *molecular surface calculations*
> - *interfaces to other programs*
>
> *Compared to standard modelling code written in Fortran, MMTK is much easier to understand, extend, and modify. For example, new force fields can be added without touching any existing code, i.e. without any risk of breaking it, and new integrators can be developed without any assumptions about force field implementations. MMTK users can also profit from a large collection of Python code developed for other applications, scientific or otherwise.*

3.7.3 Materials Studio

A commercial software package that is in use at NPL is Materials Studio from Accelrys (www.accelrys.com/products/mstudio/modeling/). See chapter 9 for a case study in the use of Accelrys.

3.8 Finite element modelling and nanoscale applications

So far this chapter has concentrated on molecular modelling and computational chemistry. However, much modelling at the nanoscale can be carried out with more traditional approaches such as finite element modelling.

A recent paper by Mackerle provides an extensive bibliography of papers on finite element modelling for nanomaterials and nanomechanics applications [56]. It cites work on nanomaterials and nanostructures and their properties, applications of nanomaterials and nanostructures; atomic force microscopy, nanoscale microscopy, lithography and pattern transfer.

Pask and Sterne [67] have also published a useful paper on finite element methods in *ab initio* electronic structure calculations.

For readers who wish to consider the use of finite element methods at the nanoscale both these papers are recommended.

4 US Computational Chemistry Roadmap

A brief introduction to this important document has been given in section 3.3 (www.ccrhq.org/vision/index/roadmaps/CompChem%20Roadmap%2092599.pdf). Although the roadmap is now several years old it contains a number of observations and recommendations that are relevant to this report.

The motivation for the roadmap study was a review of the future of the chemical industry in the United States that sought to provide a vision of what the industry would look like in the year 2020 (membership.acs.org/i/iec/docs/chemvision2020.pdf). This *Technology Vision 2020* report made a number of recommendations concerning the computational technologies needed for success in chemical engineering that relate to the remit of this report. These are quoted below:

- *Renewed effort in experimental validation is required. The development and application of computational methods are now largely separated from experimental testing of results; discrepancies and limitations are still sometimes discovered by accident rather than by design.*
- *In the area of computational molecular science (CMS), several improvements are necessary to make the tools more useful in modelling. Major improvements are needed in user interfaces for molecular modelling and design, including guidance in problem specification, method selection, computing platform selection, results visualization, and performance of ancillary computations to relate these results to observable physical and chemical properties.*
- *Integration of CMS with statistical thermodynamic and continuum methods is required for full treatment of many problems.*
- *Development of kinetic and thermodynamic modelling will allow prediction of long-term stability and performance of materials.*
- *For scientists and engineers to better model more complex fluid dynamic systems (coupling chemical reactions with multi-phase, multidimensional, simultaneous fluid, heat, and mass transfer dynamics), CFD programs can be developed to incorporate emerging advances in physical models and property databases and to provide a readily adaptable architecture.*
- *Software tools are needed that bring together a complete modelling environment, including simulation, parameter estimation from experimental data, optimization, graphical representation of results, and statistical measures of uncertainty.*
- *Increased support is required for experimental validation of (or challenges to) computational results. The technology would benefit greatly from a large coordinated program combining work on theoretical and computational methods with experimental programs designed from the beginning to challenge those methods.*

The Technology Roadmap for Computational Chemistry was designed to build on the *2020* vision. The roadmap begins by considering the role of computational chemistry or molecular modelling in the chemical industries. In addition to helping solve essentially economic problems such as shortening product and process development cycles, optimising processes and improving environmental performance and efficiency, computational chemistry can be used to design molecules, for example, by accurately predicting thermochemistry so that feasible reaction pathways can be identified. It is also able to predict a wide range of spectroscopic properties (IR, Raman, UV-Vis, NMR, EPR, photoelectron). In addition, calculations of electronic structure help in the understanding of bonding, orbital energies and shapes.

The authors divide computational chemistry into its "components" in the following manner. In their own words:

- *Quantum Scale - solves the Schrödinger equation for electronic motion in atoms and molecules either by molecular orbital or density functional theories. Predicts molecular structure, energetics, bonding, reaction rates, and spectroscopic data. Quantum effects are particularly important in chemical reactions and spectroscopy, and provide the basis for predicting interactions at the atomic and molecular scale. The results of quantum mechanical calculations are often used in the design of molecular force fields providing a connection to the next scale, that of atomistic simulations.*
- *Atomistic or Molecular Scale - computes interactions between atoms or groups using classical Newtonian mechanics and empirically determined force fields. Calculates structure and thermodynamic and transport properties, and time dependence of the structure. Calculations are usually done by molecular dynamics or Monte Carlo methods using classical "ball and spring" force fields. Properties described at this scale might range from thermodynamic properties (critical points, pressures) to transport properties (mass and heat transfer) and phase equilibria. Using statistical mechanics, the results of atomistic or molecular scale calculations can then be applied to describe behaviour at the mesoscopic and macroscopic scale (e.g., process or bulk properties)*
- *Mesoscale - in between atomistic calculations and the continuum assumption of traditional materials engineering. Typically applies to systems of millions of atoms which still reflect molecular scale phenomena.*
- *Bridging Scales - theory and models to provide an interface between scales.*

The roadmap also emphasises that it is the recent growth in computational power, together with improvements in computational techniques, that have made it possible for computational methods to be employed in addressing a wider range of problems. Computational methods are being used to "complement, guide and sometimes replace" experimental measurements.

4.1 The quantum scale

The roadmap reviews at length the current state of modelling at the quantum scale and also identifies barriers to future progress. At the time the report was written, the authors point out that computational quantum chemistry techniques were capable of calculating the heats of formation of small molecules to significantly better than 1 kcal/mol and could calculate accurate charge distributions at the *ab initio* level for molecules with more than 700 atoms. Density functional theory and correlation methods could deliver lower but useful accuracy for much larger systems.

The report provides a useful summary of the language and technical terms used in molecular modelling computational quantum chemistry and this is reproduced below, with some amendments to aid understanding.

- **ab initio Molecular Orbital Theory** - is an approximate theory that describes the electronic structure (e.g., electrons, nuclei) of molecules using rigorous quantum mechanical principles;

solution of the Schrödinger equation for electronic motion in the fixed nuclei (Born-Oppenheimer) approximation using the concept of molecular orbitals, that is, that electrons behave independently from each other.

- **Basis set** - a complete set of known functions which represent the atomic orbitals.
- **Car-Parrinello** - an approach to finding the energy and structure simultaneously by performing molecular dynamics simulations while optimizing the energy, based on a density functional theory approach.
- **Density Functional Theory (DFT)** - a theoretical model by which the energy of an N-electron system can be described as a functional of the one-particle density.
- **Electron Correlation** - defines the treatment of electron-electron interactions. These interactions are missing in the simpler Hartree-Fock approximation.
- **Hartree-Fock** - a theoretical model, based on molecular orbital theory, which solves the Schrödinger equation self-consistently using an antisymmetrized, linear combination of atomic orbitals and a single arrangement of electrons within those orbitals.
- **Heavy Atom** - any atom other than hydrogen. The number of non-hydrogen atoms is used loosely to characterize the difficulty of a quantum calculation.
- **Perturbation Theory** - a self-consistent, systematic procedure for finding the correlation energy neglected by Hartree-Fock methods, based on a perturbation expansion of the energy. Other approaches to finding the correlation energy include coupled cluster methods and configuration interaction.
- **Scaling** - describes the rate of increase in computational cost with system size. It is expressed as N^m where N is the number of degrees of freedom and m is a method-dependent exponent.

The roadmap then reviewed what it considered to be the main barriers to advances in computational chemistry. It identified the barriers to achieving high accuracy on small-to-medium sized systems (up to about 30 heavy atoms) as:

- the extremely rapid increase in computational resources required as the size of the system increases, referred to as the "N^7 scaling problem" for present high-accuracy methods;
- the need for experimental validation of new methods;
- the need for convenient, practical access to cost-effective high performance computing;
- the need for a high level of expertise in order to obtain reliable results and avoid "ugly surprises" due to mis-application of advanced methods.

Interestingly, the definition of "validation" that is being used here is:

> *The purpose of validation is not really to show agreement between experiments and computational models. It is, rather, to challenge the model - to discover the limitations and range of applicability of the model. A "validation" project which merely demonstrates agreement with experimental data is much less useful than one that shows where the model fails, as well as how it performs under a variety of conditions.*

For medium-to-large systems (500 heavy atoms or more) the barriers to good accuracy were seen as:

- lack of adequate basis sets for all atoms of the periodic table;
- the need for validation;
- the need for more accurate, consistent functionals for the density functional theory methods, which are appropriate for larger systems;
- the need for better, more fundamental and universal empirical factors, corrections, and hybrid methods;
- the need for better methods to compute the best structure or ensemble of low-energy structures for large, flexible molecules;
- the need for better methods of modelling the liquid state and the interactions of target molecules with solvents.

More generally, they argued that there was a need for:

- methods with better scaling and better solutions to the fundamental causes of error;
- combining quantum methods with other models to solve larger problems;
- accessible benchmark calculation and experimental results for selected “gold standard” reference molecules;
- expert advisory systems and more usable robust software.

They also emphasised that accounting for the effects of solvents presented a severe challenge. This is because it is necessary to average over solvent configurations to achieve converged results for the solute and also to account for interactions with solvent molecules. Modelling the effects of solvents explicitly or simulating them using approximate methods is essential for the study of chemical reactions in solution, especially in biochemistry.

The authors also commented on specific computational and validation problems. They argued that:

- there is no way for a non-expert user to optimise available modelling options to perform calculations in the most efficient way. As a result numerous unnecessary computations are performed at considerable computing expense;
- empirical parameters are lacking for a number of computational methods, so that estimation methods are used which itself increases the possibility of erroneous results and the occurrence of pathologically wrong results;
- there is a lack of validation for specific problems of interest to users. In such cases the reliability and utility of results is highly uncertain.
- the methods for predicting uncertainties in calculations are inadequate as are methods for interpreting results.

4.2 Modelling at the atomic scale

At the scale of atoms and molecules a much wider range of calculations is possible. This includes thermodynamic properties, bulk transport properties and rheology of fluids. The systems modelled may incorporate phase changes and consist of heterogeneous components.

Once again, the roadmap report provides a useful short glossary of the basic terminology of modelling at this scale, which is again reproduced below with some amendments.

- **Molecular Dynamics Methods** - atomistic molecular simulation methods in which Newton's classical equations of motion are solved numerically for a system of atoms or molecules using finite difference methods.
- **Monte Carlo Methods** - atomistic molecular simulation methods in which the equilibrium configurations of systems of atoms or molecules are sampled statistically with the help of random numbers.
- **Non-equilibrium Molecular Dynamics** - molecular dynamics method which simulates systems that are away from equilibrium and subject to external fields. Both steady-state and transient phenomena can be modelled. In steady-state non-equilibrium molecular dynamics all heat produced by the work of external fields is removed by thermostats.
- **Gibbs Ensemble Method** - method in which the conditions of phase equilibrium are directly simulated and therefore is suitable for vapour-liquid coexistence curve calculations.
- **Gibbs-Duhem Method** - method of determining phase equilibrium by integrating the Gibbs-Duhem equation
- **Intermolecular Potentials** - empirical or *ab initio* force fields used to describe interacting atoms and molecules, or sites within molecules.

The authors argue that "one of the consequences of the diversity of researchers and users of atomistic methods is that many research calculations are performed by special purpose codes rather than commercial codes, and adoption of new techniques into commercial codes is relatively slow."

They also comment that, "An increasingly important component of research at the atomistic scale is the development of intermolecular potentials suitable for a wide variety of compounds and temperature/pressure conditions. Such potentials are critical to the prediction of properties of practical importance to chemical process and product design . . . Unlike other advances in atomistic simulation, third party vendors have been relatively quick to implement leading edge codes relating to intermolecular potentials and most commercial packages reflect the current state-of-the-art."

The report sets out a vision of what would be required in computational chemistry by the year 2020. The authors envisage that by that date it will be routinely possible to model systems of one million atoms or more and length scales of 10 to 100 nanometres. This would allow the modelling of systems that were comparable to the size of specific applications, such as the simulation of 0.1 micrometre thin films.

One of the main limitations to progress that the roadmap identifies is that there is a lack of methods for estimating the intrinsic accuracy of calculations and of results. This arises both from the limited availability of experimental data and inadequacies in basic science and theories underlying the computational methods that are used.

4.3 The mesoscale

The roadmap argues that mesoscale modelling is by no means a mature discipline and that its current limitations cannot simply be solved by bigger and faster computers. Mesoscale modelling requires both the modelling of systems in such a way as to be able to predict how molecular structure determines measurable macroscopic properties and the ability to compute the properties of systems on spatial and time scales that are much larger than can be achieved in atomistic scale calculations.

The authors summarise the barriers to developments in mesoscale modelling as:

- *lack of theoretical tools for the mesoscale;*
- *lack of links to atomistic models;*
- *lack of knowledge (data) of morphology of materials;*
- *lack of experiments designed to validate modelling;*
- *lack of software for the best available methods;*
- *lack of algorithms to take advantage of future computers;*
- *cost of high performance parallel computing.*

The report argues that the most critical barrier to the use of computational chemistry tools at the mesoscale is absence of proper theoretical tools. They comment that:

> *Mesoscale computations are unique in computational chemistry because the theory to fully describe the phenomena has not yet been developed. Mesoscale refers to the length scale that lies between the atomic and bulk scales. Materials demonstrate both atomic and bulk phenomena at this scale, while often being in a non-equilibrium state due to processing conditions. The defining equations linking these regimes are complex. Current models extrapolate calculations from either the atomic or bulk scales, and involve much empiricism. This generally does not produce results that accurately describe mesoscale phenomena. Results can be difficult to interpret and link to experimentally observable properties. The few validation experiments that have been conducted at this scale show quite a difference in results between the theoretical models and the actual data. Part of this problem can be attributed to the poor sensing equipment that is used in these experiments. It is very difficult to accurately measure physical properties such as temperature and fluid velocity at this scale. Given a complex molecular structure such as that of a polymer, it is now possible to predict at some level what the properties of the material are likely to be. The accuracy of the results depends critically on the complexity of the structure as well as available information on similar structures. For example, various QSPR (quantitative structure property relationship) models are available for the prediction of polymer properties. However, the inverse of this process (designing structures given a set of properties) is far more difficult and is practised today by synthetic chemists using mostly heuristic methods, based on individual knowledge and experience. A significant amount of effort is currently being expended to develop "reverse engineering" software to solve the problem of going backwards from a set of desired properties to chemical structures.*

> *These efforts are primarily based on artificial intelligence techniques and have met with limited success.*

There are also data limitations. Here the roadmap points out that:

> *Presently there are not enough good validated measurements of the morphology of mesoscale systems. Methods to measure mass, heat, and momentum transfer in such systems have not been developed. The lack of specific experiments geared towards validating the results of molecular modelling is part of the reason that such methods have not yet been developed. One of the reasons is the fact that there is very little collaboration between molecular modellers and experimentalists, resulting in a scarcity of the data that is required by modellers.*

4.4 Bridging techniques

The final topic that is discussed in the roadmap is that of bridging techniques, computational methods that can link a range of time and spatial scales from the quantum scale, via the atomic scale to the mesoscale and from femtoseconds to hours. The aim of such methods is to use the results of a calculation at one scale as inputs to a calculation at another scale.

