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Nature doesn't solve equations, so why should we?

Mathematically-lean simulations in chemistry

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1. Introduction

During the last decade the style of university chemistry teaching has changed radically. Computers were once rarities, but are now commonplace, and their use enhances many courses. As universities compete to attract students from a limited pool, the skill with which chemistry departments can weave new technology into their courses is becoming an important consideration for many candidates.

Computers are somewhat cheaper than most scientific instruments and considerably cheaper than a professor. It is not surprising then that they are in widespread use (Table 1).

Table 1.
Typical computer use in university chemistry departments.
🔴 **Provision of access to, and maintenance of, databases of scientific data or student records**
🔴 **Automation of exam setting and marking**
🔴 **Provision of word processing and graphic design facilities for students and staff**
🔴 **Tuition and guidance of students in problem-solving**
🔴 **Numerical computation in areas such as molecular dynamics**
🔴 **Control of instruments and data acquisition**
🔴 **Analysis of data using spreadsheets or mathematical packages**
🔴 **Control and display of simulations**

The contribution which computers make varies from one department to another, depending on the machines available, local expertise, and the teaching philosophy of the department. Consequently, their impact on student learning is far from uniform.

Where the computer is used primarily as an administrative tool, for example to store student records, there is little direct benefit to the student. Similarly, when students have ready access, but the computer is used just to word process laboratory reports or assignments, it does not contribute a

great deal to scientific understanding. Students' keyboard and computer skills improve, but the computer is not helping them to understand "why things are the way they are".

Even when employed scientifically, if computers are used to help students to balance equations or follow VSEPR rules, the software may just be a disguised "programmed learning" text. The application of rules to determine molecular shapes or balance equations is, in a sense, a mechanical operation which can be carried out without knowledge of the underlying science.

The primary aim of a chemistry course must be to develop in students an appreciation of how the material world behaves, and this requires that the computer play an active, positive role in learning. The key to this is the simulation. Simulations have long been a part of chemistry, and although longevity is not in itself a persuasive argument for their use, they find a place in most courses. We argue in this paper that one of the most valuable uses of the computer in a chemistry course is to run simulations which develop understanding of the molecular world.

Detailed simulations of scientific phenomena can provide an insight which transcends a mathematical description, and an understanding of how materials behave is at least as important as being able to express that behaviour in algebraic terms. By interacting with a computer model students can develop an understanding that - at its best - becomes almost intuitive.

2. The place of simulation in the undergraduate course

At the most fundamental level, a simulation visualises the - possibly idealised - behaviour of individual atoms and molecules.

The level of detail may be limited by the facilities available, (it is a common observation that, no matter how much computer power is available to a chemist, it is never enough). Nevertheless, sophisticated simulation is not always necessary; a detailed view might conceal important generalisations, and thus be counterproductive. Consequently, both molecular level simulations and their coarser counterparts, in which behaviour in the bulk is simulated, have a role to play in a chemistry course. It is important to realise, though, that they are not equivalent. Visualisation of equations, which is essentially what most bulk-level simulations involve, is one step removed from the "real" world of atoms and molecules; we shall argue that in some ways this lessens their value and their impact in teaching.

Computer visualisation can be introduced almost anywhere in a chemistry course, but grapeshot firing of simulation into it is rarely desirable. A simulation must justify its place no less rigorously than a lecture or practical experiment. (Equally, lectures and experiments should be able to justify their existence against the competition provided by simulations). To do this, the simulation must teach concepts more efficiently, or give students a special insight into a topic, or perhaps link together disparate areas of the subject. It must not be a soft financial option whose raison d'etre is to allow administration to replace professors, or keep students quiet when there are not enough spectrometers to go around.

Variety is beneficial in learning, so a mixed diet of simulation, lecture, experiment and discussion will do much to stimulate students' appetite for chemistry.

3. Categories of Simulation

Simulation is a broad field, and much variety exists, limited primarily by the inventiveness of those who write the software. Most simulations can be placed into one of the following categories:

3.1 The Black Box Simulation

In a Black Box Simulation the computer mimics some of the behaviour of a real or imaginary instrument (Fig 1). A complete virtual instrument may be available, or even a virtual laboratory [10] ; in other cases users may select discrete components from a Grey Box and bolt them together to make their own Black Box. In this way they might, for example, construct an electrical circuit from standard items such as resistors and capacitors.
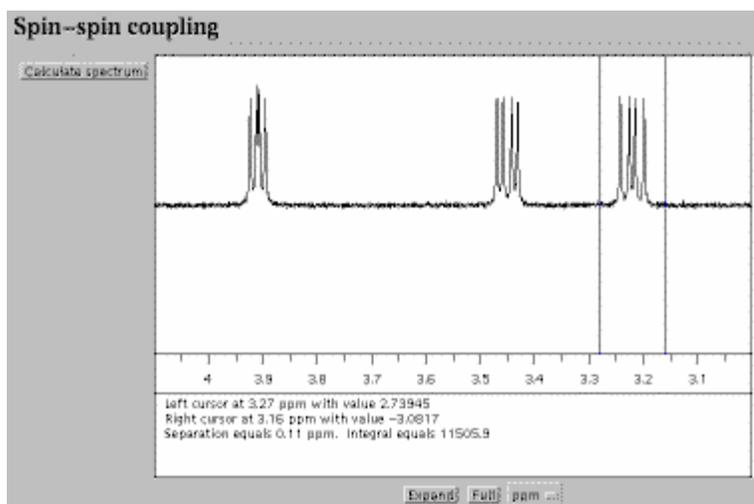

Fig. 1. The spectrum calculated by a "Black Box" NMR instrument. This display is created by a Java applet [1]. Full size version of this figure.

