# Nanotechnology Applications Guide

**accelrys**

# Introduction

'Nanotechnology is about making things, whether it be making things that are smaller, faster, or stronger, making something completely new or with additional properties, or making machines that will lead to new manufacturing paradigms' [1].

Three factors define nanotechnolgy: small size, new properties, and the integration of the technology in to materials and devices. Nanotechnology covers a broad range of science, drawing concepts, knowledge and expertise, skills, and materials from all the three classical sciences, physics, chemistry, and biology.

From an economic point of view the potential of nanotechnology is clearly vast, with the drive to be smaller, faster, lower power and cheaper. As size is reduced, overheads (materials, energy, factory and manpower requirements) are all reduced.

Recent nanotechnology products poised for near-term market realization include a molecule-sized electronic switch, improved sun cream, and a fullerene-based cancer treatment. In medicine nanoceramics are currently being used as bone replacement agents. These ceramics show outstanding osteoblast (cells that form bone) proliferation and mechanical properties [2].

One obvious area where nanotechnology has vast potential is in computing, in particular the ever-shrinking computer chip. 1965 saw the birth of Moore's law, named after Gordon Moore of Intel, who stated that the number of transistors per integrated circuit would double every 18 months [3]. Turning this on its head, the size of chips would half every 18 months. This has held true since 1965, but now, with chip sizes expected to approach the atomistic scale in the next decade or so, the need for nanotechnology to shrink the chips ever more is clearly obvious with atom-scaled circuits required.

And, of course, atom-scaled chips would go in atom-scaled computers, constructed and assembled by other atom-scaled devices. IBM is currently undertaking pioneering work in this respect with a quantum mirage of cobalt atoms forming a potential data transfer tool. HP recently reported fabrication of nanoscale molecular-electronic devices comprising a single molecular monolayer of bistable rotaxanes sandwiched between two 40-nm metal electrodes [4].

So where now for this exciting science? How to go about the exploration of the vast range of scientific and technological opportunities offered by the advances of controlling materials at the nanoscale? Challenges the researcher is faced with include the selection and screening of potentially large libraries of molecules and materials, the fact that 'almost any' molecule can be synthesized but synthesis can still be very costly, and the unambiguous interpretation of experimental information at the nanoscale level, where quantum effects are often important.

Today's computing power is proving invaluable in the research behind the miniaturization. Computer molecular modeling and simulation is being used in the drive to advance this exciting and cutting edge scientific field, enabling scientists to visualize and predict behavior at the nanoscale. And with the major cost vs. performance barrier being blown away by today's rapid computing developments, these techniques are set to become widespread throughout all research and development, not just in nanotechnology.

Computational tools enable scientists to simulate reactions and study the properties and interactions of molecules and materials at a computer interface. Once the preserve of computer experts, the widespread availability and use of personal computers, coupled with the almost exponential increase in available hardware power, has resulted in these techniques becoming a widespread research tool, resulting in many advantages.

The tools can be used to complement, direct, and refine and, in some cases, even replace experimentation. The need to use 'real' chemicals can be reduced, not only saving resources but also lessening researchers' exposure to toxic chemicals, so called 'greener' science. Non-starter reactions can be identified before valuable laboratory time and resources are wasted. Reactions that would have been difficult to study experimentally, for

example because of the time taken to complete or the requirement of toxic chemicals, can be studied with ease on the computer, with mechanistic and chemical insight obtained.

Michael York of Continental Tire North America explains the scientific advantages gained by using computational chemistry, "Experimentation takes manpower, chemicals, equipment, energy, and time. Computational chemistry allows one operator to run multiple chemical reactions 24 hours a day."

Michael York continues, "By performing the 'experiments' on the computer, the chemist can eliminate non-productive reaction possibilities and narrow the scope of probable laboratory successes. The end result is a major reduction in laboratory costs (such as materials, energy, and equipment) and manhours." See reference [5].

Deepak Srivastava [6], a leading computational nanotechnology expert, describes the advantages of these computational techniques in nanotechnology, "Theory, modeling, and simulations have provided and will continue to provide insights into what to expect next and verification/explanation of what has been done or observed experimentally. For nanoscale systems, simulations and theory in fact have provided novel properties that has led to new designs, materials, and systems for nanotechnology applications."

Srivastava references carbon nanotubes as an example of where these state-of-the-art tools are being used in nanotechnology, "For example carbon nanotubes applications in molecular electronics or computers were predicted first by theory and simulations, the experiments are now following up to fabricate and conceptualize new devices based on those simulations" he states.

The following section describes how computational techniques have been used to tackle real-life research and development challenges, in applications ranging from nanocomposites to sensors and nanoscale drug delivery systems.

## References

[1] CMP Cientifica 'Nanotech – the tiny revolution', July 2002.

[2] www.rpi.edu/dept/materials/COURSES/NANO/dulgar/nano_index.html

[3] www.intel.com/research/silicon/mooreslaw.htm

[4] Yong Chen, Douglas A. A. Ohlberg, Xuema Li, Duncan R. Stewart, R. Stanley Williams, Jan O. Jeppesen, Kent A. Nielsen, J. Fraser Stoddart, Deirdre L. Olynick, and Erik Anderson, *Appl. Phys. Lett.*, 2003, **82**, 1610.