There are two general approaches to this problem - seamless data interfaces and coarse-graining techniques.

The first of these, seamless data interfaces, refers to the ability of software to exchange data from a calculation performed at one length or time scale with a calculation at another scale. The aim is to be able to extend calculation results over a range of scales and a range of different programmes and software products.

In coarse-graining methods are theory-based approaches that allow knowledge gained from calculations at one scale to be applied at a larger scale. For example, certain degrees of freedom may be eliminated (averaged out) and replaced with the mean action, that is, in a large molecule all intra-molecular motion is frozen in an averaged configuration and the molecule is considered as a single rigid body.

The need for such approaches can be understood simply by recognising that modelling at the atomic scale concerns itself with discrete entities, but that as we move to the bulk scale, we tend to describe materials in terms of continua and continuum properties such as Young's modulus. What is needed is the ability to obtain a value for Young's modulus, say, from an atomic scale calculation and then be able to input this directly into a finite element calculation that models a much larger region or field than is possible at the atomic scale. Both these techniques, seamless data interfacing and coarse-graining, are currently very active research fields.

5 New modelling challenges in the NMS programmes

5.1 Introduction

This chapter of the report reviews some of the developments in mathematical modelling that will be needed to tackle the new challenges being faced by NMS programmes and identifies projects to which molecular modelling in particular may be able to make an important contribution. A point to note here is that in these new and developing areas it is not possible simply to rely on software - academic, freeware, or commercial - that has been developed by others. In fields such as *ab initio* modelling or in molecular mechanics and dynamics, one requires a good physical understanding of the underlying models and the ability to judge whether particular software is appropriate to the task and is producing reliable results. If one wishes to work at the leading edge of mathematical modelling, it is likely that one will be seeking to collaborate with software developers, both commercial and academic, who are writing state of the art software, rather than simply buying products and using them as “black boxes”. The identification of a set of test problems in molecular modelling, for example, for which answers are already known, or for which good experimental data exist, for use in model validation, is a key requirement.

5.2 Molecular modelling challenges

It is useful at this point to identify some of the specific difficulties that one faces in this area of research. This is particularly important when one is considering some of the newer areas of metrology such as nanotechnology, biotechnology, functional materials and photonics.

Ideally one would prefer to be able to calculate the physical and chemical properties of a material from first principles, simply from knowledge of the physical laws governing the system, and without the need to introduce empirically-determined parameters. *Ab initio*, or first-principles methods, seek to do this, albeit for systems of limited extent and with some simplifications and approximations. They are of growing importance in molecular modelling, especially as high-performance computing and grid computing become more widely used. In addition, they act as the yardstick against which methods that are applied at larger length and time scales can be tested. As NMS metrologists begin to develop molecular modelling capabilities and to seek collaborations with academic groups and commercial organisations active in this area, we will encounter a growing need to be able to understand and apply *ab initio* methods ourselves and in concert with industrial and academic partners.

A instructive introduction to the problem of simulating the behaviour of quantum mechanical systems from first principles is given in a review by Segall, Lindan and colleagues [79]. The review article uses the CASTEP (Cambridge Serial Total Energy Package) software as an example. CASTEP is based on density functional theory and is available commercially from Accelrys running under the Accelrys $Cerius^2$ modelling environment.

The authors emphasise that numerical simulations are used because of the many-body problem: the need to compute the interactions between collections of atoms or charged particles that are too large to be studied analytically. They argue that it is impossible for model systems to capture every feature of the real systems they correspond to. One works with idealized systems with the aim of representing the essence of the scientific problem. It is necessary to understand how the various choices made in setting up the calculation affect the results, and in employing density functional theory with an approximate functional, one has already made a choice which has implications for the accuracy of the results.

For reliable results one must have a good understanding of the physics underlying the model that the software is designed to solve. However, the software itself may present some problems, as the authors emphasise. They point out that the original version of the code was written in 1986 using FORTRAN77 and functional programming methods. The original developer and ten co-authors added a range of features to the code and eventually the code stood at 120,000 lines of FORTRAN77. The authors found that development of the code ground to a halt because it took longer and longer to implement changes and the structure of the code grew more and more complicated. This eventually led the authors of CASTEP to spend two and a half years specifying, designing and writing a completely new version of the code in FORTRAN90 using object-oriented design methods to attempt to overcome these difficulties.

It is clear from the experience recounted above that modelling at the level of atoms and molecules and the writing of the necessary software is not a field which can be entered without a substantial commitment of intellectual effort, time and financial resources. It is likely that the most effective manner of operation for NMS metrologists is that, once they have identified a metrology problem to which they think molecular modelling techniques may be able to make a contribution, they begin to specify in some detail exactly what the question is to which they require an answer and that they then seek collaborations with academics and with commercial software developers.

5.3 The potential for molecular modelling work at NPL and the new SR fellowship

Following the identification of a potential need for a Strategic Research fellow in molecular modelling at NPL, which was one of the recommendations from the report commissioned from Prof Quirke (see section 3.2 of this report), an email survey of NPL staff with possible interests in molecular modelling was carried out. The aim was to identify possible specific work tasks for the holder of the new post, if it were decided to adopt Prof Quirke's recommendation.

The survey was addressed to NPL knowledge leaders, members of the internal NPL nanotechnology and biotechnology email lists and to others who were known to have an interest in modelling at the nanoscale. Potential responders were asked to consider a wide definition of modelling at the molecular and atomic scale, so as not to limit requirements specifically to molecular mechanics and molecular dynamics methods. The range of topics identified by NPL staff was extremely wide-ranging. Some problems require *ab initio* modelling; others are appropriate for molecular mechanics and molecular dynamics methods and some can be tackled using more coarse-grained approaches, including techniques that have traditionally been encompassed within the domain of computational physics. Nevertheless, it was possible to identify three general themes within the email responses and within Prof Quirke's report that could form the basis of a coherent work package for the SR fellow in molecular modelling. These are:

1. Functional properties of complex systems on the nanoscale
2. Novel magnetic properties of 1D nanostructures
3. Ionic liquids and transport properties of fluids in nanopores

The objectives of the new post have been defined as:

1. to create a new capability within NPL by significantly developing and enhancing NPL's expertise in the area of molecular modelling;
2. to further raise the awareness of molecular simulation methods, and to bring NPL to internationally competitive level in molecular modelling;
3. introducing the power of molecular simulation methods to principal science areas at NPL to help NPL achieve a leadership position in nanotechnology.

5.4 Bioinformatics at NPL

Biotechnology forms a key part of the NMSD's science strategy and a useful review of bioinformatics issues relating to metrology can be found in the Software Support for Metrology *New Directions* study entitled *New Directions - Software Issues in Bioinformatics* [22]. The authors argue that biological measurements do not present new challenges for mathematicians and statisticians other than the very large amounts of data that can be generated by modern measurement technologies such as microarrays. It is likely that statistical interpretation of measurement results and the use of statistical methods in experimental design can be tackled through collaborations between NPL's biotechnology team and NPL's mathematicians and statisticians and such collaborations are already taking place in relation to the study of microarray data and of the results of circular dichroism experiments.

A developing area where it is necessary to consider whether molecular modelling can make a particular contribution to biotechnology is in relation to single molecule detection. A useful review of experimental methods for single molecule detection in biological applications in the context of NPL can be found in [13]. This report reviews two categories of experimental methods: scanning probe microscopies and applied optical spectroscopies. The report points out that scanning probe microscopies can measure physical properties such as surface conductivity, static charge distribution, localised fields, magnetic fields and elastic moduli. Atomic force microscopy can be used to examine biomolecules on surfaces to identify their orientation and structure, and by the use of molecules attached to the tip of the probe it is possible to study interactions between biomolecules. The authors argue that there are measurement and calibration possibilities in determining the orientation and morphology of proteins and other tissue materials and that it may be possible to locate and identify a ligand site on a biomolecule.

Optical spectroscopic methods can provide information at very high resolution. The main physical limitation on such techniques is the wavelength of the radiation that is employed. In principle, provided that one can use suitable short-wavelength sources, single molecule detection and perhaps imaging is possible. By means of Fluorescence Correlation Spectroscopy, for example, Brown and colleagues [13] argue that it may be possible to identify the preferred orientation of biomolecules and that this is also possible for biomolecules on surfaces using Scanning Near-field Optical Microscopy.

Mathematical models of the interactions of biomolecules with surfaces, and of the binding sites and preferred orientations of proteins and other biomolecules, can be compared with the results of single molecule measurements as part of the process of verifying both modelling and experimental work. To make progress here NMS metrologists need to collaborate with academic groups specialising in computational chemistry and biology and with providers of software, such as Accelrys.

5.5 Computational chemistry at other NMIs

It is instructive to study the approach to molecular modelling and computational chemistry adopted in other National Measurement Institutes. In the UK the Laboratory of the Government Chemist (LGC) has a statistics and chemometrics group, under the leadership of Dr Steve Ellison. In addition, LGC is the UK partner in the Virtual Institute for Chemometrics and Industrial Metrology (VICIM), which is funded by the European Community as a network of excellence in chemometrics and metrology. One of the services which VICIM plans to offer is training in visualisation and modelling allied to chemometrics. More information about VICIM can be found on their web site at www.vicim.urv.es/.

At the USA's National Institute of Standards and Technology (NIST) the computational chemistry group is part of the Physical and Chemical Properties Division of NIST's Chemical Science and Technology Laboratory. This group currently has nine staff, together with a programme of visiting researchers, mainly from Latin America, but also from Europe. A postdoctoral research programme funded by the USA's National Research Council also exists.

The rationale for the work of the group is described in detail on NIST's website at www.nist.gov/compchem/. There is a strong emphasis on industrial needs as the motivation for the work, the importance of testing and benchmarking of software, and the development of databases of results, including comparisons with experimental data. The programme of visiting researchers and the postdoctoral research programme shows the importance which the group places on maintaining strong links with academics working in computational chemistry and molecular modelling. Further information about NIST's work in this field, including lists of recent publications by the group, can be found on the NIST website.

It is highly unlikely that NPL will able to be able to devote the same level of resources as NIST to this area of research. However, we should bear in mind the three key themes that underpin the work and which were noted above: industrial relevance, the importance of validating and benchmarking software, and the maintenance of links with academic researchers.

In Germany the Bundesanstalt für Materialforschung und -Prüfung (BAM), rather than the Physikalisch-Technische Bundesanstalt (PTB), carries out much of that type of materials research which in the UK is associated with NPL, and in the USA with NIST. BAM's remit covers materials, chemistry, the environment and safety and its main technical departments are analytical chemistry, reference materials, chemical safety engineering, containment systems, environmental compatibility of materials, materials engineering, performance of polymeric materials, materials protection and non-destructive testing. BAM concentrates on experimental work. Nevertheless, its theoretical, mathematical modelling and informatics work includes:

> *Setting up and developing information systems in analytical chemistry; modelling the thermal and structural mechanics behaviour of containers and pressure vessels; numerical investigations to simulate accidental mechanical and thermal impacts on containers including those for transport of radioactive materials; numerical simulation of the deformation and damage behaviour of materials subject to complex thermomechanical loading histories; establishment of material and damage models for commercial finite element codes; inelastic 3D-FE-stress-strain analyses of complex loaded components; analysis and development of constitutive laws, damage models and failure concepts as well as their implementation into finite element codes; simulation of the behaviour of specimens and components including damage behaviour*

> *under inelastic loading; modelling and simulation and validation procedures in non-destructive testing; molecular modelling of polymer behaviour.*

What is clear from this exhaustive list of materials modelling activities at BAM is that very little work is done on molecular modelling, but that in many areas of the Institute's work there may eventually be a need to develop techniques which can handle modelling over multiple length and time scales. As far as can be ascertained from its web site, the PTB appears currently not to undertake any molecular modelling.

6 Modelling polymers at the nanoscale

6.1 Introduction

In this chapter of the report we pay particular attention to problems of modelling polymers at the nanoscale. Recent work at NPL on nano-imprint-lithography is described, which identifies the need for a better understanding of the shear properties of polymers at this scale. This is followed by a discussion of the problem of modelling amorphous polymers and, finally, group interaction modelling is introduced as a possible technique for understanding polymer properties.

6.2 NPL's background in polymers at the nanoscale

An important requirement in the development of nanotechnology applications is the need to be able to manufacture structures accurately at the nanometre scale. One technique that is suitable for this purpose is nano-imprint-lithography. This method creates patterns on a substrate by spin-coating a polymer layer on to it [18, 19, 55]. To understand and develop such processes and to gain an appreciation of the long-term dimensional and mechanical stability of nano-structures, mathematical modelling in combination with measurement is required. The scanning probe techniques that are commonly used to characterise nano-structures have limitations. These include the choice of representative test volumes and areas, lack of understanding of interactions between the tool tip and the object and lack of measurement traceability to SI units. This topic was studied in depth at NPL during a strategic research project on the shear properties of polymers at the nanoscale that was completed in 2003 and readers who require more information on this subject are referred to the work of Mendels [60].

6.3 Mechanical properties of polymers at the nanoscale

As Mendels points out [60], applying scanning probe methods to determine mechanical properties of soft materials such as polymers can be difficult. The probe generates a displacement and the resulting force is measured. This would in theory allow a Young's modulus value to be calculated but the real meaning of such a measurement is not clear, owing to the fact that force measurements at the nanoscale are not yet traceable to SI units and that models that explain the elastic response of materials at this scale are not well-developed. It is necessary to take into account both the unusual geometry and boundary conditions of the nanoscale material and the measurement environment. For materials such as polymers, the properties of nanoscale samples differ from those of bulk samples because the small samples do not contain a representative number of polymer chains. Note also, as has been emphasised before, the importance of surface effects in nanoscale samples. At such scales the ratio of surface area to volume is large, so that proportionally more molecules contribute to surface effects than is the case with bulk samples.

Polymer materials have been an important source of problems in the study of small systems. Methods based on statistical mechanics and the thermodynamics of small systems have been successful for dilute solutions. For solid-state polymers modelling is possible using several approaches: statistical mechanics, group interaction modelling and molecular modelling. Currently it is not possible to use molecular modelling methods to predict the glass transition temperature of polymers although both statistical mechanics and group interaction modelling allow this. The difficulty with molecular modelling lies simply in the size of the problem associated with deriving macroscopic properties for such large molecules.

To introduce approaches to modelling polymers the next two sections of this chapter summarise briefly some of the current techniques and challenges.

6.4 Modelling amorphous polymers

This section of the report is based on the review paper by Paul and Smith entitled *Structure and dynamics of amorphous polymers: computer simulations compared to experiment and theory* [68].

The authors point out that chain connectivity introduces a range of length scales from that of the chemical bond to the radius of gyration of the polymer chain and that this connectivity covers two to four orders of magnitude. In addition, relaxation processes in amorphous polymers range over time scales from 10^{-13} s to 10^{-3} s. In the cases of glasses, times of the order of 10^3 s may also need to be taken into account. As a result, they argue that no single simulation technique can describe all these length and time scales. For large length and time scales it is topology and entropy that govern polymer behaviour and coarse-grained polymer models can be applied here, as chain connectivity is the dominant factor at such scales.