Various factors may trigger the development of such simulations. Departments often wish to give students experience with techniques such as FTNMR, or X-ray crystallography, but are prevented from doing so by financial, technical or safety considerations. In a simulated experiment, problems which disrupt a real experiment, such as dangerous radiation fluxes or unstable samples, can be avoided. Conditions which would be difficult to produce in the laboratory can be investigated. Experiments may be interrupted in the middle to change operating conditions, or to allow the user time to reflect on what has been seen so far. The computer is thus a proxy for the real instrument, having advantages in speed, flexibility and cost.

Black Box simulations can also be used to provide remote Internet access to real equipment. The Black Box element then consists of software which allows the student to control equipment in a user-friendly fashion (Fig. 2).
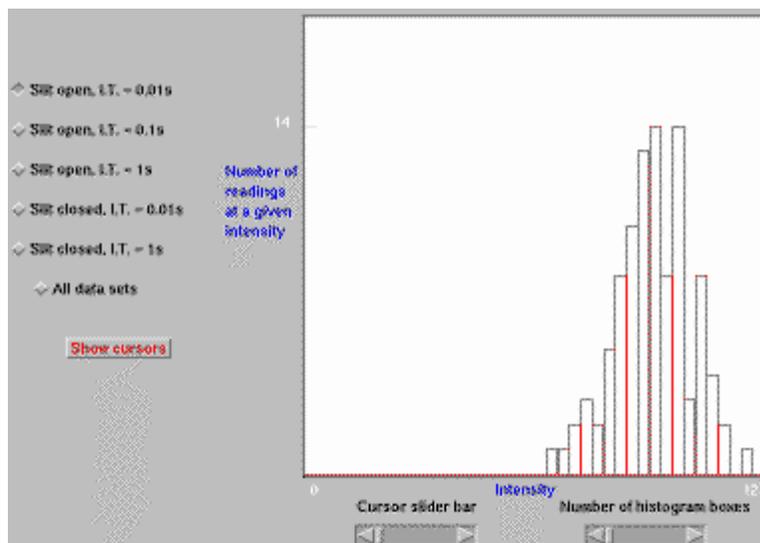
Fig. 2. Data from an on-line optical rig, gathered remotely and displayed using Java applets [2]. [Full size version of this figure.](#)

3.2 Simulation of equations.

Most of the earliest simulations in chemistry were built around the interpretation of equations describing bulk behaviour. For example, the P-V-T behaviour of an ideal gas can be understood by investigating how the volume of a gas trapped by a moveable piston changes as the pressure or temperature of the gas is adjusted. Such a simulation is independent of the behaviour of individual molecules. Indeed, even the presence of molecules is not acknowledged, since it is the behaviour of an equation which is simulated (in this case, PV=nRT), rather than the behaviour of an aggregation of molecules.

While this paper argues that simulation of equations is not always the most productive way to proceed, sometimes such an approach is unavoidable. Fig 3 illustrates a simulation of the Belousov reaction, in which calculation at the molecular level is very involved, so that bulk calculation is the only realistic way to proceed.
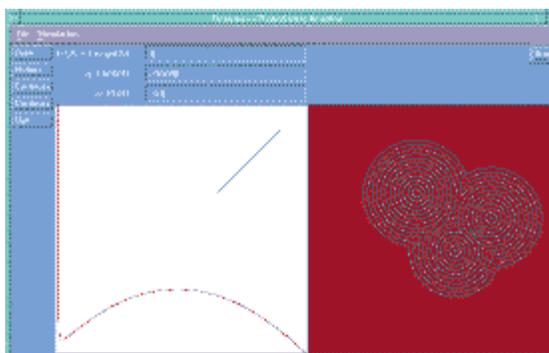

Fig 3. The development of concentric rings of concentration minima in the Belousov reaction [3]. [Full size version of this figure.](#)

3.3 Visualisation of idealised behaviour

Simulations need not be correct to be useful. From the Bohr planetary model onwards, students meet chemical models which are idealisations or approximations. On occasion it is helpful to isolate for inspection one aspect of molecular behaviour which, in a real system, cannot actually be isolated.

Molecular vibration provides an example. Even molecules of modest size have many modes of vibration (according to the 3n-5 rule for linear molecules, or 3n-6 for non-linear molecules, where n is the number of atoms in the molecule). The vibrational motion which results is complex, even in quite simple molecules (Fig. 4).
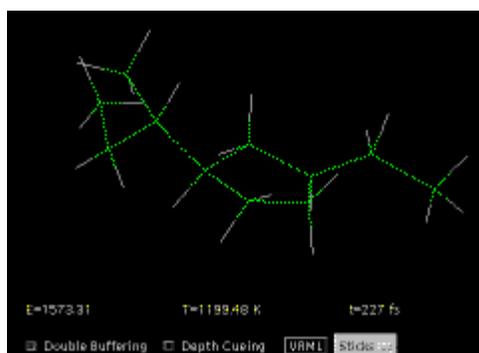

Fig. 4. A vibrating molecule displayed by a Java applet. [4] Full size version of this figure.

In any molecule all vibrations are active (though not usually excited) at room temperature, because of zero-point energy. A scientifically accurate depiction of a vibrating molecule shows all atoms moving in what appears to be chaotic motion. The amplitudes of vibration are small (of the order a few percent of the equilibrium bond lengths). The combination of these small amplitudes with the many simultaneous vibrations makes it impossible to divorce the vibration of a single segment of the molecule from vibrations of the whole.