[5] www.accelrys.com/cases/ctire.html

[6] people.nas.nasa.gov/~deepak/home.html

# Materials Studio Evaluation CD

Most of the tools discussed in this guide are operated within MS Modeling, Materials Studio's PC-based modeling and simulation environment. To obtain an evaluation copy of Materials Studio, please get in touch with Accelrys via www.accelrys.com/contact/.

# Nanotechnology Modeling Applications

## *Nanomaterials*

Carbon nanotubes have recently received increased interest for industrial applications. For example, a nanoscale thermometer has recently been reported by Japanese researchers [1]. They made a nanothermometer by filling a carbon nanotube with liquid gallium. The new device works in air, unlike previous models, which only operated in vacuum. The thermometer, which is less than 150 nanometres in diameter, could find use in a range of micro-environmental applications.

The electronic properties of nanotubes depend on their atomic structure and more precisely on the manner in which the graphene sheet is wrapped to form a nanotube. Nanotubes can be metallic, semiconducting with a very small energy gap (a few meV), or semiconducting with a moderate energy gap (few tenths of eV). Experiments probing the density of states have confirmed these predictions and conductivity measurements on single nanotubes have shown rectification effects for some nanotubes and ohmic conductance for others. These properties suggest that nanotubes could lead to a new generation of nanoscopic electronic devices.

All the potential applications call for a thorough understanding of the electronic structure of nanotubes. Nanotubes contain a large number of atoms (several hundreds) and sophisticated numerical tools are required for their study.

[1] Y Gao *et al.*, *Appl. Phys. Lett.*, 2003, **83**, 2913.

## Nanotubes: Understanding the Properties of Carbon and Boron-nitride Nanotubes

http://www.accelrys.com/cases/nanotubes5.html

### Industry sectors

**Electronics – General**
**Nanotechnology - Nanodevices**

### Organizations

**Airforce Base Research Laboratory (Wrights-Patterson)**
**Rice University, Houston, TX**

MS Modeling's quantum mechanical tools CASTEP and DMol$^3$ have been used to study the properties (structural, mechanical, vibrational, and electronic) of carbon and boron-nitride nanotubes.

If nanotube technology is to reach its full commercial potential, the ability to control and fine-tune properties such as these will be vital to manufacture of tailored devices. Carbon nanotubes are long, thin cylinders of bound carbon atoms, about 10 000 times thinner than a human hair, and can be single- or multi-walled. They have remarkable electronic and mechanical properties that depend on atomic structure and more precisely on the manner in which the graphene sheet is wrapped to form a nanotube (chirality). They can be either metallic or semiconducting.

 Carbon nanotubes are a hot research area owing to their novel properties, fuelled by experimental breakthroughs that have led to realistic possibilities of using them in a host of commercial nanoelectronic applications: field emission-based flat panel displays, novel semiconducting devices in microelectronics, hydrogen storage devices, chemical sensors, and most recently in ultra-sensitive electromechanical sensors. As a result they represent a real-life application of nanotechnology.

In addition, their high strength extends their potential application sphere to include composite reinforced materials.

Boron-nitride nanotubes also show potential for similar applications, and may even improve on the performance of carbon nanotubes; as they can tolerate heat, have a constant band-gap that is independent of tube-diameter and chirality. It has also been shown that boron-nitride coated carbon nanotubes show better field emission than non-coated ones.

Researchers at the Airforce Base Research Laboratory (Wrights-Patterson) and the Rice University, Houston, TX, used MS Modeling's density functional theory (DFT) codes CASTEP and DMol$^3$ to study and compare the properties (structural, mechanical, vibrational, and electronic) of single-walled carbon and boron-nitride nanotubes, looking at the effects (if any) of inter-nanotube coupling.

The studies concluded:

- While Resonant Raman spectroscopy has become a key experimental technique for studying the optical and electronic properties in nanotubes, theory and models are important for predictive prupoes as well as detailed analysis of observations. This work demonstrates various ways in which DFT methods can impact on this, including (a) testing and validation of simpler model relationship between nanotube structure and RBM, (b) quantifying the effect of tube interactions, and thereby the difference between single and multiple tube materials, (c) prediction of RBMs beyond the case of carbon nanotubes, here including boron-nitride nanotubes. For example, the study reveals that a model proposed by Bachilo et al. for predicting RBMs of isolated semiconducting tubes does not hold for large diameter tubes

- DFT methods give a detailed picture of variation in the structural, mechanical, and electonic properties of both C and BN nanotubes as a function of their radius, chirality, and interactions. It reveals features with potentially significant impact for applications. The location of the van Hove singularity, which for example impacts optical transitions, was studied, revealing that tube interactions do not always lead to an outward expansion with respect to the Fermi energy, but to an inward shift for tubes of smaller radius.

**Reference**

[1] W. W. Adams, B. Akdim, X. Duan, and R. Pachter, *Phys. Rev. B*, 2003, 67, 245404.