Paul and Smith comment that the defining characteristic of linear polymers is that they look like threads. They therefore ask: *“How does the structure of spaghetti differ from that of a box of billiard balls (simple liquids)? Will polymer threads orient locally or even show a transition from anistropic liquid to a nematically ordered solid?”*

They ask how, at the largest length scale, do chains move past each other or disentangle, and note that disentanglement seems to play no role in polymer motion as long as chains do not exceed a certain length. They claim that the dynamics of short chains are described well by the Rouse model [75] that is now more than 50 years old, and which treats chain motion in melts as if it were the Brownian motion of a chain of points connected by entropic springs in a viscous background. Beyond a certain chain length (known as the entanglement molecular weight) the dynamic response of polymer melts changes drastically.

The authors then review what they call the “levels of modelling” required within conventional approaches using either molecular dynamics (integrating Newton’s equation of motion), or Monte Carlo simulations (using stochastic methods to investigate all the configurations of a process). They point out that physical problems such as chemical reactions that explicitly involve electronic degrees of freedom or depend on quantum mechanical zero point fluctuations, such as the low-temperature structure of polymeric crystals, require different modelling approaches.

To make modelling chemically realistic, accurate potentials are needed if quantitatively correct prediction of behaviour and properties of real polymers are required. Nevertheless Paul and Smith observe that even *qualitative* conclusions drawn from simulations employing inaccurate or unvalidated potentials can be problematic. However, it will be the properties of interest to the researcher performing the simulation that will determine the form of the potential that is used. If it is necessary to reproduce static, thermodynamic and dynamic properties of non-reactive organic polymers, then the chosen potential must accurately represent molecular geometry, non-bonded interactions and conformational energetics. They comment that relatively simple representations of potential energy work well for these properties.

They summarise the main types of interaction that occur in polymers, which include bond stretch, intramolecular nonbonded, intermolecular nonbonded, dihedral twist, and valence angle bend interactions. A simulation would also typically include non-bonded interactions between all atoms of different molecules and between atoms of the same molecule separated by more than two bonds.

Of course, as the authors argue, the most convenient way to obtain a force field for a calculation is to utilize an existing one. Polymer force fields can be separated into three categories:

- force fields parameterized based upon a broad training set of molecules such as small organic molecules, peptides or amino acids;
- generic potentials that are not parameterized to reproduce properties of any particular set of molecules;
- specialised force field carefully parameterized to reproduce properties of a specific compound.

Some useful advice on force fields can be found at msdlocal.ebi.ac.uk/docs/mmrefs.html.

As one would expect, high level quantum chemistry calculations are the best source of molecular level information for force field validation and parameterization. However, the authors argue that such calculations are not currently possible for high polymers but are feasible for small molecules that may represent repeat units of polymers and of oligomers (low molecular weight polymers in which the number of repeat units is between two and ten).

It is important to recognise that coarse-grained polymer models neglect the chemical detail of a specific polymer chain and only employ excluded volume and topology as properties that determine universal large-scale behaviour of polymers. For all coarse-grained models, the repeat unit or monomer represents typically four to six backbone atoms of a chemically realistic chain. Molecular dynamics techniques are employed to study off-lattice models and Monte Carlo methods are used for lattice models and for efficient equilibration of continuum models.

Where the bead-spring type of coarse-grained model is employed, it is common to use a potential of the Lennard-Jones type.

This section of the report has given an overview of the key issues in modelling amorphous polymers based on the review paper of Paul and Smith. The next section considers a specific method of modelling polymers - group interaction modelling

6.5 Group Interaction Modelling

Group Interaction Modelling uses the interaction energy between groups of atoms in adjacent polymer chains to predict properties of condensed polymers as a function of chemical composition and macromolecular structure. This section of the report is based on the textbook by Porter [70] which describes the technique of Group Interaction Modelling for predicting the properties of models. Readers who require more information should consult the text itself. As an introduction to the topic Porter provides a review of the main issues that arise in modelling polymers and it is this review that is used in this part of the report to help identify a number of the issues that are important for polymer modelling.

Porter argues that a measure of the “correctness” of any model is its ability to explain and predict as many observed phenomena as possible and to use parameters as variables in the model that can be traced back to fundamentally sound first principles. He also points out that the use of an empirical potential function is in itself not “fundamental”.

The increase in speed and memory capacity of computers has been the driver for advances in modelling of polymer structure and properties in recent years and many user-friendly commercial software packages for modelling polymers now exist. Much of the development in molecular modelling was pioneered by the pharmaceutical industry, as accurate prediction of molecular structure of protein macromolecules and active small molecular drugs is important in identifying potentially interesting drugs.

As has already been mentioned in this report, the range of time and length scales that molecular modelling needs to be able to tackle is very large. Porter points out that no part of this range can be ignored by polymer designers since changing one atom in a characteristic mer unit can have dramatic consequences on the end-use and fabrication properties of the polymer in question.

The author then reviews the molecular modelling tools open to the polymer designer, pointing out that at the atomic scale quantum mechanics methods allow the energy and effective dimensions of a molecule to be calculated from the electron cloud distribution around each of the constituent atoms. The electron cloud mobility and distribution determine the polarisability and dipole moment of a molecule, and thus produce the electrostatic forces that cause the van der Waals forces between mer units. The van der Waals dispersion and polar forces then determine many of the mechanical properties of a polymer. Quantum mechanical modelling can also calculate interatomic forces and the energetics of chemical bond deformation by stretching, bending and torsion. In turn the energetics of the chemical bond determine the vibrational frequencies of a polymer molecule and the ability of a polymer chain backbone to adopt a number of different conformations at a given total energy level. Thermal energy is stored in oscillations in atomic groups or collective skeletal chain vibrations and quantum mechanics enables thermal properties such as specific heat to be calculated.

Group Interaction Modelling employs information derived from quantum mechanical modelling but is in itself not a “fundamental” modelling method. The technique regards the most important component of a polymer for engineering properties as a mer unit surrounded on all sides by other single identical mer units. In practice the basic building block of the model is a component consisting of nine mer units: one central unit, two intra-chain chemically bonded neighbours and six adjacent but non-chemically bonded neighbours. In these nine mer units the most important single element is taken as a pairwise inter-chain mer unit interaction because engineering properties tend to be dominated by the weakest link van der Waals forces between molecules.

For engineering purposes and for modelling techniques such as finite element and finite difference methods, one is concerned with continuum mechanics methods on which engineering is founded. Group Interaction Modelling can predict the following basic properties of engineering polymers: moduli, dynamics of deformation, creep, temperature limit of glass transition, yield point, and viscosity.

Porter argues that although the minimum energy configuration of an assembly of polymer molecules is interesting in itself, many important engineering properties are time dependent and the ability to model the effects of molecular mobility upon properties at the larger scale is necessary. Polymer properties such as molecular diffusion, segmental relaxation events, temperature dependent properties and stress relaxation dynamics can be tackled using molecular dynamics methods, where kinetic velocity distributions are assigned to atoms and the potential functions between atoms are solved as a function of time. Available computing power restricts the time scales which can be simulated even for small assemblies of polymer chains - simulations of the order of picoseconds are normal, but this is too short to allow the computation of bulk dynamics processes.

When the behaviour of large numbers of long polymer chains is of interest, e.g. the study of chains in an amorphous polymer melt, Monte Carlo methods may be preferable to molecular mechanics approaches and are computationally more efficient. Monte Carlo methods allow the construction of random systems of long chain molecules from characteristic rigid segments of a number of mer units. Rigid segments are joined by flexible links that allow free or restricted rotational movements to construct a random walk of a chain through configuration space. Chain segments can interact by means of van der Waals forces in the same way as in molecular mechanics and the end result of a simulation is a time-averaged coarse-grained assembly of chains in space. The use of large molecular units enables calculations that can be orders of magnitude faster than molecular mechanics methods for large systems. Porter claims that dynamic Monte Carlo simulations allow time scales of simulation that begin to be significant for the understanding of macroscopic phenomena.

In this chapter of the report has been possible to give no more than a flavour of some of the mathematical modelling issues that are relevant to modelling polymer properties. As polymers are a key group of engineering materials, it is vital that NPL gains expertise in modelling polymers at the nano and micro scales. The link between experiment and theory is also important here. Our experimental work in nanoscale measurement can be used to evaluate the results of modelling and *vice versa*.

7 Multi-scale modelling of nanostructures

Multi-scale modelling for extended length and time scales will become more and more important as one attempts to link nanoscale modelling to methods that require bulk properties as inputs or which represent materials as continua. A study of the research topics currently supported by the Engineering and Physical Sciences Research Council shows that this is currently a very active topic in UK universities. At the time of writing this interim report a search using the term *multi-scale modelling* on the EPSRC's current grants portfolio produced 31 projects in UK universities worth collectively over £8m.

This chapter of the report describes briefly some of the key aspects of multi-scale modelling using as its basis a recent review paper by Dimitri Vvedensky of Imperial College [106]. This paper also contains more than 200 references relevant to multi-scale modelling that provide a useful resource for this topic. It is recommended as an excellent introduction to multi-scale modelling.

Why has multi-scale modelling emerged? One reason is that there are materials phenomena such as crack formation and growth that are characterised by a continuous feedback between atomic and coarse-grained degrees of freedom. Secondly, there are processes that are well-understood at the macroscopic scale but manifest themselves quite differently at the atomic scale, which significantly affects behaviour of nanoscale structures. Thirdly, as has been emphasised several times in this report, the modern growth in computing power makes it possible to begin to tackle problems that were previously considered intractable.

Vvedensky also points out that experimental methods of materials design and synthesis are costly and time-consuming, leading to long development times. Modelling and simulation can be used to optimise processing parameters and to interpret results at the atomic scale - especially important where phenomena are too fast or too complex to image. Simulations based on large-scale quantum mechanical calculations and molecular dynamics can be stopped and examined at any time.

7.1 Hierarchy of methods

The paper argues that the traditional approach to multi-scale modelling is what can be described as the *divide and conquer* strategy, that is, methods appropriate to particular length and time scales are used to address phenomena that operate only over those scales. The main methodologies here, which we have already met, are:

- *ab initio* density functional theory,
- molecular dynamics,
- statistical methods based on Monte Carlo algorithms,
- continuum mechanics.

Vvedensky then provides a useful summary of the mathematical basis of the first three methods listed above, in which he sets out the basic equations, the assumptions on which they are based, and the limitations of each technique. The reader who requires further information or who is interested in understanding the methods in more detail is referred to the paper itself [106] and to the references cited by the paper.

Finally he reviews the methods of modelling materials as continua. His ideas are summarised below.

7.2 Continuum equations

Continuum equations, either deterministic or stochastic partial differential equations, are the final stage in the multi-scale modelling hierarchy. One ignores the underlying atomic structure of matter and considers only continuous properties of a material. The behaviour of a material is embodied in differential equations, derived from basic physical principles, such as the conservation of energy or momentum.

Vvedensky argues that the advantage of modelling materials as continua is essentially the ability to examine macroscopic regions in space over extended periods of time. There are many numerical methods for integrating deterministic and stochastic differential equations. One method that is very frequently employed is the finite element method. This is a method for solving differential equations in which the region of interest represented by a mesh that is made up of contiguous components called “elements”. The solution of the differential equation is discretised on the mesh points, called nodes, and interpolated within the elements. The finite element representation of the displacement field is defined at the nodes of the elements, and shape functions are used to extend this field throughout each element. A commonly used shape function is linear interpolation, in which the basis function has the value unity at a given node and decreases to zero linearly at the nearest neighbour nodes, and is zero elsewhere. This approach is a convenient choice for coupling to methods with atomic resolution because it permits a one-to-one correspondence between nodes and atoms. For atomic-size elements, the mass can be defined to be at the nodes rather than being uniformly distributed.

Modelling at the continuum scale has been studied extensively within the Software Support for Metrology programme and readers who require further information and advice on how to solve finite element and finite difference problems and to validate the results of their modelling are referred to the reports produced by the SS*f*M programme [35, 36, 37].

7.3 Methods of multi-scale modelling and the future

There are two basic strategies for combining single-scale methods into multi-scale modelling.

- Sequential methods take information from a calculation over a particular length and or time scale and use this as input to a more coarse-grained method. This assumes, of course, that the phenomenon of interest can be separated into processes that operate at distinct length and time scales. Methods of sequential modelling include: sequential parametrization, interface propagation and systematic coarse graining.
- Concurrent multi-scale modelling combines the individual scales into a single hybrid scheme, typically involving atomistic and continuum calculations. As Vvedensky comments, the main theoretical challenge is to merge the two descriptions in a manner that avoids any spurious effects due this heterogeneity. Concurrent methods combine an atomistic method, such as an ab initio density functional calculation or molecular dynamics, with continuum equations that are solved using finite element method or another method of discretisation.

Finally, Vvedensky identifies three main challenges facing future development of multi-scale modelling. These are, to quote from his paper:

- *Simulations at finite temperatures. Many of the methods . . . are confined to zero temperature, wherein the basic quantity is a Hamiltonian for the system expressed in terms of the appropriate degrees of freedom. In principle, Hamiltonian methods can be extended to equilibrium at finite temperatures by using the free energy, but inherently nonequilibrium situations are fundamentally different and a general approach is not close at hand.*
- *Time scales accessible by means of molecular dynamics. The bottleneck for macroscopic time simulations remains the small time step used in classical and quantum molecular dynamics. While this may be side-stepped in certain applications, and acceleration strategies are available for particular situations, a general acceleration methodology would have revolutionary implications that would stretch across many disciplines.*
- *Mode transmission across atomistic/continuum interfaces. In methods with a sharp interface between atomistically resolved and (finite element) continuum regions, high frequency modes emanating from the molecular region must be accommodated by the continuum region. However, the finite elements are unable to resolve the small wavelengths of the atomistic region and, since such multi-scale methods are based typically on a Hamiltonian formulation, which means that energy is conserved, the modes are reflected back into the atomistic region, which can lead to spurious results.*

8 Molecular modelling in pressure balances: a case study

8.1 Introduction to the case study

In this chapter of the report we present a detailed case study of the application of molecular modelling to pressure balance metrology. The aim is to demonstrate in some depth how molecular modelling can help clarify aspects of device behaviour and of the calibration uncertainty budget that cannot be tackled by the conventional methods that have previously been applied in pressure metrology. The case study also shows how, in an apparently mature area of mechanical metrology, new insights can be gained from nanoscale modelling, and how an experienced molecular modeller approaches a specific problem. The work reported here was carried out by means of a collaboration between the Department of Chemistry at Imperial College London and NPL's pressure and vacuum group.

8.2 Modelling of gas flow on nanoscale

An example of a metrology problem where molecular modelling assists in identifying sources of uncertainty and enables metrologists to make further progress is the study of gas flows in piston-cylinder pressure balances calibrated by the cross-floating method [89, 88]. Gas-operated pressure balances, in which known masses are applied to pistons of defined area to generate a reproducible (traceable) pressure up to 20 MPa, are used as primary sources to produce accurate (with a typical uncertainty of 25 ppm[1]) static pressures [30, 32]. This accuracy has been satisfactory for the last two decades. However, recent technological developments and improved manufacturing standards require significantly higher accuracy, in the 10 ppm range or better, and meeting these requirements presents fundamental difficulties.