When students meet normal modes and characteristic frequencies, it is helpful to discuss the vibrations of functional groups as though a group were capable of vibrating in isolation from the rest of the molecule. This can be illustrated using an idealised model in which only one mode is active. This qualitative picture - though unrealistic - both clarifies the concept of characteristic functional group frequencies, and can be used to show how one specific vibration affects the symmetry of the molecule, thus leading into selection rules. What is essentially a scientifically unjustifiable simulation can in this way be of value.

3.4 Simulation at the molecular level

Simulations at the molecular level - that is, those in which each molecule in the simulation is treated individually - encapsulate all simulations which describe the behaviour of material in bulk, since bulk behaviour is the aggregation of the behaviour of the constituent particles.

Such simulations are computationally demanding, and represent the practical limit of simulations at present, since a further dissection into the movement of electrons and nuclei leads to intractable calculations. As an example of such a simulation, Fig 5 shows the establishment of a concentration gradient for argon atoms above a solid surface under the influence of (very strong!) gravity.
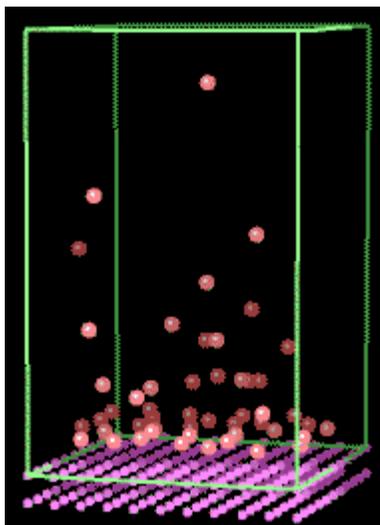
Fig. 5. Simulation of the movement of gas phase argon atoms above a solid surface. [5] [Full size version of this figure.](#)

In this simulation every atom (both in gas phase and solid phase) is treated individually, and no "bulk" equations are used.

There are various advantages to such a simulation, which we shall shortly consider. We can note immediately that minimal assumptions are made in the calculation: we assume only that

- *collisions are elastic and that*
- *energy is a function of vertical position.*

Complex behaviour (such as the Maxwell-Boltzmann distribution of molecular speeds, or the Boltzmann variation of density with height) emerges readily from the simulation, and it is the way in which detailed physical behaviour can be shown to be the result of simple physical interactions that represents one of the most potent features of molecular-level simulation

4. Advantages of simulations.

A simulation is of course just one way of allowing students to use computers to understand science. However, simulations in general have a number of special advantages.

4.1 Visual Power

Among the most noteworthy advantage is that simulations can generate images of considerable power (Figs. 6 and 7). Such images can help students remember details in a way which equations cannot. (Many of us will remember some striking simulation or visualisation, but - to take an example at random - were any of us struck at first sight by the form of the van't Hoff Isochore?).
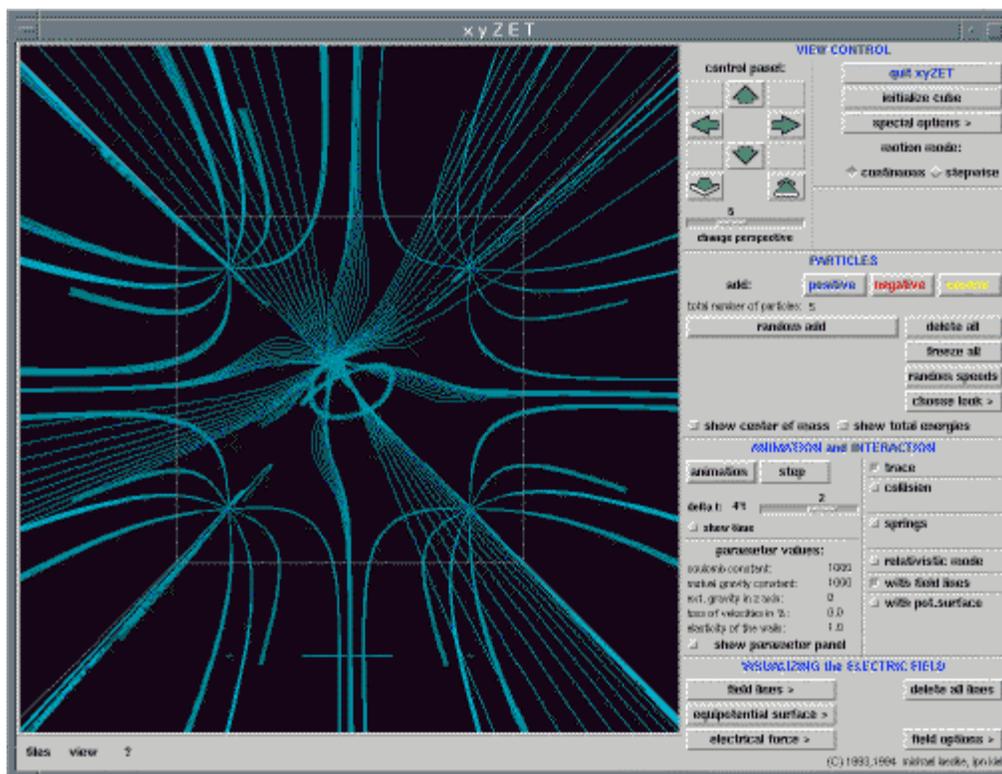
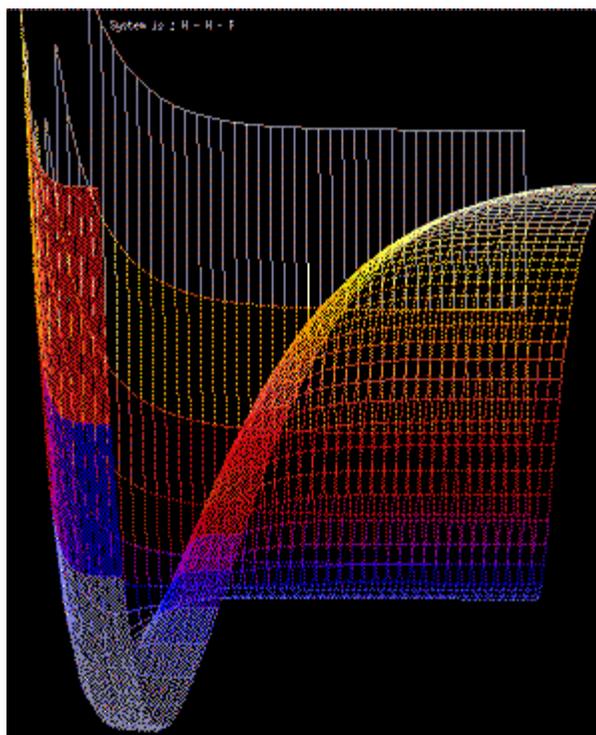*Fig. 6. The radiation field around a group of moving point charges [6]. Full size version of this figure.*