## Nanotubes: Further Examples

For further examples of nanotube properties determined by simulation, see http://www.ncnr.nist.gov/staff/taner/nanotube/

## Nanocomposites: Molecular Dynamics of Polymer Nanocomposites

http://www.accelrys.com/cases/nanocomposites.html

**Industry sectors**

**Chemicals**

**Organizations**

**Cornell Center for Materials Reseach http://www.ccmr.cornell.edu/**
**Emmanuel P Giannelis research group**
**epg2@cornell.edu**

Molecular Dynamics simulations using Cerius$^2$ software package were used to study the static and dynamic properties of 2:1 layered silicates ion-exchanged with alkyl-ammonium surfactants.



Figure 1: Schematic of the polymer layered silicate nanocomposite (PLSN) morphologies: (a) intercalated and (b) exfoliated [1].

Polymer-silicate nanocomposites exhibit good mechanical and thermal properties, and can be used in a variety of applications. Molecular dynamics simulations using Cerius$^2$ software package were used to study the static and dynamic properties of 2:1 layered silicates ion-exchanged with alkyl-ammonium surfactants.
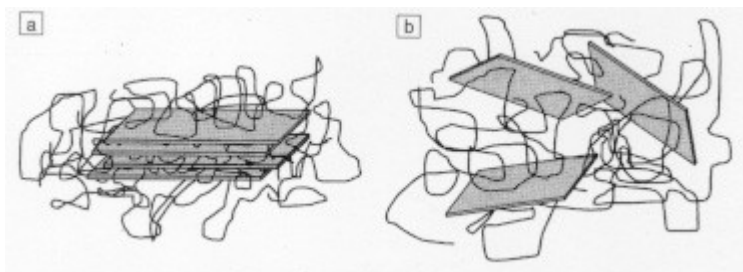
By studying the systems at the experimentally measured layer separations, computer modeling provides the structure and dynamics of the intercalated surfactant molecules, which can assist in the design of polymer-silicate nanocomposite systems.

A major challenge in developing nanocomposites for systems ranging from high-performance to commodity polymers is the lack of even simple structure-property models. Without such models, progress in nanocomposites has remained largely empirical. The large internal interfacial area between the polymer and the silicates together with the nanoscopic dimensions between nanoelements differentiates Polymer Nanocomposites (PNCs) from traditional composites and filled plastics [1].
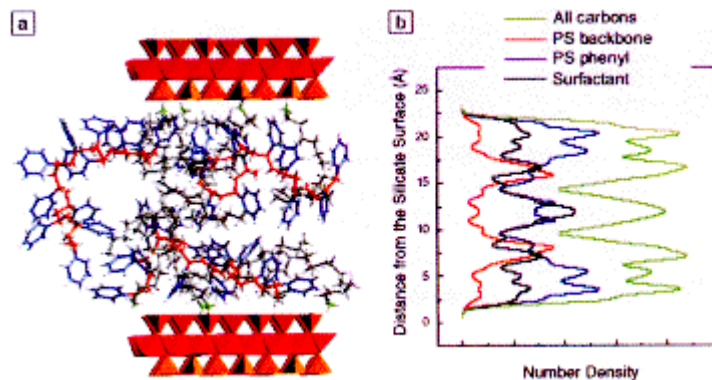


Figure 2: (a) Molecular Dynamics simulation 'snapshot' of a silicate-surfactant-polystyrene nanocomposite. (b) The corresponding ensemble-averaged, number density of carbon atoms as a function of distance. [1], [2].

Monte Carlo and molecular dynamics simulation give insight into the structure of nanocomposites on the atomic level. Figure 2 reveals that when confined to a nanoscale gap or near a surface, the polymer chains order into discrete subnanometer layers. This is useful in understanding the intercalation process and the source of some macroscopic properties such as ionic conductivity. Knowledge gained from simulations can be used to better engineer the polymer-silicate interaction.

### References

[1] R.A. Vaia and E.P. Giannelis, *MRS Bulletin*, May 2001, volume 26, No 5.
[2] D.B. Zax, D.-K. Yang, R.A. Santos, H. Hegemann, E.P. Giannelis, and E. Manias, *J. Chem. Phys.*, 2000, **112** , 2945.

## Nanostructured Blends: Binary Blend Compatibility and Nanostructure: An Atomistic and Mesoscopic Approach

http://www.accelrys.com/cases/rhodia1.html

### Industry sectors

Food, cosmetics, chemicals, plastics, detergents

### Organization

Rhodia

Researchers at Rhodia have used a combined atomistic and mesoscopic approach to study the binary blend compatibility of polyamide6 and poly(vinyl acetate) with different degrees of hydrolysis.

The compatibility of binary mixtures of polymers is an increasingly important area in materials science. Synthesis of novel polymers is expensive and can be avoided if a blend of existing species can be formulated and shown to have the desired properties. For partially miscible systems, the microphase separated structure critically determines the material's

final properties, since processing frequently 'freezes-in' these morphologies. When miscibility of copolymers is concerned, obtaining optimal copolymer compositions would require a prohibitive amount of synthesis. Molecular modeling routes to determination of the effect of composition are clearly very valuable.