It has been observed by many researchers that there are differences in the apparent distortion coefficients (which describe the manner in which the effective area of a pressure balance varies as a function of pressure) of nominally identical devices of the order of several parts per million per MPa. The present level of theoretical understanding of pressure balances, summarised in the book by Dadson *et al.*[26] is based on phenomenological hydrodynamics and the theory of elasticity. (See section 8.3 of this report for a more detailed explanation of how pressure balances operate and are modelled.) Several simplifying assumptions made in this theory, such as the assumption of axial symmetry and neglect of rotational effects, were discussed in more recent publications. They, however, cannot explain the observed effects, and further progress in improving the accuracy of pressure calibration is limited by several factors. Foremost among them is a lack of knowledge concerning pressure balance distortions, which is required to help determine the effective area of the piston-cylinder (p-c) unit. Several simplified and empirical methods are currently used to evaluate this coefficient [26, 62] based on linear approximations. More recently, nonlinearity in pressure dependence has been studied using finite element methods [15, 110, 109]. Some progress has been made by examining the undistorted molecular surfaces of the piston and cylinder and the inclusion of the properties of the materials (Young's modulus, Poisson's ratio) in the calculation of distortion and correcting the results to account for nonlinearities in the effective area. However a major problem which requires special attention is the fluid flow conditions. Moving fluid induces a frictional drag force on the vertical surface of the piston and the magnitude of this force depends intricately on the details of intermolecular interactions. As has become clear from recent

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[1] 1 ppm$\equiv 1 \times 10^{-6}$

investigations [84, 85], the usual macroscopic hydrodynamic boundary conditions cannot be simply transferred to flow in micro-capillaries. In the typical range of gap width between engaging surfaces of the piston and cylinder (0.04 μm to 2 μm) a rich variety of boundary conditions can be found. To understand this behaviour, improved modelling of pressure balances, including modelling at the molecular level of flow under a pressure gradient, with realistic gap sizes and real geometry, is required. To make significant progress in the analysis of a pressure balance, a new and more fundamental level of theory is required based on the molecular approach.

Molecular transport of fluids[2] through porous media has been the subject of sustained experimental and theoretical interest for several decades [21, 47]. Understanding of transport phenomena has advanced considerably as a result of the application of kinetic theory [16] and its recent generalizations [27, 71] to problems of fluid transport through pores [8, 72], to the interpretation of experimental results [17] and through comparison of these with simulations [7, 23, 65, 102].

A key parameter characterising the applicability of the continuum equations is the Knudsen number Kn, defined as the ratio of the molecular free path to the transverse dimensions of the system. Computer simulation studies of Couette and Poiseuille flow in model slit pores [97, 100, 103] have shown that the flow of fluids in the small Kn regime is described remarkably well by macroscopic phenomenological hydrodynamics even for pore widths down to ten molecular diameters. It is therefore a good approximation for gas flow in typical pressure balances where at ambient pressure Kn does not exceed 0.1 for a gap of 0.04 μm. What has remained unanswered by phenomenological theories, however, is the question of the precise relation between molecular properties of the interface and the hydrodynamic boundary conditions inevitably appearing when the solid is approximated by a continuum [42, 96, 9, 51, 3, 2]. The usual assumption made in continuum fluid dynamics is that the fluid velocity vanishes at the solid wall: the so-called ‘no-slip’ boundary condition. In molecular models where the solid is modelled as a continuum, the boundary conditions are usually specified by postulating a scattering law, such as diffuse [23] or Knudsen’s cosine law [93, 104] boundary conditions.

The determination of the hydrodynamic boundary conditions appropriate to Newtonian fluid flow has recently attracted much attention [20, 84, 3, 5, 24]. In particular, it has been shown that the assumption of a no-slip boundary condition usually made in phenomenological hydrodynamics is not always valid. Thus, it has been known for some time that slip exists in liquid flow between partially wetting solid surfaces and depends on wettability [20, 84, 5]. More recently, in a computer simulation study of fluid flow in a graphite pore with a realistic model for graphite structure [84] it was demonstrated that large slip persists even for strong adsorption potentials, that is, wetting surfaces). Significant slip was also detected in recent experiments on the hydrodynamic drainage force between aqueous fluid and relatively hydrophilic surfaces [24]. The no-slip condition obtained in other simulations of Poiseuille flow [102, 103, 51] shows that slip depends on the solid structure, and that a large degree of surface corrugation (roughness) could suppress molecular slip. Besides the relative strength of the solid-fluid interactions (governing wetting conditions), several other factors contribute to conditions at the boundary, including temperature, fluid density, and the degree of the lateral corrugation of the solid-fluid potential. In relation to the p-c unit, molecular slip at the piston/gas interface will result in reducing the drag force on the piston, and this effect needs to be included in the calculation of the effective area.

High pressure p-c units are often manufactured from sintered cobalt tungsten carbide (WC) hard alloys which have a rich morphology of surface structure and a broad distribution of the grain sizes of carbides. It is impossible to predict the type of boundary conditions in this complex picture

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[2] **fluids** include both liquids and dense gases.

without thorough and detailed analysis based on computer simulation with validation and comparison of the predictions with experimental data (for example, flow rate, which can be estimated from the p-c geometry and the fall rate of the floating piston as a function of the slip length).

Two different experimental techniques exist for the determination of the effective area of a p-c assembly [26]. In the first (the so-called "absolute method") the effective area is calculated using computational methods from directly measured diameters of the piston and cylinder. The second (comparative) is based on a cross-floating experimental determination of the effective area by comparison with a pressure standard. The underlying basic theory, as described in the book[3] of Dadson *et al.* [26] published more than twenty years ago, was developed in the decades preceding publication and is used practically without modifications since then. There has not been much theoretical development since the book was published. A physical model extending the classical theory to account for gas species and mode-of-operation effects has been proposed by Schmidt *et al.* [78] and a model for drag forces in the crevice of piston gauges in the viscous and molecular flow regimes was proposed by the same group recently [77]. They are discussed below.

8.3 Basic theory of the gas-operated pressure balance

Pressure balances, or piston gauges, as they sometimes called, are used to generate reference pressures from the fundamental relationship

$$p = \frac{M\, g}{A_{\text{eff}}}, \tag{1}$$

where M is the total mass of piston plus all weights placed on it, g is the local acceleration of free fall, and A_{eff} is the *effective area* of the p-c unit. (See figure 2 for a schematic diagram of a piston-cylinder system.) The accurate determination of the effective area is a highly nontrivial problem since it depends on many parameters including surface properties of the piston and cylinder material, temperature and pressure itself, and is the primary aim of the current research. The measuring element in the balance is a cylindrical piston rotating freely in a closely matching cylinder, lubricated by the gas that escapes from the space below the piston through the small clearance (width usually $< 1\mu$m) between piston and cylinder bore. The gravitational force exerted by the piston mass and a concentric stack of annular weights acts on the piston in the direction of its axis. This force is balanced by the force exerted by the pressure acting on the 'effective' bottom surface of the piston, that is, on the effective area of the p-c unit. To enable the measurement of absolute pressures, the p-c unit and the weights are mounted inside a bell jar that can be evacuated. Allowance must be made for the residual pressure p_{res} under the bell jar. If $p_{\text{res}} = p_{\text{ambient}}$, the pressure balance measures gauge pressures, and buoyancy corrections must be applied to the floating parts.

The effective area A_{eff} of a p-c unit is estimated from the ratio of the sum of the forces acting on the piston in the direction of its axis to the pressure to be measured. It can be calculated from numerical data describing the deviations of the radial surfaces of the piston and the cylinder bore from a perfect cylindrical form, assuming that rotational symmetry is retained, as outlined in reference [26]. Let x denote the coordinate along the coinciding (vertical) axes of piston and cylinder. The measured position-dependent radii of the piston, $r(x)$, and of the cylinder bore, $R(x)$, are written in terms of reference radii, r_0 and R_0, and corresponding deviations, $u(x)$ and $U(x)$;

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[3] Often referred to as the "Brown Book".

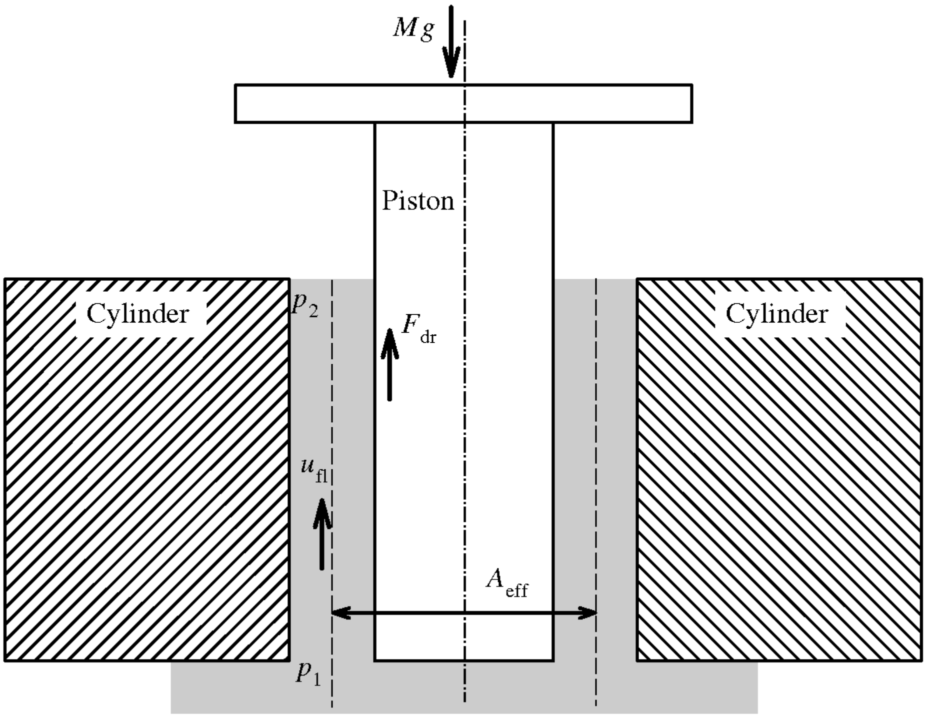

Figure 2: Schematics of a simple piston-cylinder assembly of the gas-operated piston gauge. The gas flow in the clearance between piston and cylinder induces a drag force on the vertical surface of the piston.

$r(x) = r_0 + u(x)$ and $R(x) = r_0 + h_0 + U(x)$ with $u(0) = U(0) = 0$ where $R(0) - r(0) = h_0$ (initial width of the clearance). Piston and cylinder are engaged in the range between $x = 0$ and $x = l$ and the piston is at its working position in the cylinder. Under these conditions the following result is obtained,

$$A_{\text{eff}} = \pi r_0^2 \left\{ 1 + \frac{h_0}{r_0} - \frac{1}{r_0(p_1 - p_2)} \int_0^l (p(x) - p_2) \frac{d(u(x) + U(x))}{dx} dx \right\}. \tag{2}$$

This formula can be evaluated if the pressure in the clearance between piston and cylinder, $p(x)$, is known in the interval $0 < x < l$ with boundary values $p(0) = p_1$ and $p(l) = p_2$. An expression for $p(x)$ can be derived from the equation of continuity describing the amount of fluid escaping through the clearance between piston and cylinder. The cases of compressible and incompressible fluids have to be distinguished. The result obtained for the effective area using (2) is valid for a rigid p-c unit or in the case of small pressures p_1.

The pressures measured in the plane of the bottom surface of the piston of a gas-operated pressure balance for the gauge pressure and absolute pressure cases are:

$$p_{\text{e}} = \frac{g \sum_i m_i (1 - \rho_{\text{air}}/\rho_{m_i})}{A_0(t_{\text{R}}) \left[1 + (\alpha_{\text{p}} + \alpha_{\text{c}})(t - t_{\text{R}})\right]}, \tag{3}$$

$$p_{\mathrm{abs}} = \frac{g \sum_i m_i}{A_0(t_{\mathrm{R}})\,[1 + (\alpha_{\mathrm{p}} + \alpha_{\mathrm{c}})(t - t_{\mathrm{R}})]} + p_{\mathrm{res}}. \tag{4}$$

Here, g is acceleration of gravity; m_i is the mass of weight i (including piston and weight carrier); ρ_{m_i} is the density of the weights; ρ_{air}, the density of the ambient air; $A_0(t_{\mathrm{R}})$, the effective area at zero pressure and reference temperature t_{R}; $\alpha_{\mathrm{p}}, \alpha_{\mathrm{c}}$ are the coefficients of thermal expansion of piston and cylinder; and p_{res} is the residual pressure under the bell jar.

The smallest uncertainty achievable in the values m_i is discussed in [28] and can be neglected. Local acceleration of gravity is known to better than 1 ppm. The uncertainty in α_{p} and α_{c} is less important when work is carried out at the reference temperature. The overall measurement uncertainty of a gas-operated primary pressure balance standard is therefore mainly determined by the uncertainty in the effective area, and at low pressures by a small unknown additional force acting on the piston. The accuracy can be substantially degraded by aerodynamic forces acting on the rotating weights when gauge pressures are measured. Small axial forces may also be produced by certain imperfections of the surface of the piston rotating in a viscous medium, by the action of an automatic drive mechanism or by a small magnetization of piston and/or cylinder. In addition to such experimental sources of error the limitations of the theory applied to calculate the effective area may give rise to an increased systematic uncertainty. Thus, a fluid friction term contributing to the forces acting on the piston is usually derived for an assumed viscous flow in the clearance between piston and cylinder. The whole derivation relies upon several significant assumptions whose nature is not clarified sufficiently in the Brown Book [26]. For example, the drag force on the surface of the piston is calculated with the assumption that “the fluid velocity in the interspace will be zero at each of the bounding surfaces” ([26], p. 21). The idea of a ‘neutral surface’ (*Ibid.*) as a midway position where the “frictional force between adjacent layers of fluid will be zero” is unclear (a simple argument is that, if it were so, then the middle layer which experiences the driving force and no viscous friction would be accelerated infinitely, which is absurd). Instead, the ‘effective area’ should be considered as a device to hide our ignorance of what happens at the boundary. It is an idealised area on which the total weight is acting to produce the required (measured) pressure. The calculation of Knudsen numbers for typical p-c units operated at absolute pressures in the atmospheric pressure range shows that the gas flow in the clearance is in the transition region between viscous and molecular flow [107]. This fact may cause unexpected differences between effective area values measured in the gauge mode and in the absolute mode, and unexpected dependences of the effective area on the gas used and on the pressure. Such effects have been observed [107, 98]. For calculations see also chapter 10 of [26] and [94]. An example of a thorough uncertainty calculation for absolute piston gauge pressure measurements with specially prepared instruments is given elsewhere [108].