Fig. 7. The potential energy well for reaction between a hydrogen molecule and a fluorine atom [11]. Full size version of this figure.

Interactivity is also a powerful argument in favour of simulation. Users quickly become bored if they are just passive consumers of information. They learn better when they need to respond frequently to, and have control over computer software.

It should be appreciated, though, that interactivity carries with it some dangers. A conventional program

which channels all users along a pre-defined track depends on that track being chosen with care, and on it being suitable for almost every user. Interactive software by contrast presents the user with many facilities and numerous choices. This flexibility may remove from the user any sense of direction, so that they become lost within the software package. The academic objectives of the work may become unclear, and the user may wander inefficiently through attractive but meaningless exercises. Interactive software must therefore be sufficiently structured that users do not lose sight of the educational target.

The use of html wrappers and embedded Java applets can provide this essential structure, though there are of course other equally effective ways of ensuring that users are not submerged in a complex, multi-faceted simulation.

4.2 Flexibility in topic ordering

In any set of computer-mediated exercises the instructor must decide upon the most suitable order in which topics are to be presented. In mathematically-based or rule-based exercises a progression from mathematical simplicity to sophistication may be used.

Exercises might progress from point masses to masses of finite volume and eventually to molecules. This may be a justifiable course, but there is no reason why an order determined by an increase in mathematical complexity should coincide with the order which is academically most desirable. It might instead be desirable to present a comprehensive simulation initially, and gradually uncover its mathematical basis as the underlying science is studied.

4.3 Development of scientific intuition

Other, more controversial, arguments also exist in favour of simulation.

Women are under-represented in most areas of science, particularly in the physical sciences. For many people who teach at school, college or university, this is a cause of concern, and much effort has been devoted to searching for ways to increase the number of women in science.

The limited number of female science teachers and professors, and the rarity of female scientists on the television may have an effect, but there are probably other factors at work. Anecdotal evidence - drawn from observation of a group of students at Oxford - suggests that female students are often harder working than male students, but may have less "flair" for science at the university level.

By contrast, their male compatriots sometimes seem to have a greater sense of scientific "intuition". What does this mean? Suppose that, during a walk in the country or on a beach, we come across a stream blocked by a child's dam. We can assess whether it is a "good" dam (in the sense of being strong enough to hold the water back) without considering any hydrostatic or hydrodynamic equations. Indeed, the problem of whether a particular sticks, stones and mud dam is "good" would present a testing computational problem.

But how then do we assess the quality of the dam, if not by using equations? Presumably, through having built dams - or having seen them built - and in so doing, having gained practical experience of what a "good" dam looks like. We have accumulated a fund of knowledge which is ill-defined, incomplete and fuzzy, yet still useful scientifically. This is not "intuitive" knowledge in the normal sense, but a collection of experience which gives us a feel for how things behave.

Those students who possess this sort of scientific intuition have built this up from childhood, perhaps through building dams, throwing stones and falling off trees, but also - crucially - through the challenge provided by science teachers whose approach is first to get their students to understand the physical principles of science, and only later to learn the rules, facts and equations.

Scientific intuition may help when students have to evolve appropriate ways to tackle a novel

problem, or rationalise a newly-discovered equation, trying to understand why it has some particular form. Inasmuch as simulations allow the user to experiment and interact with the material world, they will stimulate the development of this intuition. Simulations thus teach not only a single topic, but provide also broader scientific experience.

5. Advantages of mathematically-lean simulations

Much science depends upon the interpretation and use of equations. Simulations of equations have a role to play, but the understanding which students gain from them is different from that which they derive from molecular simulations.

Of course, all simulations make use of equations and rules. Without a prescription to determine how objects appear on the computer screen and interact with each other, there could be no simulation. In a mathematically-lean simulation, these equations and rules are kept to a minimum.

For example, returning to PV=nRT , a molecular simulation of gases requires us only to assume that gas molecules move, that they do not interact except during collisions, and that collisions are elastic (no energy loss). If we wish to introduce non-ideality, we can allow the molecules to have non-zero size, or interact with a Morse or a 6-12 potential. Notice that our assumptions are physically based. That is, we are assuming properties of the components which make up the physical system, not assuming equations which describe observed behaviour, such as the van der Waals equation. This is the key idea behind mathematically-lean simulations.