The length and time scales associated with microphase separation of sparingly miscible blends are too large for traditional atomistic routes to be effective. A coarse-grained representation of the system is sought, which increases the physical dimensions and time-step of the simulation without sacrificing the chemical nature of the species involved. Accelrys offers MesoDyn [1], a dynamic algorithm, which replaces a full atomistic description of polymers by a Gaussian chain, and solves Langevin equations for density fields of the various chemical species involved. These species interact via an effective pair-potential related to the energy of mixing of the binary pairs.

The energy of mixing can in turn be determined from atomistic modeling. Using Discover molecular dynamics simulations with the COMPASS force field [2] one is able to determine cohesive energies (and solubility parameters) with high accuracy. The Flory-Huggins interaction parameter chi is a closely related value, which is used as input to MesoDyn.

Theodora Spyriouni and Caroll Vergelati at Rhodia used this combined atomistic and mesoscopic approach to study the binary blend compatibility of polyamide 6 (PA6) with poly(vinyl alcohol) (PVOH), poly(vinyl acetate) (PVAC), and partially hydrolyzed PVAC (h88-PVAC containing 88% VOH groups, and h75-PVAC containing 75% VOH groups) [3]. The Flory-Huggins interaction parameter chi, calculated for these mixtures over a wide range of compositions, showed that favorable interactions develop for PVAC with a low hydrolysis degree for a specific composition, and also for compositions rich in either component (Fig. 1).
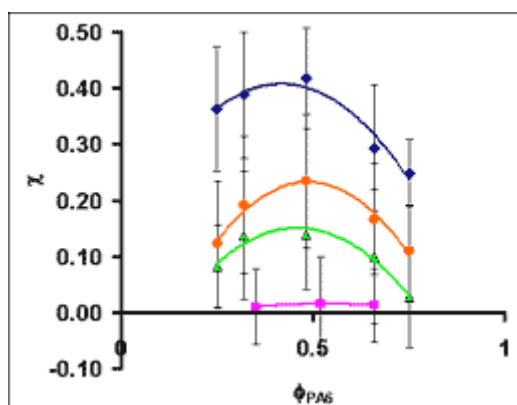


Fig. 1 Flory-Huggins interaction parameter chi as a function of the PA6 volume fraction for the binary blends of PVOH (blue, diamonds), h88-PVAC (red, dots), h75-PVAC (green, triangles), and PVAC (pink, squares).

For all mixtures, the highest chi values were observed for the equimolar composition. The PVAC/PA6 mixtures had the lowest $\chi$ value for all compositions examined, while the highest values were obtained for the PVOH/PA6 mixtures. The $\chi$ parameters for the hydrolyzed PVAC/PA6 mixtures were found between the two. Hence, on the basis of $\chi$, improved mixture compatibility is predicted in the direction of increased content of acetate groups (low hydrolysis degree) at a specific composition, and for compositions rich in either component. The influence of the degree of hydrolysis on the mixture compatibility was explained in terms of the reduced ability of the acetylated chains to form intramolecular hydrogen bonds, and in terms of the bulky side groups that resulted in more extended conformations (more open structure) of these chains.

The cohesive interactions and other atomistically derived parameters were supplied to coarse-grained simulations: MesoDyn. In these mesoscopic simulations, the dynamic evolution of phase separation of high MW blends was observed over time scales of the order of ms. Only mixtures having very small $\chi$ parameters were found to be miscible (Fig. 2). This is explained by the negligible entropy that large polymers gain upon mixing, and the consequent need for very favorable interactions in order to mix. The incompatible mixtures

gave macrophase separation with density profiles of each component varying between 0 and 1.
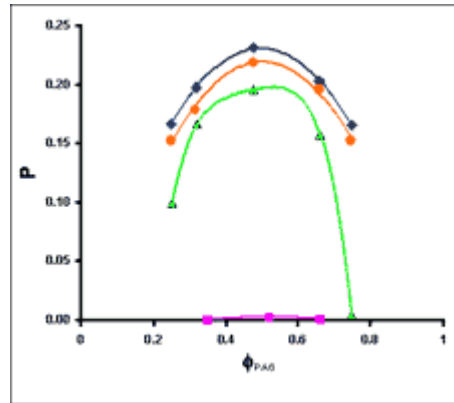


**Fig. 2 Mesocale order parameter, indicating the degree of phase separation, as a function of the PA6 volume fraction for the binary blends of PVOH (blue, diamonds), h88-PVAC (red, dots), h75-PVAC (green, triangles), and PVAC (pink, squares).**