8.3.1 Effects of elastic distortion on the effective area

At elevated pressures it is essential to know the effect of elastic distortion of the piston-cylinder units, *i.e.* the distortion coefficient of their effective area, with adequate accuracy. Both theoretical and experimental methods have been developed to determine the distortion coefficient. This effect can be discussed as follows. The load applied to the piston adds a term independent of x to the width of the clearance, *i.e.* to the effective area. This term is proportional to the measured pressure p_1. If it is assumed that the radial deformations of the piston and the cylinder due to the pressure $p(x)$ in the clearance are proportional to this pressure, *i.e.* if $du/dx = k \cdot d(p - p_2)/dx$ and $dU/dx = K \cdot d(p - p_2)/dx$, then, with $p_2 = 0$ for simplicity, it can be seen from equation (2) that again terms proportional to the measured pressure are created. Therefore, if the result obtained for the effective area at zero applied pressure is denoted by A_0, the pressure-dependent effective area can be written as $A_{\text{eff}}(p) = A_0(1 + \lambda p)$. It is customary to obtain expressions for the various contributions to λ from standard formulae of the elementary theory of elasticity applied to cylinders and thick-walled tubes loaded by external and internal pressure (see for instance [43] p. 154). The result obtained for λ in this way may however need justification. Starting from an arbitrary pressure distribution in the clearance of a p-c unit, it is not possible to obtain an exact solution of the elastic differential equations. The special cases of a linear and a quadratic pressure distribution are tractable however. It was shown [50] that in both cases with adequate boundary conditions the above result for the distortion coefficient is obtained if the deformations calculated from the elastic differential equations are used along with the assumed pressure distribution to calculate λ from equation (2) according to $\lambda = (A_{\text{eff}}(p)/A_0 - 1)/p$. The derivation of eqn. (2) starts from explicit expressions for the forces acting on the piston [25]. The frictional force acting on the flanks of the piston is

$$F = -\pi r_0 \int_0^l h \frac{dp(x)}{dx} dx \tag{5}$$

with all symbols having their usual meaning as in equation (2). For constant clearance h this equation can be derived from a solution of the Navier-Stokes equations applied to the fluid flow in the clearance of the p-c unit. Equation (5) is then assumed to be valid also for $h = h(x)$. It is not possible to obtain an exact solution of the Navier-Stokes equations for this case. Using some approximations, a solution can however be derived for a linear dependence of h on x (converging channel model [48]), which is a realistic first approximation to describe a distorted p-c unit of perfect cylindrical symmetry. If the pressure distribution $p(x)$ calculated for constant viscosity from the theory of the flow in the converging channel is used along with the linear dependence of h on x to derive the frictional force F from equation (5), the result agrees with the force obtained from the calculated velocity $u(x, r)$ of the fluid [49]. Therefore the application of equation (5) to distorted p-c units seems to be justified at least within the limitations of these model calculations, and this in turn supports the validity of equation (2). The fluid friction term contributing to equation (2) does not include the fluid viscosity which therefore does not explicitly appear in equation (2). The pressure dependence of the viscosity influences, however, the pressure distribution in the clearance and consequently the distortions generated. The distortion coefficient λ may therefore depend on the fluid properties to some extent if the assumption of proportionality between the deformations and the pressures at some level x in the clearance is not exactly valid [25, 26]. This effect may become more pronounced when the pressure profile in the clearance changes drastically with increasing measured pressure as must be expected in the range up to 1 GPa.

Since the pressure distribution and the fluid flow in the clearance and the distortion of the p-c unit are interdependent, an adequate solution of the distortion problem is a self-consistent solution of the Navier-Stokes and the elastic differential equations. An iterative procedure was developed to solve the differential equations describing the deformations of piston and cylinder, due to the pressure distribution in the clearance, and to calculate the latter, starting from the appropriately modified Navier-Stokes equations in which the pressure-dependent fluid viscosity and the width of the distorted clearance are both taken into account [61]. The geometrical (profiles, roundness) and elastic data of piston and cylinder, the density, and the dynamic viscosity of the fluid, including its dependence on temperature and pressure, and the volume flow through the clearance are needed as initial data. When convergence is obtained in the deformations $u(x)$ and $U(x)$ of piston and cylinder bore and in the pressure distribution $p(x)$, the distortion coefficient is calculated from equation (2).

The distortion of the outer surface of the cylinder can be measured by different methods [6, 61]. If a method were at hand to find the pressure distribution in the clearance that generates the measured external distortion, then it would be possible also to derive the distortion of the internal surface of the cylinder and the piston distortion, so that λ could be calculated from equation (2). A numerical method to solve the elastic differential equations applied to a p-c unit starting from a known pressure distribution in the clearance is described elsewhere [53].

The results of the theoretical methods developed to determine the distortion coefficient can in principle be checked against the results of the 'Similarity Method' or the 'Flow Method' developed by Dadson and coworkers [25] which allow determination of the distortion coefficient empirically. This requires however two identical p-c units made of different materials (Similarity Method) or a cylinder that can be used with two different pistons (Flow Method). Since generally this type of equipment is not available, a detailed discussion of these methods is omitted. The results of the experimental work of Dadson *et al.* suggest that satisfactory agreement may be expected between the distortion coefficients obtained theoretically and empirically if the design of the p-c units justifies the assumption of proportionality between local deformations and pressure in the clearance and if a high degree of geometrical accuracy of piston and cylinder bore can be achieved.

In the original theory described in the Brown Book [26] the viscous drag force on the piston was calculated within the framework of hydrodynamics, assuming that properties of the fluid do not vary near the interface. This was also the starting point for further development by Schmidt *et al.* [78, 77] who developed a model for azimuthal and axial drag forces acting on the rotated piston. Their derivation implied knowledge of viscosity at the wall, and equation (1) in [77], which is used to define the drag force, can be employed, in fact, as an equation for the 'interfacial viscosity' η from the known (measured) drag force F_d. In the molecular-flow regime (their equation 8a) an assumption was made that all statistical (macroscopic) momentum along the flow direction is transferred to the wall. This is an unrealistic approximation as will be shown in the slip flow section.

The reduction of uncertainties in the effective area of gas-operated piston gauges appears to have reached a plateau at the 10 ppm to 20 ppm level. Below this level a number of compelling, sometimes intertwined, effects become significant and further progress will be limited until the effects are better understood. Thus, one of the assumptions usually made is that the flow in the gap is laminar viscous flow, which is a crude assumption even in gauge mode operation. Better understanding of such effects requires better physical and mathematical models of the piston gauge system.

8.3.2 Molecular hydrodynamics of Poiseuille flow

There are two basic approaches to the dynamics of fluids: macroscopic, based on the 'continuum matter theory' of fluids, and microscopic, where the molecular structure of the matter is taken into account and the dynamic equations of motion are formulated in terms of intermolecular forces. Both approaches give consistent results apart from a small difference in the phase boundary/high density case where deviations from the macroscopic predictions were observed. When considering the fluid flow in the gap between the piston and the cylinder along the engagement length, several simplifying approximations could be made. It is reasonable to assume that macroscopic hydrodynamics is valid and to accept flat geometry for the system. If, for example, we take 1.5 mm as a piston diameter in a typical assembly and a gap of 50 - 100 nm, which again is typical for such dimensions of piston-cylinder assembly, the ratio of the gap to the surface curvature radius would be in the range $0.67 - 1.3 \times 10^{-4}$. If we take now into account that molecular correlations in dense gases and simple liquids have correlation length 2 nm or less, then the cubic sample with edge length equal to the gap width would be representative of the system. The curvature effects on this scale would be similar to the curvature of the earth's surface on a scale of one third of a mile due to the sphericity of the earth. Consider therefore Poiseuille flow in flat geometry where the fluid is driven along the y direction by a thermodynamic force, as sketched in figure 3. The thermodynamic driving force acting on the fluid is usually associated with the gradient of thermodynamic potential, chemical potential in this case. Quite often the conditions of flow are expressed in terms of pressure gradient, which is related to the chemical potential differential via the Gibbs-Duhem relation.

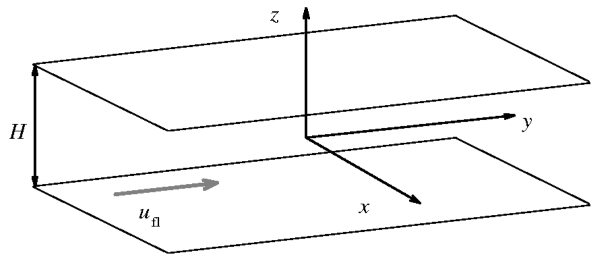

Figure 3: Sketch of the system. H is the gap width and the fragments of the cylinder and piston surfaces are shown as planes.

The Navier-Stokes equations are obtained when the balance equations for mass, momentum, and energy are supplemented by the corresponding constitutive equation. Thus, from mass conservation, one has

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \tag{6}$$

where $\rho \equiv \rho(\mathbf{r}, t)$ is the local density, $\mathbf{u} \equiv \mathbf{u}(\mathbf{r}, t)$ is the velocity field, and boldface is used to denote vector quantities. The momentum equation expresses Newtonian law for an elementary volume of fluid

$$\frac{d\mathbf{u}}{dt} = \rho \mathbf{g} - \nabla \mathbf{\Pi}, \tag{7}$$

where $\mathbf{g}$ is the fluid acceleration due to a homogeneous external field, and $\mathbf{\Pi}$ is the pressure tensor. It is defined from the constitutive equation, which for a Newtonian fluid, ignoring the bulk viscosity, is

$$\mathbf{\Pi} = p\mathbf{I} - \eta(\nabla \mathbf{u}). \tag{8}$$

Here, p is the hydrostatic pressure, $\mathbf{I}$ is the identity matrix and η is the shear viscosity.

In the continuum picture, the velocity field entering these equations is usually taken as Eulerian velocity. However, as has been recently shown, [11, 12] it is the volume-average (Lagrangian) velocity that enters the equation (6), and the two velocities are distinct in the inhomogeneous case. This is due to the fact that element of fluid (or *material fluid particle* [11, 12]) contains different molecules at different times. We will demonstrate here that the difference is measurable.

Assuming that the fluid is incompressible and that the flow is laminar, we can apply the standard laws of hydrodynamics to describe the flow. Thus, for this particular geometry, the steady hydrodynamic balance equations are

$$\frac{\partial P_{yz}}{\partial z} = \frac{\partial P_{zz}}{\partial z} = 0,$$

$$P_{yz}\frac{\partial u_y}{\partial z}+\frac{\partial q_z}{\partial z}=0. \tag{9}$$

If the gradients are small,

$$\begin{aligned} P_{xx}=P_{yy}=P_{zz}, \qquad P_{yz}=-\eta\frac{\partial u_y}{\partial z} \\ q_y=0, \qquad q_z=-\kappa\frac{\partial T}{\partial z}. \end{aligned} \tag{10}$$

The Navier-Stokes (NS) equation for an incompressible, Newtonian fluid is

$$\rho(\mathbf{r},t)\left(\frac{\partial\mathbf{u}(\mathbf{r},t)}{\partial t}+(\mathbf{u}(\mathbf{r},t)\nabla\mathbf{u}(\mathbf{r},t))\right) = \nabla p+\eta\,\nabla^2\mathbf{u}(\mathbf{r},t)+\rho(\mathbf{r},t)\mathbf{g} \tag{11}$$

For a stationary state gravity-driven flow in a circular cylinder it reduces to

$$\nabla^2 u_z(r)=-{}^{\rho}\!/_{\eta}\,g_z \tag{12}$$

and is supplemented by the boundary condition either in the Dirichlet form (no-slip boundary condition)

$$u_z(R)=0, \tag{13}$$

or in the form of the Neumann boundary condition when a finite slip exists

$$\left.\frac{\partial u_z(r)}{\partial r}\right|_{r=R}=-\delta^{-1}u_z(R_{-0})=-\delta^{-1}u_0. \tag{14}$$

Introducing $Kn=\lambda/H$, and considering $Kn\ll 1$ we obtain a parabolic solution of the NS equation

$$u_y(z)=\frac{\rho g_y}{2\eta}\left(h^2-z^2\right)+u_0 \tag{15}$$

that could be expressed in terms of slip length δ (see figure 4),

$$u_z(r)=\frac{\rho g_z}{4\eta}\left((\delta+R)^2-r^2\right) \tag{16}$$

8.3.3 Molecular slip flow

The type of hydrodynamic boundary conditions for viscous fluids appropriate at the nanoscale generated rich discussion recently, and much controversy exists in the literature about its nature. The continuum approach is firmly based on the so-called no-slip boundary conditions. This is a consequence of the continuity of stresses [4] and furnishes thus a Dirichlet boundary condition, $\mathbf{u}'\ (\mathbf{r})|_{\mathbf{r}=\sigma}=\mathbf{0}$, where $\mathbf{u}'$ is the relative velocity of the fluid at the solid-fluid boundary σ. Kinetic theory, on the contrary, suggests that there should be a finite slip at the solid-fluid interface [58] and this finding is supported by the large body of experimental evidence [64] and revealed in simulation studies [97, 3, 112]. The apparent paradox has a simple explanation, however. Finite slip appears only when we consider the wall collisions on purely kinetic arguments, that is, for hard molecules colliding with a hard wall, where the volume of the system is well defined. For a soft solid-fluid

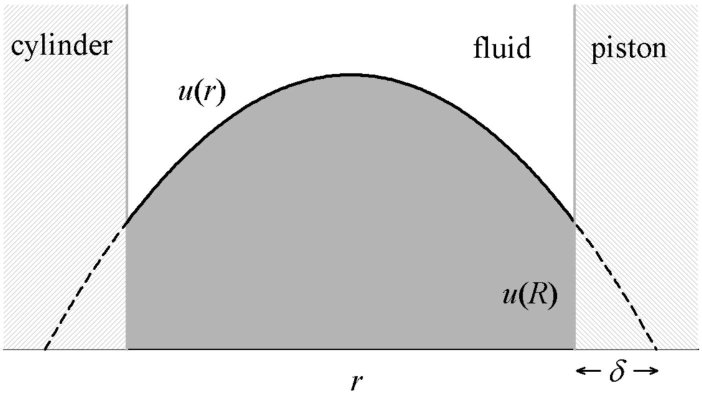

Figure 4: Velocity profile in the p-c unit gap. For a given fluid, the slip length δ is a property of the substance and it should be equal for a cylinder and piston made from the same material.

potential $w(\mathbf{r}) < \infty$ the definition of system volume is less clear cut, since there is a non-zero probability $\sim \exp(-\beta w(\mathbf{r}))$ that the fluid particle is visiting $\mathbf{r}$, even if $\mathbf{r}$ is situated in the solid. As a result, the velocity field is defined (exists) everywhere, and the fact that the density of fluid is diminishingly small is immaterial since the velocity field is an intensive property. In Maxwell's original consideration of the conditions to be satisfied by a gas at the surface of a solid body [4] he considered two extreme cases of collision: first, when the gas molecule penetrates the surface layer of the solid (a "stratum" with "fixed elastic spheres") during the collision, and second, when the colliding molecule is perfectly reflected, and added that the condition of the rebounding molecules will be intermediate between these two cases. This is clearly the case; the degree of surface corrugation depends critically on the collision speed, and the deeper the colliding molecule penetrates the surface layer, the stronger the lateral interaction ("friction") it experiences during the collision, which depends, of course, on the lateral velocity. The streaming velocity at the boundary comprises the streaming velocity of incident particles and that of scattered particles. When particles collide with the wall, they transfer part of the momentum in the direction of flow to the wall. On the molecular level the boundary conditions therefore define a discontinuity in streaming velocity rather than fix a value at the boundary. On a phenomenological level this corresponds to Neumann boundary conditions for the macroscopic velocity field. However, when the solid is considered within the continuum approximation, there are certain effects, which Maxwell called 'oblique stresses against real surfaces' that are completely ignored. Inclusion of these effects in the model requires a special device to couple the lateral motion of the solid and the fluid thus introducing interfacial friction, or frictional drag. In the appendix to his paper on stresses in rarefied gases, published in 1879 [57], Maxwell developed a theory in which slip boundary conditions were obtained as a consequence of the molecular corrugation of the solid. This theory is based on the assumption that a particle colliding with the wall is thermalised by the wall with some probability α, or specularly reflected with probability $(1-\alpha)$, resulting in a scattering law, which is a mixture of slip and stick boundary conditions. Since the derivation was made within the framework of the kinetic theory of gases, the theory does not, of course, include the effects of adsorption. Beginning with the work of Tolstoi in the early 1950s [101] it became clear that molecular slip could exist at a non-wetting surface and that it becomes more pronounced for narrow capillaries. A large surface slip was observed in the experiments of Churaev *et al.* [20] on mercury and water flow in narrow (radius about 1 μm) quartz capillaries and was attributed to a decrease in viscosity in the molecular boundary layers next to a solvophobic surface. Bocquet and Barrat [3] have demonstrated in a computer simulation that when a liquid only partially wets the solid, a large slip effect is observed. Other simulation studies [42, 96, 51, 3] have found a variety of other types of boundary conditions, ranging from no-slip [102, 100, 51], to stick-slip [74] and even to immobilized layers at the wall [96]. It emerges from these studies that the slip velocity depends critically on how the solid surface is modelled. In all previous studies where the molecular structure of the solid is taken into account, the solid was modelled either as a rigid framework of atoms, or as an Einstein solid, in which atoms are tethered to the lattice sites by harmonic springs. A representation of the solid by a collection of atoms at a surface density of $\rho\sigma^2 = 0.8 - 0.9$, where σ is the van der Waals diameter of fluid particles, is acceptable for molecular crystals, but introduces an unrealistically high degree of surface corrugation for metallic or covalent solids, where the surface density is typically several times higher (*e.g.* $\rho\sigma^2 = 5.54$ for graphite basal plane).