We have noted in section 3.4 that, from simple assumptions, complex behaviour can be derived. We now consider some further advantages of molecular-level simulation.

5.1 Visualisation of behaviour "hidden" in equations

Equations exist which accurately describe a huge range of phenomena. Science attempts to identify those aspects of the natural world which behave in a predictable fashion, and to rationalise them by constructing equations which describe that behaviour.

Although these global equations encapsulate the behaviour of the system which they describe, it may be hard for students to extract from them that detailed behaviour.

Let us consider an example from mechanics. Fig 8 shows a beam, hinged at its base, falling under gravity.
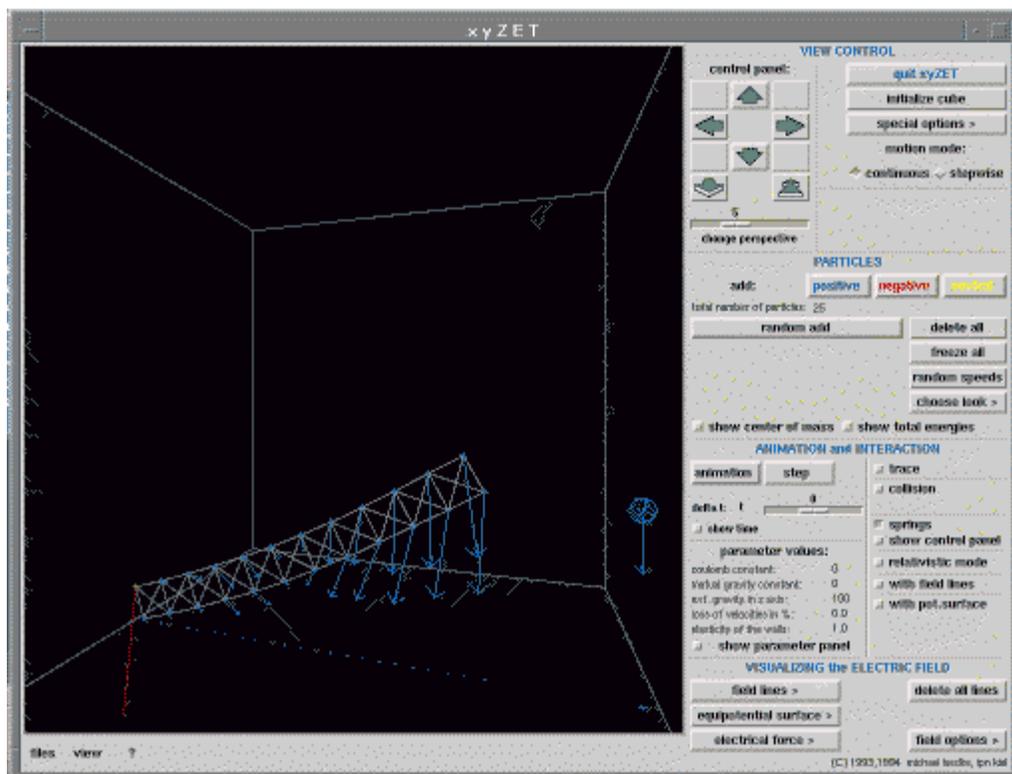
Fig. 8. A frictionless hinged beam falling under gravity. [6] [Full size version of this figure.](#)

> *The beam is constructed of a number of masses, connected by springs which obey Hooke's law. Although the edges of the beam are initially straight, it is apparent that gravity causes the beam to bend slightly.*
>
> *Let us allow the beam to fall; how will it strike the floor? There are three options:*
>
> - *the end of the beam furthest from the hinge will strike the floor first;*
> - *the beam will have recovered its shape and be exactly linear when it strikes the floor, so that all points along the lower edge will make contact simultaneously;*
> - *the bending shown in the figure will remain, as gravity is constant, so there will be a "rolling collision" in which contact is made first by points closest to the hinge, and contact spreads along the beam towards the end.*
>
> *Which of these possibilities is correct? The equation which describes the behaviour of a such a beam of connected masses would tell us, but doubtless this equation is complex, and it would be no simple matter to determine from it how the shape of the beam varies. It is simpler to run a simulation, the results of which are shown in figures 9a to 9e below.*
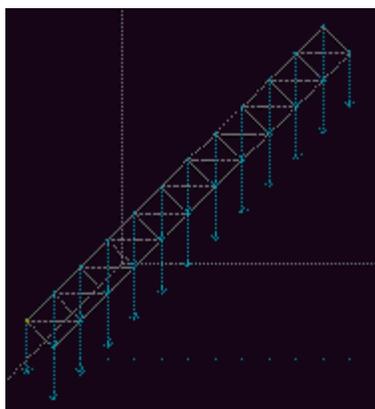
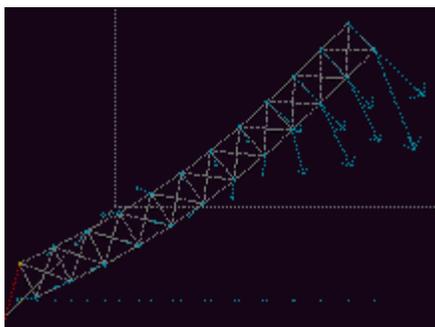*Fig 9a. The initial configuration of the beam. [Full size version of this figure.](#)*

Fig. 9b. Considerable curvature is apparent shortly after the beam begins to fall. [Full size version of this figure.](#)
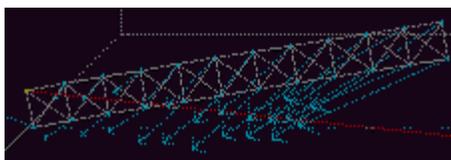