As an example of a macroscopically separated mixture, in Figs. 3a and 3b are shown the density profiles of the h88-PVAC/PA6 mixture at a composition of 67% PA6 after 1000 and 6000 time steps (2400 and 14400 ms), respectively. Slices of the density profile at three faces of the periodic box are shown. The periodic boundary conditions are evident in these figures. The size of the periodic box is around 0.4 mm at each side.
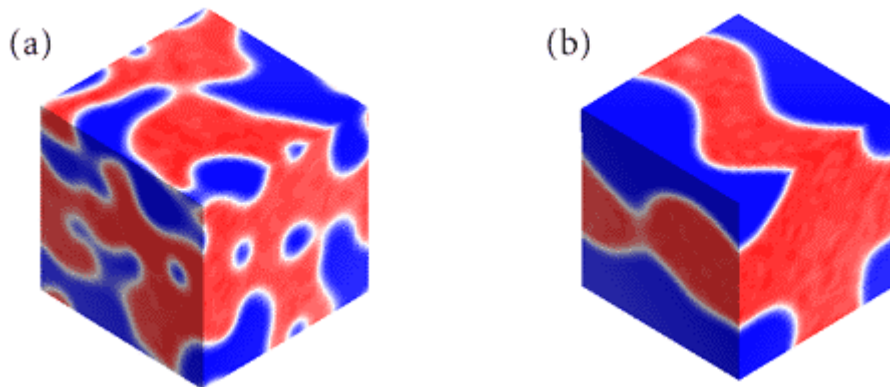


**Fig. 3 PA6 density profile slices (red color), on three sides of the periodic box, for the h88-PVAC/PA6 mixture at composition 1/2. Snapshot after (a) 1000 and (b) 6000 time steps, where the phase separation is complete. The red areas contain pure PA6 (r=1), the blue areas contain the other component, and the light shading corresponds to the interface between them.**

Figs. 4a and 4b show the evolution of the density profile of the h75-PVAC/PA6 mixture at a composition of 25% PA6, after 2000 and 15000 time steps (4800 and 36000 ms), respectively. The phases formed by the PA6 chains (red) remain dispersed in the h75-PVAC phase, even after a long simulation time (Fig. 4b). This is probably due to the low concentration of the PA6 chains in the mixture along with a small interaction parameter. The morphology in Figs. 4a and 4b is reminiscent of the nucleation and growth mechanism during polymer phase separation. The inclusion of hydrodynamics facilitates the process of diffusion and coalescence of the phases, and thus, helps the system to attain an equilibrium morphology.

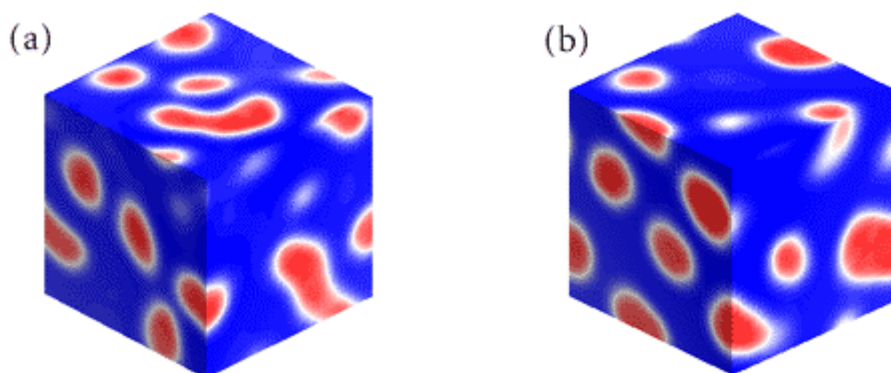**Fig. 4 PA6 density profile slices for the h75-PVAC/PA6 mixture at composition of 3/1, after (a) 2000 and (b) 15000 time steps. The notation of the colors is the same as in Fig. 3.**

All PVAC/PA6 blends and the h75-PVAC/PA6 mixture at composition 1/3 v/v were found to be miscible with order parameters close to zero. Overall, the order parameter of the phases formed were shown to decrease in the order PVOH < h88-PVAC < h75-PVAC < PVAC, for a given composition, indicating that the acetylation of the PVOH chains facilitates mixing with PA6. The above trends were found to compare well with experimental tests performed at Rhodia using transmission electron microscopy [3]. Furthermore, the dynamic evolution of the structures is obtained and can lead to novel processing schemes to achieve desired morphologies.

## Conclusion

The use of a combination of Discover®/COMPASS and MesoDyn to determine phase separation of sparingly miscible polymer blends has permitted Rhodia researchers to:

- Map out mixing behavior over the whole composition range
- Gain insight into the length scales of decomposition
- Predict the likely phase behavior of untested copolymer compositions
- Screen candidates for compatibilization of the species and interpret TEM data.

## References

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[3] T. Spyriouni and C. Vergelati, *Macromolecules*, 2001, 34, 5306.

# *Devices and Electronics*

Nanomaterials, especially nanotubes of various kinds as well as nanodots, exhibit unique combinations of properties that make them prime candidates for a range of device applications. However, conventional device models tend to fail, since at the nanoscale, electrons no longer flow through electrical conductors like rivers – conventional physics and 'water-through-a-pipe' modeling thus no longer applies. At this scale quantum mechanical modeling tools are required. For example, MS Modeling's DMol³ ideally combines the efficiency and accuracy needed for such investigations. In particular, its new multiple k point capability allows for the efficient study of infinite nanotubes and the transition state searcher facilitates the study of surface chemistry which is known to modify the conductance and field emission properties. Accuracy and efficiency can be conveniently tuned by using a real space cut-off radius allowing for simulations of very large structures.

The case studies below demonstrate how these tools are applied in some topical areas of device and nano-electronics development.