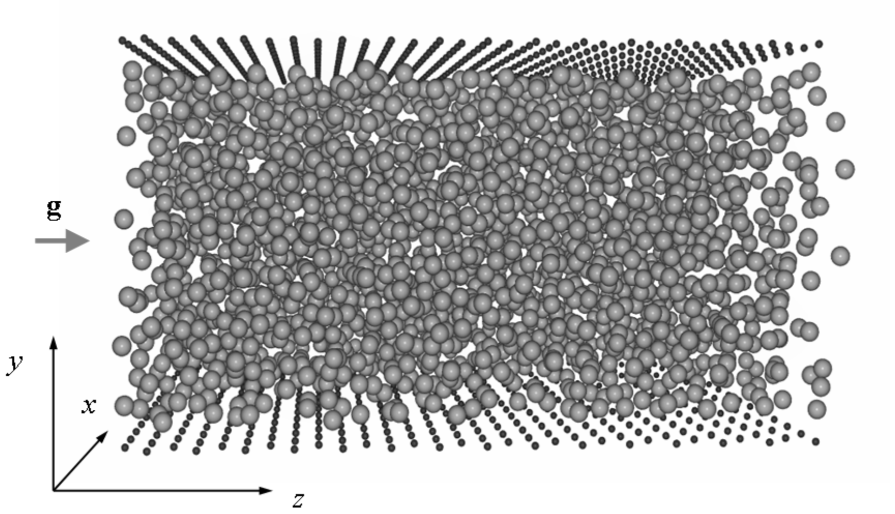

Figure 5: Sketch of the MD system. Flow is along the z direction. The solid walls are located at $y = \pm H/2$, in x and z periodic boundary conditions are applied.

In our recent work we used a nonequilibrium molecular dynamics (NEMD) technique to simulate Poiseuille fluid flow in a graphite slit pore, in which the atomic structure of carbon layers is taken into account explicitly via the many-body bond-order Tersoff–Brenner potential [95] and compare the results with rigid walls at surface density $\rho\sigma^2 = 1.1$ (the so-called 'rare-gas' wall; see figure 5). As far as we are aware, this was the first simulation of fluid flow in a confined space of simple geometry using a realistic model for the solid. Previous simulation work using simplified models for the solid have assumed that there is no slip at the wall in systems of this type. We show below that existence of slip at the walls depends critically on the model of the solid surface, and that by using a realistic model for a graphite surface we arrive at a different conclusion. The analysis of the streaming velocity profile in this case enables us to formulate the most appropriate boundary conditions for flow where the solid surface is to be represented as a smooth wall.

According to Maxwell's theory of slip, the distribution function for the velocity component parallel to the wall in the direction of flow is a linear combination of specularly reflected particles and those thermalised by the wall,

$$f_M(v_\parallel) = (1 - \alpha) f(v_\parallel - u_{\text{in}}) + \alpha f(v_\parallel), \tag{17}$$

where it is assumed that both distributions can be described by the Maxwellian,

$$f(w) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mw^2}{2kT}\right), \tag{18}$$

and u_{in} is the mean streaming velocity of the particles approaching the wall. The transverse component, parallel to the wall and normal to the flow, is always $f(w)$, and the distribution for the normal components is

$$g(v_\perp) = \frac{m}{kT} |v_\perp| \exp\left(-\frac{mv_\perp^2}{2kT}\right); \tag{19}$$

$$u_w = (1 - 0.5\,\alpha)\, u_{in}. \tag{20}$$

In order to relate the macroscopic (phenomenological) boundary conditions and microscopic (molecular) motion we inspected the sub-ensemble of particles colliding with the wall (see figure 6) and calculated the streaming velocity as a function of time from the collision.

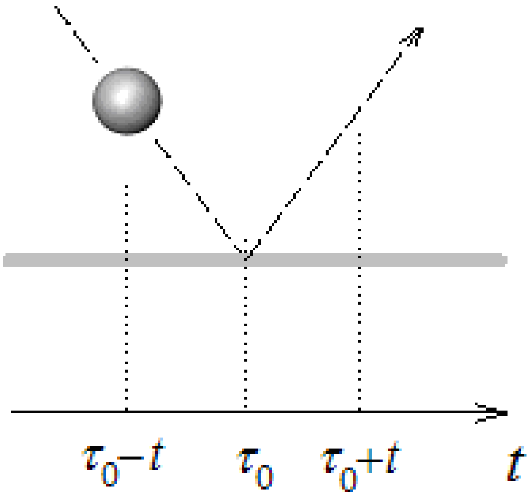

Figure 6: Collision of a particle with the wall. Time is measured relative to the collision moment τ_0 and velocity evolution along the flow direction is analysed.

We found that molecules during the collision lose a fraction of their velocity in the direction of flow. If, following Maxwell, we introduce a coefficient α, to describe the fraction of molecules thermalised by the wall, then diffuse boundary conditions [66] used in a computer simulation with continuum walls correspond to the extreme case $\alpha = 1$ which in most cases we have found to be unacceptably high [85].

Assuming that the slip velocity is small compared to the (mean temperature) velocity, a simple relationship between the mean velocity components in the direction of flow just before, u_{in}, and immediately after, u_{out}, the collision can be established

$$u_{\text{out}} = (1 - \alpha)\, u_{\text{in}}, \tag{21}$$

which gives the relation between microscopic properties and 'reflectivity' of the wall. The coefficient α never reaches a value of one, even for a slit pore with a high degree of corrugation (rare-gas wall) $\alpha = 0.66$ and for a graphite wall α is two orders of magnitude smaller. Clearly, the nature of the interaction between particles and the wall is very sensitive to the details of the wall structure and the determination of the Maxwell coefficient requires full-scale molecular modelling.

The deviations from hydrodynamic behaviour in the proximity of the wall are caused by the variation of fluid properties in this region and is noticeable usually within one molecular diameter from the wall, within the first adsorbed layer of atoms. Its main features can be captured by a Knudsen boundary layer with a characteristic length scale of 1σ, where σ is the diameter of a fluid particle but with unknown viscosity. An alternative way is to reformulate the boundary condition in terms of slip length, a distance from the wall where the extrapolated velocity profile decays to zero. The idea goes to Navier [63] who obtained the following boundary condition for the velocity field (the last equation on p. 415 of his paper),

$$\eta \left. \frac{\partial u_z(y)}{\partial y} \right|_{y=H/2} = \beta u_z\left(H/2\right) \tag{22}$$

introducing the empirical parameter β that enters the slip length $\delta = \eta/\beta$. Incidentally, he arrived at this condition within the field approach while considering particle arguments. Characterization of the boundary conditions by a slip length is just a convenient way of hiding all the complexity of the problem under the single parameter, which needs to be defined either empirically or from simulation. In hydrodynamics it plays the role of the surface excess in classical thermodynamics, describing the adsorption phenomena to a first order. Boundary slip in Newtonian liquids under various conditions has attracted much attention in recent years and many details of conditions at the wall have been clarified. In particular, it has been found that slip is a nonlinear function of the dynamic state [97] and exists even in the strongly wetting case [64]. However, the fundamental problem of estimation of its magnitude from molecular properties still remains a major challenge.

8.4 Viscous drag force on a piston

Modelling fluid flow in complex geometries at a full molecular level of description presents a challenging problem in interpreting data and requires large computational resources. The presence of the solid modifies the transport properties of fluids in channels of molecular dimensions in a rich and intricate way with many influencing factors, including the strength of the solid-fluid interactions, geometry of the channel, and morphology of the solid interface (surface heterogeneity and anisotropy). In order to make progress it is necessary therefore to use simplified assumptions and the usual way to tackle the statistical problem is to decompose it into a primary region treated with molecular details, and the remainder, where the continuum description is sufficient. Quite generally, in the case of a plane solid surface the interaction potential between the adsorbate at $\mathbf{r}$ and the adsorbent can be expanded in a power series and, by retaining the first two terms only, written as [90]

$$U(\mathbf{r}) = U_0(z) + U_1(z)\ f(\mathbf{s}). \tag{23}$$

Here the first term, $U_0(z)$, is a potential of a statistically averaged solid and it defines the normal stress in the fluid. Its functional form has been well studied in the past [14] and for covalent solids it can be described, for example, by the Steele's '10-4' potential. The second term includes the periodic function of the two-dimensional lateral vector $\mathbf{s}$ ($\mathbf{r} \equiv (\mathbf{s}, z)$) with z-dependent amplitude, and describes the surface corrugation. This term, which is responsible for lateral stresses in the fluid, has been largely ignored in previous treatments of equilibrium and non-equilibrium fluids in contact with the solid wall. In the above simplified picture a complex two-phase problem is reduced to a more manageable task of a fluid in an external field, which includes, however, the lateral forces. At equilibrium, the local fluctuations at the interface give rise to fluctuating stresses and to local currents, but the corresponding macroscopic field is averaged to zero. Away from equilibrium the local viscous stress $\eta\,\partial u/\partial z$ at the boundary takes some finite value and the hydrodynamic boundary conditions can be described by a macroscopic friction field. The phenomenological viscous friction law for fluids postulates a linear dependence of the friction force on the fluid velocity at the interface (slip velocity), u_{s} [83],

$$F_y = \xi u_{\mathrm{s}}, \tag{24}$$

where $\xi = m/\tau$ is the damping factor, m is the mass of the fluid monolayer at the wall, and τ is the slip time. Recent experiments in nanotribology [83, 52] show that on the microscopic scale the solids exhibit friction behaviour strikingly different from the predictions of Amonton's law and Coulomb friction for macroscopic solids. While the analytic models developed for wearless friction between the solids provide much insight into the phenomenon of dynamic friction between the solids on the molecular level, there is no microscopic theory of the viscous friction. The development and formulation of the kinetic theory of friction implies further development of statistical methods for the non-equilibrium steady-state ensemble. Progress can be made either using approximate mode-coupling approaches or considering the work done against dissipation and equalising microscopic and macroscopic expressions.

Among several mechanisms of energy dissipation at the solid-fluid interface, which includes in the general case, the surface corrugation, phonon excitations and electronic excitations in the solid as well as irreversible changes of the surface, the corrugation of the adsorption potential due to atomic structure is probably the dominating mechanism for metallic solids. Inclusion of the molecular motion of the solid results in two counter-acting effects: decreasing friction due to decreased apparent surface corrugation as seen by the colliding particle and increasing friction due to phonon excitation in the solid. The combined effect will depend on the relative importance of these two mechanisms and this will be examined and compared with molecular simulation results, obtained with both the molecular model for the solid and our continuum approach for the solid with a friction field. Another task will be the development of numerical techniques for friction field simulations including extensions of the method to include surface heterogeneity on different spatial scales. The goal is to understand how these factors affect the hydrodynamic boundary conditions.

The total potential energy of a system containing N_1 fluid particles and N_2 atoms in the solid in pairwise approximation consists of three different contributions,

$$W = \sum_{j>i}^{N_1} w_{\mathrm{ff}}(\mathbf{r}_j - \mathbf{r}_i) + \sum_{j>i}^{N_2} w_{\mathrm{ss}}(\mathbf{r}_j - \mathbf{r}_i) + \sum_{i,j}^{N_1,N_2} w_{\mathrm{sf}}(\mathbf{r}_j - \mathbf{r}_i), \tag{25}$$

where w_{ff}, w_{ss}, and w_{sf} are pair interaction potentials (which could also implicitly include many-body terms) for fluid-fluid, solid-solid, and solid-fluid interactions, respectively. When a simplified model for the solid is used, the last sum in (25) is replaced by a sum of one-particle interactions which correspond to statistical averaging over the degrees of freedom of the solid. In this case the second term disappears and the problem is reduced to a fluid in a static external confining field,

$$W = \sum_{j>i}^{N_1} w_{\mathrm{ff}}(\mathbf{r}_j - \mathbf{r}_i) + \sum_{i}^{N_1} E(\mathbf{r}_i). \tag{26}$$

This approximation is particularly successful when the density of the solid is high, as in the case of graphite carbon walls.

For an infinite plane of the rigid lattice the last term in (26) can be expanded in a Fourier series[90]

$$W = \sum_{j>i}^{N_1} w_{\rm ff}(\mathbf{r}_j - \mathbf{r}_i) + \sum_{i}^{N_1} E(\mathbf{r}_i). \tag{27}$$

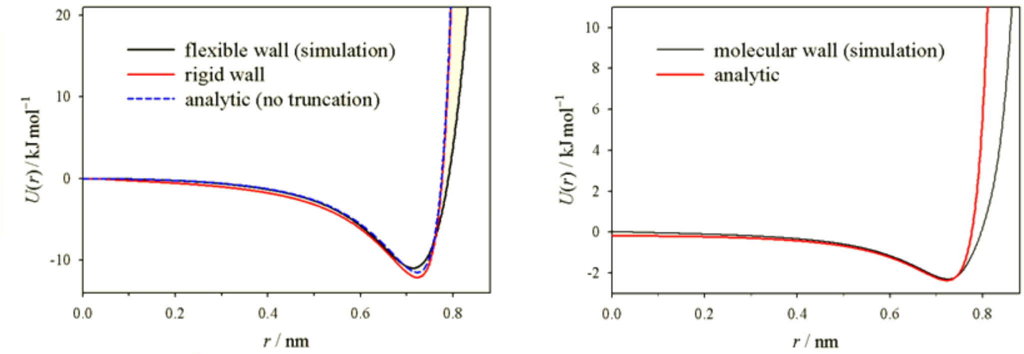

Figure 7: (a): Solid-fluid potential curve for methane – (16,16) carbon nanotube. Full line, mean potential as seen by a fluid particle in a MD simulation with a flexible model for the solid; grey line, potential for a rigid nanotube; dashed line, analytic 10-4 potential for a smooth cylinder. (b): Solid-fluid potential for a rare-gas nanotube. Full line, molecular wall; grey line, analytic 10-4 potential.

where $\mathbf{r}$ is decomposed into normal, z, and in-plane, $\mathbf{s}$, components ($\mathbf{r} \equiv (\mathbf{s}, z)$), and it is assumed that the potential is periodic with Fourier components at the reciprocal lattice vectors, $\mathbf{q}$, only. For a graphite surface this series converges rapidly and in order to represent methane-graphite interactions adequately it is sufficient to take the first six shortest vectors [91]. Explicit expressions for the Fourier coefficients in (27) for the Lennard-Jones (12-6) potential contain the modified Bessel function of the second kind and they are given in the original paper of Steele [90]. For our purposes we can rewrite (27) in the form

$$E(\mathbf{r}) = E_0(z) + E_1(z) f(\mathbf{s}) \tag{28}$$

where $E_1(z)$ is the amplitude of the corrugation potential and lateral dependence of the potential is hidden in periodic function $f(\mathbf{s})$.