Fig. 9c. The combination of gravity and the unequal stretching of the sides of the beam, shown in figure 9b, are forcing it to straighten. [Full size version of this figure.](#)
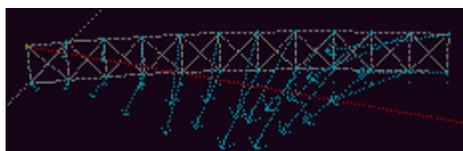

Fig. 9d. The curvature of the beam has been over-corrected, and the beam is now nearly horizontal. [Full size version of this figure.](#)
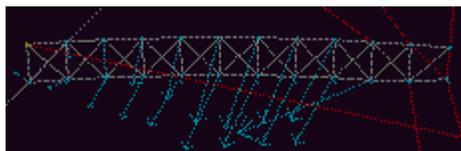

Fig. 9e. At the point of impact, crushing of the right-hand end of the beam is apparent. [Full size version of this figure.](#)

That the first point of contact is furthest from the hinge surprises many people. The simulation shows in a graphic and simple way what the complexity of equations would largely hide.

5.2 Freedom in variable adjustment

Simulations whose role is to display the behaviour of equations usually allow the user to specify only the values of parameters which appear in the equation. There is little point in allowing the user to set other parameters, which do not affect the calculation.

In a molecular-level calculation, the few equations which underlie the calculation are usually hidden from the user, and often contain "within them" further equations (section 5.3). The user can then be permitted to vary a wide range of parameters to investigate whether or not they influence the system.

For example, the screen shot in Fig 10 is taken from a CoLoS demonstration program dealing with fractal growth in solution. It shows the semi-random motion of copper ions in a solution in which three electrodes at an equal potential have been placed. The user can investigate how the rate of growth and the form of copper fractals depends upon temperature, solution viscosity, concentration, potential difference and other factors. By making minimal assumptions, but providing maximum flexibility, it is possible to investigate combinations of parameters which the software designer might never have considered. By calculating the movement and interaction of ions at the most basic level, rather than using equations which describe fractal deposition directly, the user has considerable freedom to discover how fractal growth is influenced by the various parameters.
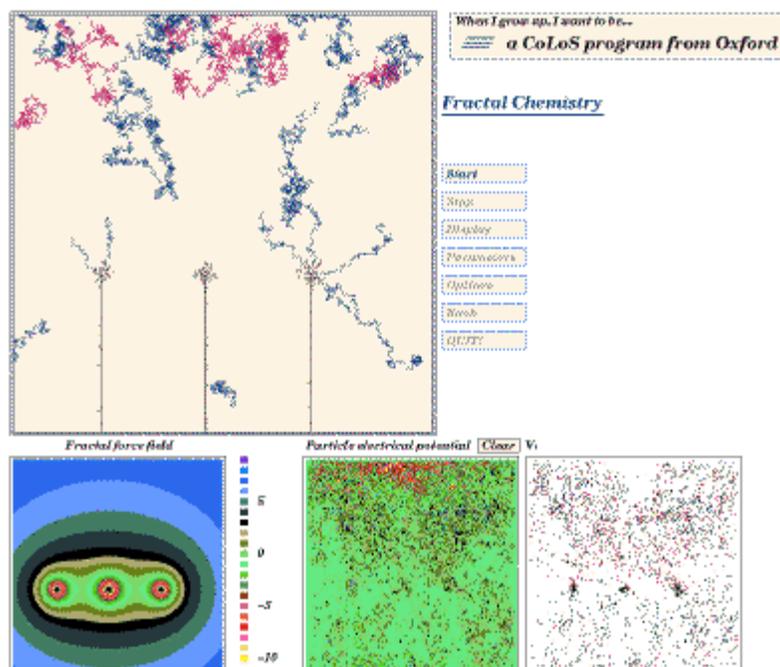

Fig. 10. The development of fractal growth at electrodes arising from the movement of copper ions in solution [7]. Full size version of this figure.

5.3 Avoidance of mathematical complexity

A strong mathematical background is an asset to an honours chemist. Nevertheless, many students find the language of mathematics difficult or obscure. Simulations provide a means by which the mathematics can be made less intimidating and the chemistry more palatable and understandable.

Students can, for example, learn qualitatively about the relationships between the temperature of an assembly of molecules and the vapour pressure without first (or ever!) meeting the Clausius-Clapeyron equation. They can develop an understanding of heat capacity, or colligative properties, from simulations such as that shown in Fig 11.
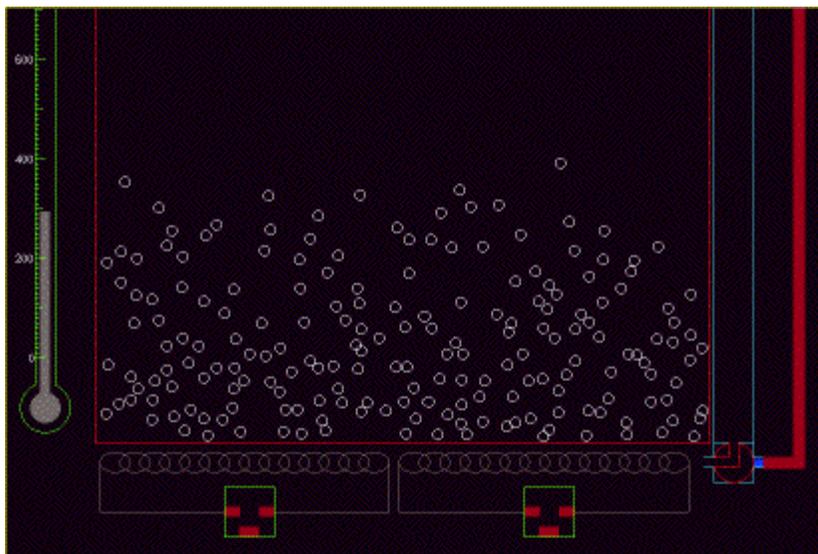
Fig 11. A display of a cold gas about to condense to a liquid; pairs of molecules have already begun to form [8]. Full size version of this figure.