## Opto-electronics: Oxygen Manipulation of the Structural and Optoelectronic Properties of Silicon Nanodots

http://www.accelrys.com/cases/nanodots.html

### Industry sectors

**Electronics – General**
**Nanotechnology - Nanodevices**

### Organization

**University of Modena and Regio Emilia, Italy**

Researchers have used MS Modeling's CASTEP to study the role of oxygen on the structural and optoelectronic properties of silicon nanodots.

Such an understanding will enable these properties to be manipulated, leading to commercially viable nanoscale solid-state lighting devices - a major commercial application of nanotechnology.

Nanodots, also known as quantum dots, consist of 100s-1000s of atoms of inorganic semiconductor nanoparticles and are approximately one billionth of a meter in size. Developed in the mid-1980s for optoelectronic applications, they have interesting structural, electronic, and optical properties - they strongly absorb light in the near UV range and re-emit visible light that has its color determined by both the nanodot size and surface chemistry. And as the size of nanodots can be controlled during synthesis with nanoscale precision, so the optical properties can be manipulated. In addition, nanodots have a longer life than organic fluorophores, and have a broad excitation spectrum. These factors combined make the use of quantum dots as light-emitting phosphors a strong candidate for a major application of nanotechnology in the future [1].

Silicon nanodots have, in particular, have emerged over the last 10 years as a hot area of research due to the fact that a reduction in size of this semiconducting material to the nanometer scale dramatically alters their physical properties. In addition, the 1990 discovery that porous silicon exhibits photoluminescence properties, has led to a flurry of research activity, with commercially viable solid-state lighting devices made from Si nanostructures seemingly within reach [2].

As porous silicon reacts with the atmosphere, leading to major structural (and thus optical properties change), the theoretical role of different passivation species (to passivate is to coat (a semiconductor, for example) with an oxide layer to protect against contamination and increase electrical stability) must be fully understood.

With the knowledge that silicon nanocrystals dispersed in $SiO_2$ show an optical gain [3] researchers at the University of Modena and Regio Emilia, Italy, used MS Modeling's CASTEP to study the role of passivating oxygen on the structural and optoelectronic properties of silicon nanodots [4,5,6].

Marcello Luppi and Stefano Ossicini used denisty functional theory (DFT) to investigate:

- The changes in the optoelectronic properties when O is absorbed onto hydrogenated Si nanocrystal

- The different role played by single and double Si–O bonds

- How a $SiO_2$ matrix influences the physical properties of a Si nanocrystal.

Using CASTEP, the scientists showed:

- In hydrogen covered Si nanocrystals single-bonded oxygen atoms lead to small variations in the electronic properties yet large changes in structure

- However, double-bonded oxygen atoms lead to small geometry variations yet a large energy gap reduction, explaining the huge photoluminescence red shift observed in high porosity silicon after oxygen exposure.

The studies on Si nanocrystals embedded in a $SiO_2$ matrix revealed:

- The prescence of the nanocrystals only slightly deforms the $SiO_2$ cage determining the formation of an interface region of stressed SiO2 between the nanocrystals and the matrix

- New electronic states originate in the $SiO_2$ band gap

- Both nanocrystal Si atoms and interface O atoms affect optical properties.
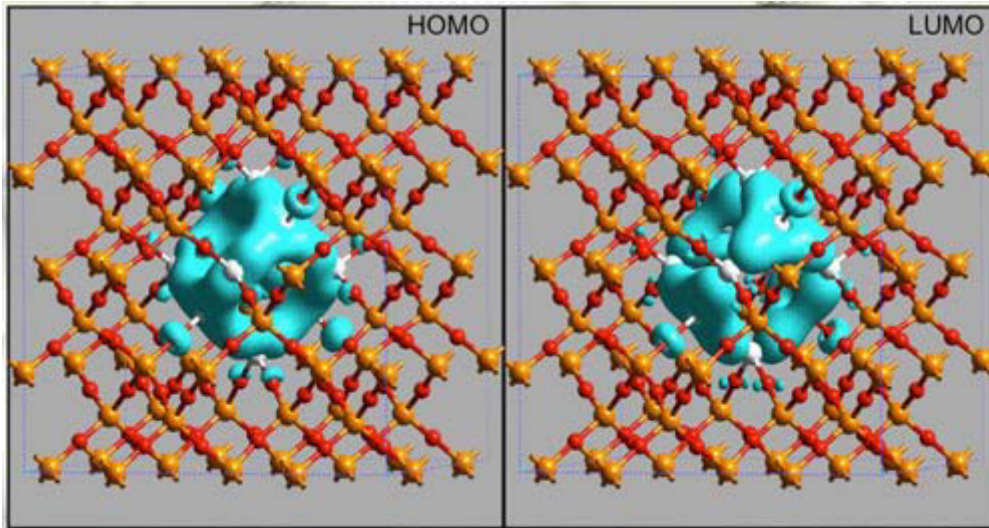


The HOMO and LUMO isosurfaces at fixed value show that the distribution is totally confined in the Si NC region with some weight on the interface O atoms. These dot-related states originate strong absorption features in the optical region. These features are entirely new and can be at the origin of the photoluminescence observed in the red optical region for Si nanocrystals immersed in a $SiO_2$ cage.