In many cases the expansion (27) is truncated at the leading term, which corresponds to $\mathbf{q} = \mathbf{0}$ and describes the interaction with a surface spatially averaged over the area of unit cell. For a graphite plane such truncation is known to be reliable due to the high surface density of carbon atoms and integration over an infinite plane gives the familiar (10-4) potential [90]. In the case of cylindrical symmetry ($\mathbf{r} = \{r, \theta, z\}$) as for nanotubes, the integration can be performed analytically [99]

$$\begin{aligned} E_0(r) = \quad & 3\pi^2 \rho_{\rm s}\, \varepsilon_{\rm sf} \left[\tfrac{21}{32} R^{-10} \left(1-\beta^2\right)^{-10} F\left(-{}^9\!/_2, -{}^9\!/_2, 1; \beta^2\right) \right. \\ & \left. - R^{-4} \left(1-\beta^2\right)^{-4} F\left(-{}^3\!/_2, -{}^3\!/_2, 1; \beta^2\right) \right]. \end{aligned} \tag{29}$$

Here, $\beta = r/R$ is the reduced distance from the cylinder axis, $\rho_{\rm s}$ is the surface density of atoms in the solid, $\varepsilon_{\rm sf}$ is the energy parameter for the solid-fluid interactions, and $F(..)$ is a hypergeometric function. For the simulations the external potential was used in a tabulated form using three-point interpolation and therefore needed to be calculated once only. This approximation becomes less accurate for surfaces of a lower density, where a statistical (Boltzmann) average should be used instead.

The boundary condition for the fluid flow is defined by the repulsive part of the solid-fluid potential as probed by molecular collisions. The motion of the atoms in the solid usually has no effect on equilibrium properties and the preceding discussion is generally applicable to problems of hydrostatics, but it cannot be ignored when the hydrodynamic condition of the fluid is to be determined. This is particularly true in the case of solid interfaces, where the mobility of atoms in the surface layer is different in different directions. To illustrate this point we present in figure 7 (in colour in on-line version of this report) the average solid-fluid potential as a function of distance from the cylinder axis in the case of a flexible solid, a rigid lattice and calculated analytically using (29) for a (16,16) carbon nanotube and a 'rare-gas' tube of the same dimensions. The average potentials were obtained from the simulation using

$$\bar{E}(r) = Q^{-1} \int\limits_{0}^{2\pi} d\theta \int\limits_{-L_z/2}^{L_z/2} dz\, E(r,\theta,z) \exp\left(-\beta E\left(r,\theta,z\right)\right), \tag{30}$$

where the second integration is over the periodic cell in z-direction,

$$Q = \int\limits_{0}^{2\pi} d\theta \int\limits_{-L_z/2}^{L_z/2} dz\; \exp\left(-\beta E\left(r,\theta,z\right)\right),$$

and

$$E(r,\theta,z) = \sum_i w_{\mathrm{sf}}(\mathbf{r}_i - \mathbf{r}),$$

depend on the thermodynamic state of the fluid, *i. e.* they are effective potentials. They were obtained for the Lennard-Jones fluid at a reduced density of 0.485 in the (16,16) carbon nanotube at 300K. In figure 7(a) the analytic potential is practically indistinguishable from that calculated in computer simulation of the rigid tube, reflecting the low degree of corrugation that is characteristic of a graphite surface [90]. The small difference in the fluid-solid potential for the rigid wall, near the potential minimum, is a result of the finite cut-off (1.05 nm) used in the simulation and is the only observable consequence of the corrugation of the graphite potential. In the flexible case however the situation is completely different. As a result of the molecular motion of the solid, the repulsive part of the potential is much softer and therefore the standard integration method (29) introduces a large error. In the simulation with a smooth wall designed to be equivalent to a flexible wall we used a polynomial fit to the average potentials obtained using (30). For the rare-gas tube the potential averaged over unweighted configurations and Boltzmann-averaged potential are different. Uniform integration within the repulsive part of the wall potential introduces a bias towards high-energy configurations where the fluid particle is in front of carbon atom in the solid, configurations of very low statistical weight at ambient temperature.

Each simulation started from the uniform initial condition $\mathbf{u} = \mathbf{0}$, and as a result of balance between the driving and velocity-dependent dissipative forces, a steady state was usually developed within 1 – 2 ns of the MD time. Under stationary Poiseuille flow all forces acting on a fluid element are perfectly balanced (the Eulerian velocity field is time independent throughout the system). This is one of the underlying principles and a necessary condition for the stationary flow. The viscous forces in the flowing fluid can be monitored by a small test particle, co-moving with the fluid, and in molecular simulation the natural choice of such a test particle is the molecule itself. The stationary condition in the Lagrangian formulation, however, implies that the time derivative of the particle velocity taken along the particle trajectory vanishes and the stationary Eulerian flow can be realized when each particle is systematically accelerated in one region and decelerated in another.

When a molecule moves through the viscous fluid it experiences a hydrodynamic drag, whose magnitude can be calculated directly from the intermolecular force field [69]. This drag force is related to viscosity [69] and other transport coefficients [113]. We considered two different contributions of the drag force

$$\begin{aligned} f_i^+ &= \sum_{y_j > y_i} f\left(\mathbf{r}_{ij}\right) \\ f_i^- &= \sum_{y_j < y_i} f\left(\mathbf{r}_{ij}\right) \end{aligned} \tag{31}$$

where f_i^+ (f_i^-) is the projection of the total instantaneous force acting on molecule i due to fluid molecules j with $y_j > y_i$ $(y_j < y_i)$ on the direction of flow, together with the force f_i^{sf} due to the solid-fluid interactions.

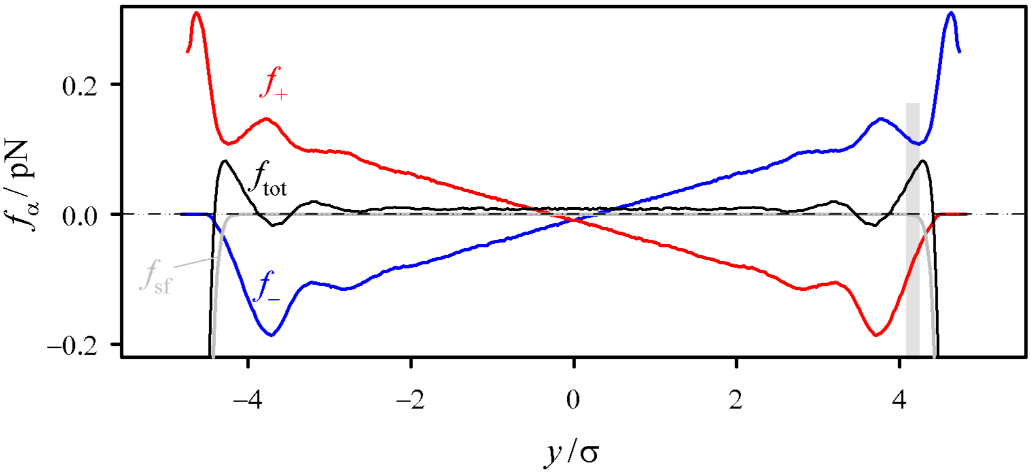

Figure 8: Profiles of the components of the shearing force on a molecule and a hydrodynamic friction force profile.

Each component α was averaged independently, $f_\alpha(y) = \overline{f_i^\alpha(y,t)}$, with the bar denoting the time average. Figure 8 presents three contributions for the density $\rho\sigma^3 = 0.5848$, as well as the total force profile, f_{tot}, which includes also constant external force contribution. The components of the net force acting on a particle (color online) scale linearly with the distance from the channel midpoint, and the corresponding shearing force, $f_+(y) - f_-(y)$, also scales linearly, in accordance with macroscopic hydrodynamics. In the middle of the channel the shearing force vanishes. The total force, however, is nonzero, and according to hydrodynamics, it should be equal in magnitude and oppositely directed to the external driving force. The total force is positive and almost constant in the central part, where the density is uniform (see figure 8), and shows an oscillating profile near the interface. The number of resolved oscillations and their amplitude depends on the wetting conditions (strength of the adsorption potential) and surface corrugation, and for a particular system, it depends on fluid density (normal pressure). Thus, at the interface there are regions where the fluid molecules are subject to a net accelerating drag force, and there are regions where they are decelerated, and the location of these regions correlates directly with the positions of maxima and minima in the density profile. For the system considered, the net accelerating force acting on fluid molecules in the first adsorption monolayer is actually stronger than the external drag force and is therefore a result of shearing force between the first and second monolayers of fluid. Our results for a Poiseuille flow along the chemical potential gradient [86] in the equivalent system produce similar oscillations in the force profile. The origin of particle acceleration is also clear from an inspection of two contributions to the shearing force shown on the lower graph. In the acceleration area $f_+(y)$ is negligible since there are practically no fluid molecules on the right of it; the solid-fluid friction is also insignificant here since it decays exponentially and is a very short-ranged force, so the main contribution comes from $f_-(y)$, slightly weakened here as the number of nearest neighbours in the adjacent fluid layer is reduced. The overall steady-state conditions of the Poiseuille flow are maintained by a constant circulation of molecules between two regions. The stationary velocity in the acceleration region results from the time average in the space fixed frame over the molecules entering the region with lower average velocities and leaving it accelerated.

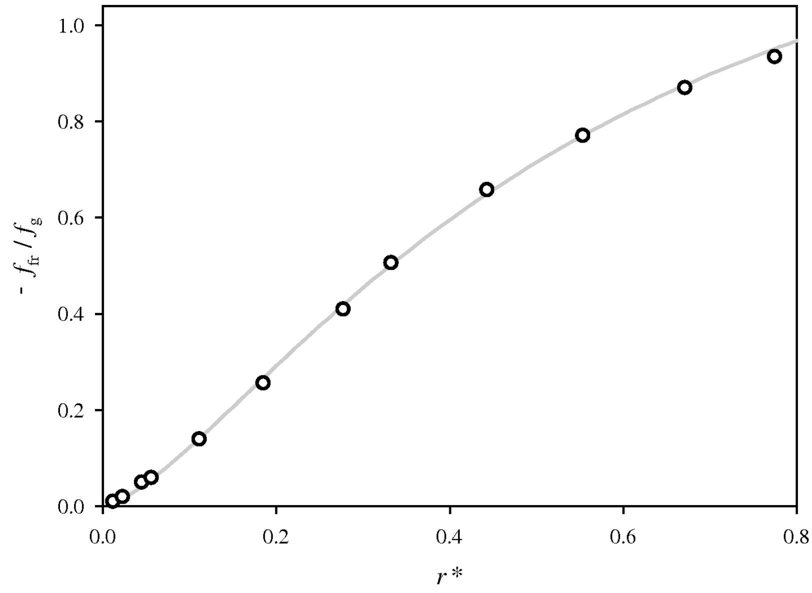

Figure 9: Ratio of the hydrodynamic friction force on a moving molecule to the driving force as a function of density.

The density dependence of the drag force is shown in figure 9, where its magnitude is shown as a fraction of the driving force. The effects of rarefaction are usually described by expanding the properties of the system in a power series of the Knudsen number *Kn*. Using kinetic theory expressions for hard spheres, flow conditions at a reduced density $\rho\sigma^3 = 0.5848$ correspond to $Kn = 0.01$, whereas the difference between the driving force and a friction force amounts to 23%. Clearly, this effect cannot be described by rarefaction solely. The observed effect shows also that the Stokes-Einstein relationship between the diffusivity and viscous friction is violated in small channels.

Details of the molecular collisions with the wall can be clarified by studying the temporal velocity profile of the sub-ensemble of particles colliding with the wall [85]. We have observed previously in molecular dynamics simulations [87] that, just before a collision with a confining wall, particles accelerate in the direction of flow. A similar effect was observed in flow in carbon nanotubes [85], however there was no real explanation given for this effect. Figure 10 presents the temporal velocity profile of colliding particles, centered at the moment of collision with the wall, dashed line (blue online), right scale, together with the corresponding profile for the particle distance from the wall (solid black line, left scale). Using these profiles the initial speed-up (vertical shadowed area) is mapped onto a range of distances from the wall (horizontal shadowed area), and that gives the shadowed area on figure. The lateral acceleration of colliding particles corresponds thus to a region where the fluid is constantly accelerated due to the imbalance of shearing forces, where the decelerating f_+ is replaced by the solid-fluid force f_{sf} which is shorter-ranged, creating thus a "gliding layer" over the surface in the low-density region. This argument shows the importance of the "gas" layer at the boundary predicted by de Gennes [29].

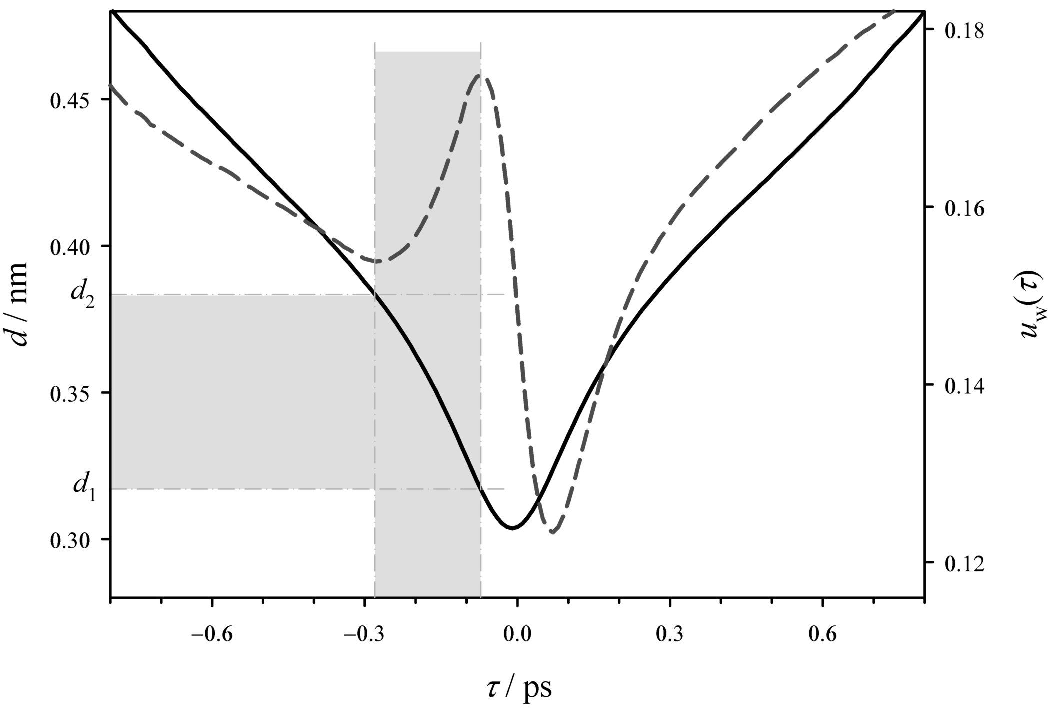

Figure 10: Temporal profiles of the streaming velocity of the sub-ensemble of colliding particles and collision depth profiles.