The Clausius-Clapeyron equation expresses the dependence of vapour pressure of a volatile solid or liquid on temperature. It contains differentials (or logs in the integrated form). It is an important equation in thermodynamics, but though it is not particularly complex, it still presents students with difficulties, and they may not appreciate that vapour pressure rises approximately exponentially with temperature. A simulation of a collection of molecules, assuming a simple interaction potential, will allow students quickly to investigate the dependence of vapour pressure on temperature.

The experimental behaviour is not "built-into" the simulation - indeed thermodynamic properties are defined only for bulk systems, and the simulation is of individual molecules. Nevertheless, with a sufficiently large number of molecules, the user can measure vapour pressure and investigate P/T relationships.

In a two phase (gas/solid) system, one can illustrate the principles of Langmuir or BET behaviour using again simple interaction potentials. (Fig 12).
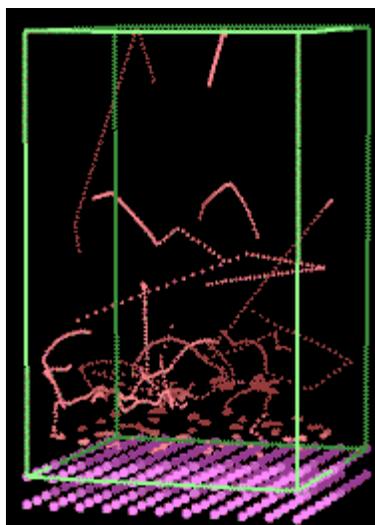

Fig. 12 Simulation of argon above a charcoal surface. The movement of the argon atoms is illustrated by the tracks. [5]. Full size version of this figure.

This leads us to a further point of crucial importance:- molecular simulations also simulate what we do not see.

This sounds like nonsense. What can it mean? Although the primary role of the simulation shown in Fig 12 might be to allow students to study adsorption on solids, further physical phenomena may be investigated using the same model. For example, the molecular tracks in Fig 12 hint that the molecules adsorbed on the surface are not actually stationary, but move around a little. This behaviour is not "what we are looking for" if we are using the simulation to study Langmuir adsorption; indeed, this movement across the surface could not be observed if the simulation was based solely on the Langmuir equation. In this sense then, the molecular level simulation may include within it behaviour we are not looking for (and may not even notice). The sudden discovery by a student of quite unexpected phenomena, such as movement of adsorbed molecules, is both a stimulant to learning, and often a source of delight to the student.

5.4 Insight into the physical origin of equations

Let us return to the ideal gas law. A simulation whose function was to allow students to understand the behaviour of ideal gases could be visualised either at the molecular level, or through direct interpretation of the ideal gas equation.

Most students need to memorise and be able to regurgitate equations in an exam. But they need also to appreciate the physical origin of gas pressure, that is, the bombardment of the walls of a container by molecules. There is more fundamental understanding to be gained by realising that, if the volume is restricted the number of collisions of molecules with the walls per second must increase, than by simply learning that P depends inversely on V.
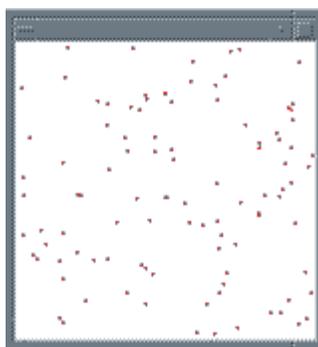
Fig. 13 A simple simulation of gas molecules confined to a small container. [9]. Full size version of this figure.

5.5 Revelation of complex behaviour from simple equations

It is clear that complex behaviour can often result from simple equations. The growth of fractals in solution, for example, can be simulated using a random walk model in which ions in solution are attracted to, and deposited on an electrode.

With the simplest of equations, quite complex behaviour can be modelled. Fig 14 shows the symmetrical fractal obtained when a centro-symmetric field is provided by an electrode in a dilute solution.
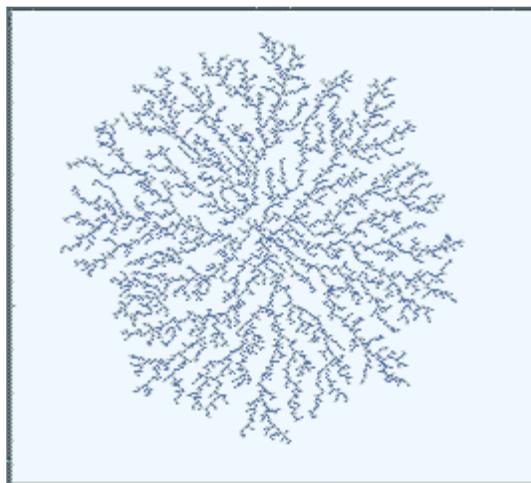
Fig. 14. Fractal growth resulting from a small centro-symmetric field applied to an electrode in a dilute solution of copper ions [7]. Full size version of this figure.
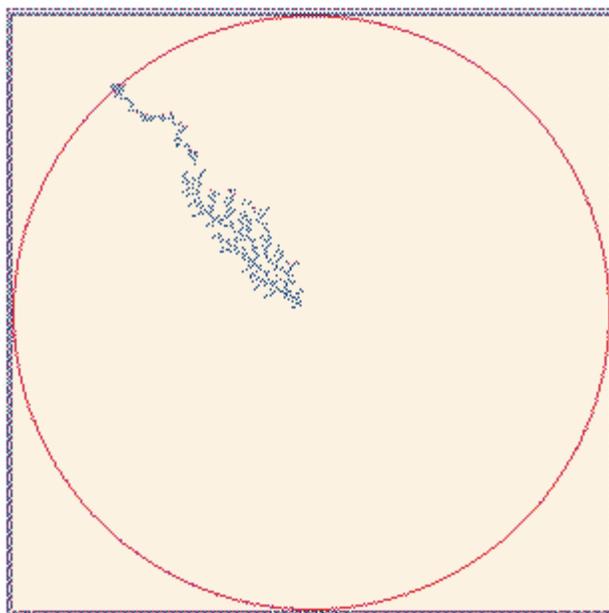