These findings help to explain experimental optical property observations, and should lead to the fine tuning of nanodot optical properties - paving the way to commercially viable solid-state lighting devices based on nanodot technology.

Dr Marcello Luppi comments, "The use of CASTEP enabled us to perform a first principle study on semiconductor nanodots embedded in an insulator host matrix in which for the first time the whole system has been geometrically optimized. Thanks to the performance of the code we were able to handle hundreds of atoms and to study the electronic and optical properties of the system in a very accurate and efficient way. The graphic user interface was the perfect tool for drawing our models and for analyzing the results".

### References

[1] See www.sandia.gov/news-center/news-releases/2003/elect-semi-sensors/quantum.html
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[6] M. Luppi and S. Ossicini, *J. Appl. Phys.*, 2003, **94**, 2130.

# Electromechanical: Application of Carbon Nanotubes as Electromechanical Sensors

http://www.accelrys.com/cases/nanotubes3.html

**Industry sectors**

**Electronics**

**Organization**

**NASA Ames Research Center**

Researchers have used Accelrys' DMol$^3$ to examine bonding differences between two types of nanotube deformation: (1) bending, and (2) pushing with atomically sharp AFM tips.

Such an understanding should lead to a better design of ultrasensitive sensors that could detect even the smallest mechanical perturbations, and also the design of new types of strain gauges based on carbon nanotubes.
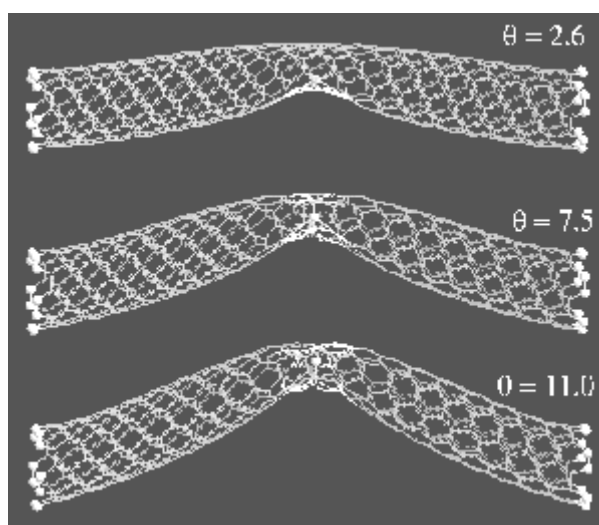


Structure of a (5, 5) tube (fixed ends) when a tip-constrained atom in the middle (in ball representation) is displaced to various tip-deformation angles. At a critical angle of 7.5°, a top atom forms a bond with the tip-constrained atom leading to sp$^3$ coordination. Larger deformation leads to a complex defect with dangling bonds

Carbon nanotubes have recently turned into a hot area of research activity, fuelled by experimental breakthroughs that have led to realistic possibilities of using them in a host of commercial applications: Field emission-based flat panel displays, novel semiconducting devices in microelectronics, hydrogen storage devices, chemical sensors, and most recently in ultra-sensitive electromechanical sensors.

An important experiment with regards to developing electrochemical sensors involved a metallic nanotube suspended over a 600 nm long trench. When the middle part of such a suspended nanotube was pushed with the tip of an atomic force microscope (AFM), the conductivity was found to decrease by almost two orders of magnitude [1]. This drop in conductance was much higher than previously computationally predicted values for tubes bent under mechanical duress.

The DFT code DMol$^3$ in combination with classical molecular dynamics and the Universal Forcefield (UFF) has been used to examine bonding differences between two types of nanotube deformation: (1) bending, and (2) pushing with atomically sharp AFM tips. Bent tubes maintain an all-hexagonal network up to large angles. AFM-probed tubes, in contrast, display a more complex behavior, which depends on the details of how the AFM-tip is represented in the simulations [2, 3].

More recently, the electrical response of carbon nanotubes was computed under the two types of deformation. It was shown that bent tubes do not display large changes in conductance. In contrast, AFM-pushing led to a net tensile stretching of the tube [3], which for zigzag tubes opened up an energy gap at the Fermi level, and led to a significant drop in the room-temperature electrical conductance [4].

This work has prompted nanotechnologists to explore the design of new types of strain gauges and pressure sensors based on carbon nanotubes.

Ongoing collaboration with the nanotechnology group of NASA Ames Research Center, Moffet Field, USA, is expected to yield more interesting results in the near future. The work has prompted nanotechnologists to explore the design of new types of strain gauges and pressure sensors based on carbon nanotubes.

The work (reference 4) received NASA-CSC's best paper award in Applied Science for the year 2002.

### References

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[3] A. Maiti, *Phys. Stat. Sol. B,* 2001, **226,** 87.
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## Gas Sensors: Understanding the Nitrogen Dioxide Sensing Mechanism of Tin Dioxide Nanoribbons

http://www.accelrys.com/cases/nanoribbons.html

### Industry sectors

Electronics – General
Nanotechnology - Nanodevices

### Organizations

Brookhaven National Laboratory
Lawrence Berkeley National Laboratory
Accelrys

MS Modeling's DMol$^3$ has been used to investigate the nitrogen dioxide sensing mechanism of tin dioxide nanoribbons.