The acceleration arising in Poiseuille flow should be observable for a broad range of substances and can be detected in principle using molecular tagging velocimetry experiments [92] or similar techniques. In the case of electrolyte solutions it could lead to a detectable high frequency electromagnetic field generated by accelerated/decelerated charged species.

9 Materials Studio software testing case study

In this chapter we review a popular commercial molecular modelling software package, the *Materials Studio* suite of programs from Accelrys, that is in use at NPL. The review concentrates on usability questions to aid readers in deciding whether this software might be of use to them in tackling particular molecular modelling challenges that they faces. More information about Accelrys and about the software itself can be found at www.accelrys.com/.

9.1 About the software

Materials Studio is a software package for molecular visualisation, simulation and modelling. The software includes a range of tools that can be used to design molecules and polymers, simulate their interaction with other molecules and surfaces, and predict their behaviour and properties. The software tools are accessed via a Windows-based graphical user interface (GUI).

The software package is similar to many modern simulation packages because it does not require the user to have an understanding of the equations underlying the model, or of the methods used to solve the equations. This approach is increasingly common amongst providers of finite element software, for example.

9.2 Test problem and tester

The chosen test problem was the simulation of the interaction between a single molecule of Irganox 1010 (a relatively complicated organic molecule, see figure 11 for structure) and a silver surface. This problem has been modelled by experts in molecular modelling as part of an NPL Strategic Research project, so the problem solution was known. The reference result was the final configuration of the molecule on the surface, since this was well-defined and known to be independent of the initial position of the molecule.

The software tester had a very basic knowledge of chemistry, including an elementary understanding of molecular structures and the forces affecting molecular mechanics, but with little knowledge of crystalline structures and behaviour of surfaces at an atomic level.

9.3 Setting up the calculation

Setting up the calculation required the following steps:

1. Creation of the Irganox 1010 molecule.
2. Creation of the silver surface.
3. Joining the molecule and the surface in a single model (the two are created separately).
4. Definition of suitable boundary conditions.
5. Definition of other parameters affecting the calculation.

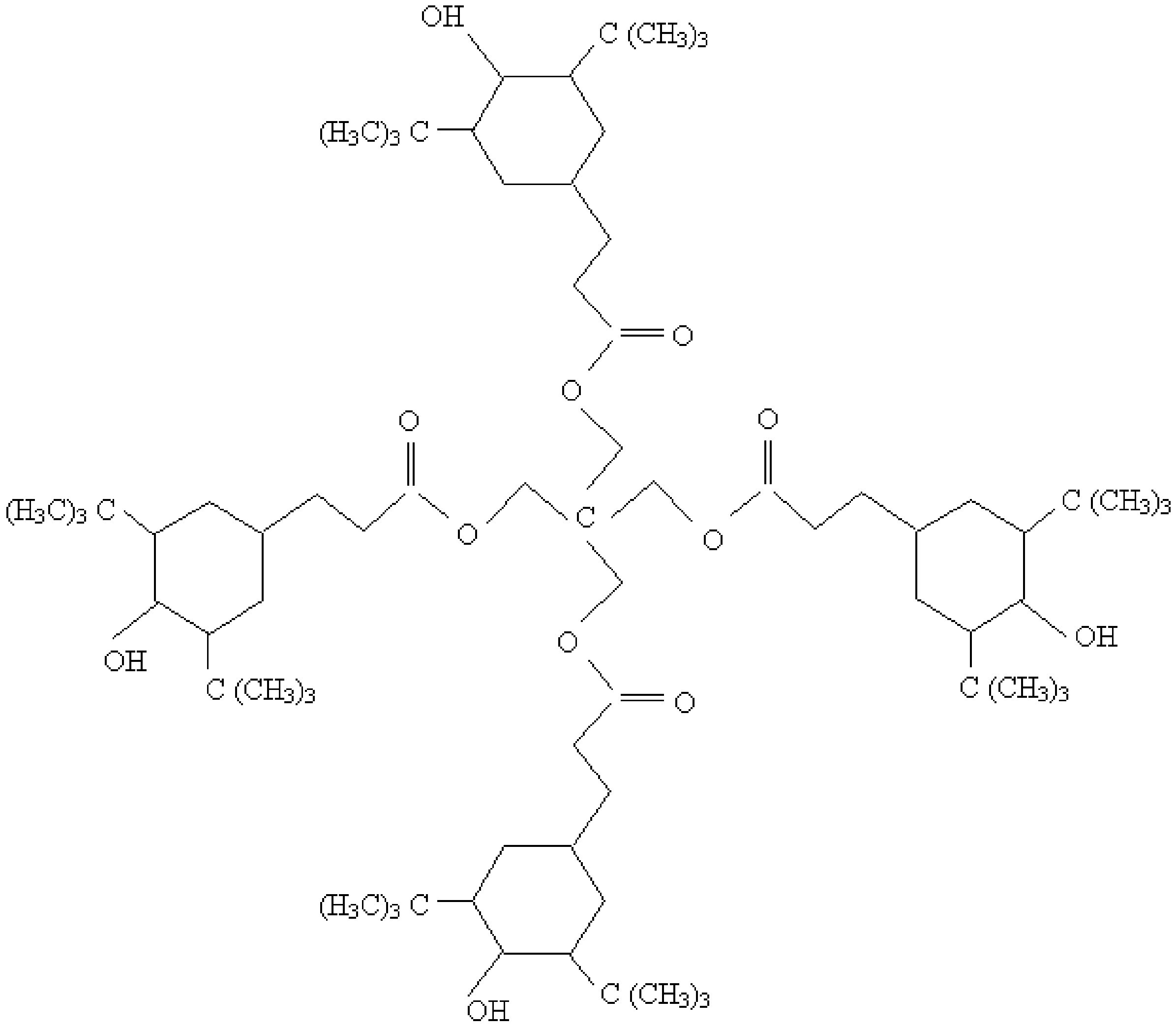

Figure 11: Structure of the Irganox 1010 molecule

Molecules in *Materials Studio* are created by using a simple point-and-click interface to place and join atoms. Once an atom has been created, its properties can be altered by double-clicking on it to access its properties menu, so if the wrong atom is added it is simple to correct the mistake. Similarly, bond properties can be accessed and altered through a properties menu. The visualisation tools for molecular structures are good.

The software includes a number of tools that are useful for the creation of large complicated molecules. If a molecule features a repeated sub-unit (as is the case for Irganox), this sub-unit can be created and saved separately, thus speeding up the creation process. In addition, the software includes a number of common molecular fragments that can be used to construct complete molecules. If an organic molecule is being created, it can be helpful to build the main structure without adding the hydrogen atoms since this often makes visualisation clearer, and the software package has a tool that automatically adds the maximum possible number of hydrogen atoms to a molecule.

The creation of the silver surface was helped by two features of *Materials Studio*. The first feature was the existence of a pre-defined pure silver structure with an appropriate configuration that could be read in, so that it was not necessary for the user to know the correct atomic spacing for silver. The second feature was the tutorials included in the help files, specifically the tutorial “Polymer interactions with a metal oxide surface”. This tutorial takes the user through the steps needed to set up and run a model of the interaction of a polymer and a metal oxide surface, a problem that is clearly very similar to the test problem.

This tutorial was used without the user being certain that all of the steps in it were necessary, and without any certainty that no extra steps were required. This lack of certainty is the main problem for the user with little knowledge of molecular interactions.

Further evidence of the importance of understanding the problem in the correct terms was provided during the creation of the silver surface. This required the user to cut a crystal cell by defining a plane through the cell that would form the new free surface. The software required the plane to be defined in terms of units related to the crystal structure rather than the on-screen display axes, which led to some confusion. A user with more knowledge of crystal structure terms would not have had this problem.

The main factor that had to be considered when combining the molecule and the surface was that the surface unit that had been created was a lot smaller than the molecule. The software has a tool for the creation of arrays of a repeated unit, so it was easy to construct a larger surface (called a “supercell”) for the interaction. When the supercell was created, the boundary conditions of the problem were defined to be periodic in all three dimensions.

The molecule was combined with the surface by using the *Layer builder* tool and a large vacuum was added above the surface in order to avoid the unwanted effects of the periodic boundary conditions in the direction normal to the surface.

The calculation method chosen was a molecular dynamics simulation within the *Discover* module of the software. The calculation is an iterative process that calculates the forces on the molecule, updates the position at the end of each time step accordingly, and then recalculates forces. The long-term position of the molecule, in the absence of external forces, should be the most energetically favourable configuration.

The parameters required for this calculation are temperature, time step, and total dynamics time (or number of time steps). The temperature was held fixed at 298 K throughout, and the time step was held at 1.0 fs. Initially the job was run for 50,000 steps (a time of 50 ps), and two subsequent runs of one million steps (a time of 1 μs) were tried. All other options were kept at default values, including those in the *Discover* Setup menus, such as choice of force field. It is not clear whether this choice of time step was the most appropriate for the chosen problem. The advice on time step choice in the software help files suggested that any molecule containing a C-H bond would require a time step of 0.5-1.0 fs to produce good results.

9.4 Running the calculation

The calculation was easy to start, and supplied regular updates of current position and energy. After the successful completion of the initial 50 ps test run, the configuration of the molecule was not the same as the reference result, but it exhibited some similar features. It was likely that the time period chosen was not long enough, and so a longer calculation period was chosen.

However, a number of problems occurred during the longer calculation process. During the first lengthy calculation, the software ran extremely slowly even when the computer was not in normal use. Additionally, the calculation failed after 0.99 μs, restarted from the initial conditions, and overwrote all useful results that had been calculated up to that point. After some investigation, it was found that the software did not interact well with the NPL distributed computing software.

The NPL distributed computing (DC) software uses the excess capacity of desktop PCs to carry out calculations. The DC software checks the processor usage of a PC in order to determine whether that PC is available for a DC calculation. It seems that the *Materials Studio* calculation was either a low priority calculation or used a negligible amount of the processor, since the DC software found that the PC running the molecular dynamics calculation was available for a DC calculation. The DC calculation then used all of the available processor and so the calculation speed of the molecular dynamics calculation decreased sharply. It was also suspected that the DC calculation could have caused the failure of the molecular dynamics calculation.

The PC was removed from the DC network and the molecular dynamics job was restarted from the beginning. In order to speed up the calculation further, the frequency at which the visualisation of the molecule's current position was refreshed was reduced. The restarted run had no calculation speed problems, but it failed under the same circumstances as before. The software help files suggested that the problem was either lack of disk space (unlikely), lack of memory (possible) or a communication failure. The error log file generated by the software seemed to state that communications failure was to blame, which is somewhat surprising as the software was running on a single PC and so communication should not be an issue.

As a result of both the long runs failing unexpectedly, no useful results were created from the test. However, since the test was partly an assessment of usability, useful information was still obtained.

9.5 General comments

The visualisation tools in *Materials Studio* are good. Atoms and bonds can be visualised in a range of different ways so that an appropriate visualisation can be found for the information that is required. The user interacts with the visualisation via the mouse, making rotation, translation and zooming of the view simple and easy to control. The updated view appears seemingly instantaneously, making detailed control of the view simple.

The interface is easy to use for anyone familiar with Windows-based GUIs as it consists of familiar drop-down menus and buttons with icons. The design of the GUI is clear and any doubts can be resolved by consulting the help files. In general the help files are very good, giving explanations of many of the technical terms and providing useful case studies and tutorials to guide the novice user.

9.6 Conclusions

The software is user-friendly, and includes a number of features that make setting up a calculation straightforward:

- the software includes a wide range of pre-defined complete and partial molecular and crystalline structures so that the user does not have to define every aspect of the problem from scratch;
- the software's help files and online manual contain a number of case studies and worked examples that take the user through the steps required to set up a calculation correctly, and the examples are sufficiently generic that they can be easily adapted to apply to other similar problems;
- the tools for definition of molecules are easy to understand and include useful features such as automatic addition of hydrogen (useful for organic molecules), fragment saving for construction of molecules with repeated units, and polymer creation;
- the visualisation tools make checking the model simple.

The danger of this user-friendliness is that it is easy for a user to set up and run a job with very little idea of whether the right steps have been taken. This is clearly not a fault with the software, since user-friendliness is a positive quality, but it is an important factor in assessing whether a calculation is likely to be correct or not. The software should only be used by people who are aware of all of the factors that could potentially affect the results of the calculation.

A number of problems were experienced with running the software. The calculation crashed twice during long time-scale calculations. In both cases the software package did not crash, and it automatically restarted the calculation from the initial conditions. The restarted calculation appeared to delete the results calculated during the crashed calculation, which meant that potentially useful information was lost.

10 Conclusions

This report has reviewed current challenges in mathematical modelling at the nanoscale. It has set out the reasons for the growing interest in nanoscale modelling among metrologists, identified sources of help for modelling at this scale and provided specific advice on modelling polymers and on multi-scale modelling. In addition, it has included two case studies, one on the modelling of gas flows in pressure balances and the other on the use of a commercial molecular modelling software package.

As was emphasised in the introductory chapter, this report has been drafted with metrologists from other NMSD programmes in mind. It has set out the most important mathematical modelling issues that metrologists who need to tackle nanoscale problems should take into account. The report has provided advice for metrologists on how to assess the potential contribution that nanoscale modelling techniques may be able to make and how to identify sources of help with modelling problems. It has described some of the software available and suggested ways in which non-commercial software may be used to gain experience in modelling at the nanoscale.

Key observation and recommendations from the work reported here are summarised below.

- The pressure balance modelling case study demonstrated that it is not easy to define the necessary molecular modelling tasks unless one has a very clear understanding of the physical problem one is trying to solve and a detailed appreciation of the scientific background to the metrology problem of interest. It appears that such work should be led by computational physicists, chemists and materials scientists rather than by mathematicians.
- The key questions identified by the *New Directions* study[33] are still relevant for nanoscale modelling.
  - How many atoms can be handled using the proposed method?
  - How many different properties and material types can be handled simultaneously?
  - How well do the various nanoscale modelling approaches overlap - if at all?
  - How is it possible for nanoscale models to be validated and benchmarked?
  - Are the approximations used in a particular technique reasonable for the problem of interest?
  - Are current computing resources adequate to tackle large calculations or is there a need to move to parallel processing, grid or distributed computing techniques to speed up computation times?
- At the quantum scale there is a need for accessible benchmark calculations for selected “gold standard” reference molecules.
- A barrier to the development of molecular modelling at the quantum scale is the lack of validation of results, and inadequate methods for predicting uncertainties in calculations.
- At the mesoscale there is a need to develop methods for applying statistical and stochastic methods.
- The identification of a set of test problems in molecular modelling for which answers are already known, or for which good experimental data exist, for use in model validation, is a key requirement.

- It is impossible for model systems to capture every feature of the real systems they correspond to. It is necessary to understand how the various choices made in setting up the calculation affect results
- The NIST aims for its modelling work at this scale should be incorporated into NMS strategies in this area, that is:
  - there should be a strong emphasis on industrial needs as the motivation for the work;
  - testing and benchmarking software is important;
  - the development of databases of results, including comparisons with experimental data is needed.
- As polymers are a key group of engineering materials, it is vital that NPL gains expertise in modelling polymers at the nano and micro scales. The link between experiment and theory is also important here. Our experimental work in nanoscale measurement can be used to evaluate the results of modelling and *vice versa*.

Acknowledgements

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