Fig. 15. Fractal growth by deposition of ions released from a point source. Full size version of this figure.

Fig 15 shows the fractal arising when the solution contains only a small concentration of copper ions, and fresh copper to replace that deposited at the electrode is available only at a single point on the northwest side of the ring. The figure shows the path of a typical copper ion as it moves towards the growing fractal. It is easy to appreciate that, the stronger the electric field produced by the electrode, the more linear and less fractal in appearance the copper deposit becomes.

Fig 16 shows a fractal that results when we assume that the central electrode provides a potential concentrated along the Cartesian axes. The resulting 4-fold symmetry is striking.
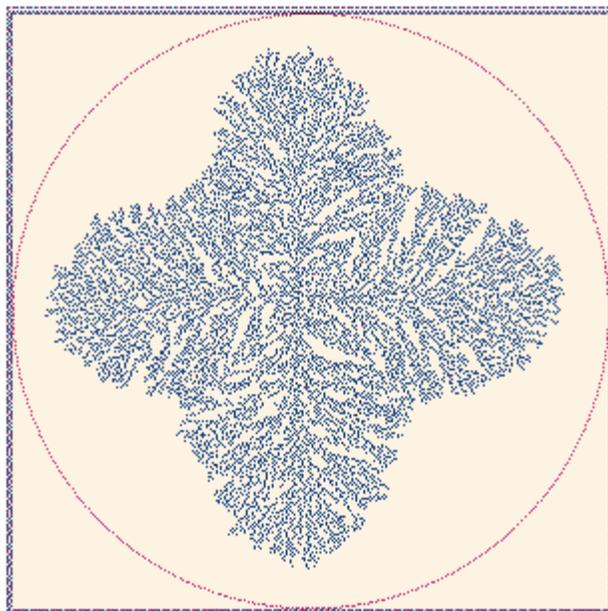
Fig. 16. A fractal growth generated by an electrode which provides a field aligned along the x-y axes. [Full size version of this figure.](#)

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6 Comment

It would be unreasonable to expect simulation to sweep away the need for students to be able to understand and use equations. However, an appreciation of the physical world, promoted by interactive simulations, can lay the basis for a deeper knowledge of the raft of equations which chemists must know.

A chemist who understands only equations is really a mathematician. A chemist who has a feel for the way in which molecules behave, and who thinks that he or she knows what molecules want to do is a scientist.

Appendix A: The CoLoS group

Several of the screen shots in this paper are from work by members of CoLoS. CoLoS brings together scientists from many disciplines in a variety of different countries, who share an interest in the effective use of the computer in understanding science.

Readers who share this interest may like to know that CoLoS is offering prizes for innovative scientific software available through the Internet. First prize is one thousand dollars, travel from anywhere in the world to a CoLoS conference, and day-to-day expenses for attendance at the conference.

The closing date for applications is expected to be February 1st 1998.

- *[Further details of the prizes.](#)*

- *[Further details of CoLoS.](#)*

References and background information.

1. Taken from an [experiment in NMR spectroscopy](#) under development in the Physical and Theoretical Chemistry Laboratory at Oxford University.

2. Taken from an on-line experiment in error analysis under development in the Physical and Theoretical Chemistry Laboratory at Oxford University. Data are generated by [connecting to an optical rig](#) through the Internet.

3. Data from Computer simulation of the Belousov-Zhabotinsky reaction, Chi Ho Lam, Chemistry Part II thesis, Oxford, 1996

4. A [java applet](#) showing a vibrating molecule: http://www.pc.chemie.th-darmstadt.de/java/

5. Screen shot from a simulation written using X, C and Motif. Pete Bennett, Mathematical modelling and computer simulation of aspects of surface science, Chemistry Part II thesis, Oxford University, date.

6. An experiment under the control of the [CoLoS](#) program [xyzet](#), developed at Kiel University, Germany.

7. Screen shot from an experimental [CoLoS](#) program on fractal growth, developed at Oxford University.

8. A screen shot from a [CoLoS](#) demonstration program on the thermodynamics of simple liquids. Andy Armstrong, Computational modelling and simulation of molecular phase dynamics. Chemistry Part II thesis, Oxford University, June 1995.

9. A screen shot for a simple simulation of gas-phase molecules.

10. The virtual lab in Oxford is at [http://neon.chemistry.ox.ac.uk](#)

11. An interactive computer simulation of collisional potential surfaces, Russell Strevens, Chemistry Part II thesis, Oxford University, England, 1995