Understanding the sensing mechanism will enable the efficient design and manufacture of nanoscale chemical sensors - an important commercial application of nanotechnology.

Practical challenges with carbon nanotubes involving cost of synthesis, control of chirality and diameter, separation from bundles, and attachment of functional groups have prompted researchers to explore other types of one-dimensional nanostructures. Two of the most promising candidates in this regard are nanowires and nanoribbons. As the name suggests, nanoribbons are solid objects (unlike nanotubes, which are hollow) with a near-uniform rectangular cross-section.

So far, nanoribbons have primarily been synthesized from the oxides of metals and semiconductors. In particular, $SnO_2$ and ZnO nanoribbons have been materials systems of great current interest because of potential applications as catalysts, in optoelectronic devices, and as chemical sensors for pollutant gas species and biomolecules. Although they grow to tens of microns long, the nanoribbons are remarkably single-crystalline and essentially free of dislocations. Thus they provide an ideal model for the systematic study of electrical, thermal, optical, and transport processes in one-dimensional semiconducting nanostructures, and their response to various external process conditions.

Recent experiments with $SnO_2$ nanoribbons [1] indicate that these are highly effective in detecting even very small amounts of harmful gases like $NO_2$. Upon adsorption of these gases, the electrical conductance of the sample decreases by more than an order of magnitude. More interestingly, it is possible to get rid of the adsorbates by shining UV light,

and the electrical conductance is completely restored to its original value. Such single-crystalline sensing elements have several advantages over conventional thin-film oxide sensors: low operating temperatures, no ill-defined coarse grain boundaries, and high active surface-to-volume ratio.

To be able to fully commercialize their potential, it is important to better understand the sensing mechanism of such systems.

With this goal in mind, researchers at the Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, and Accelrys used MS Modeling's DMol[3] to investigate the nitrogen dioxide sensing mechanism of $SnO_2$ nanoribbons.

Reporting in *Nano Letters* [2], the researchers examined the $NO_2$-sensing mechanism of $SnO_2$ nanoribbons with exposed (1 0 `1) and (0 1 0) surfaces.
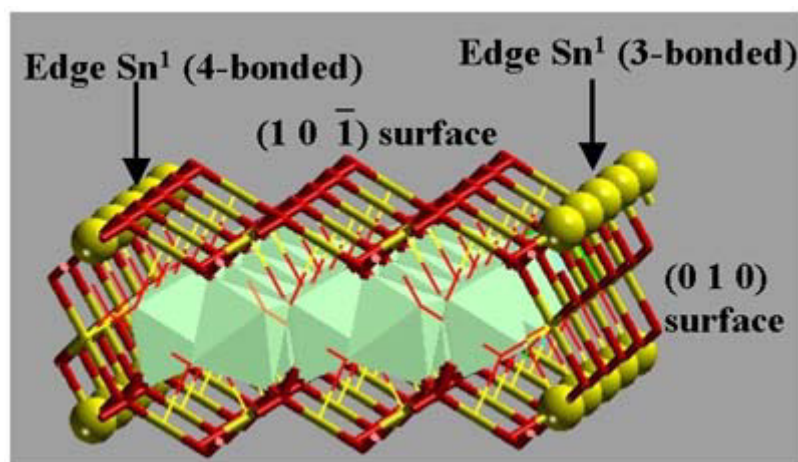


Molecular model of a $SnO_2$ nanoribbon, showing its exposed surfaces and edges. Periodic boundary condition was employed in the actual calculations. See ref. [2].

The density functional theory (DFT) calculations revealed that:

- The most stable adsorbed species involved an unexpected $NO_3$ group doubly bonded to Sn centers

- An orders-of-magnitude drop in electrical conductance can be explained by significant electron transfer to the adatoms

- Computed binding energies were consistent with adsorbate stability up to 700 K, with X-ray absorption spectroscopy indicating predominantly $NO_3$ species on the nanoribbon surface.

The ability of the nanoribbons to sense $O_2$ and CO was also investigated.

In the case of $O_2$, the response of the nanoribbon was highly sensitive to the concentration of O-vacancies on the surface. Thus, in the absence of any surface vacancies, the calculation predicted negligible charge transfer. However, when surface vacancies were present, an $O_2$ molecule can adsorb as a peroxide bridge, and withdraw a significant amount of electronic charge from the nanoribbon surface, thereby decreasing its electrical conductance.

In the case of CO adsorption, there was a net electron transfer from the CO to the nanoribbon surface. Thus the calculation predicted an increase in nanoribbon electrical conductance upon CO-adsorption, in agreement with experimental results.

### References

[1] M. Law, H. Kind, F. Kim, B. Messer, and P. Yang, *Angew. Chem., Int. Ed.*, 2002, **41**, 2405.

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## Field Emission: Effect of Adsorbates on Field Emission from Carbon Nanotubes

http://www.accelrys.com/cases/nanotubes2.html

### Industry sector

**Electronics**

Researchers at Motorola have used Accelrys' DMol$^3$ to investigate the interaction of water with a nanotube tip. Such an understanding is critical in designing commercial quality flat panel displays based on carbon nanotubes.
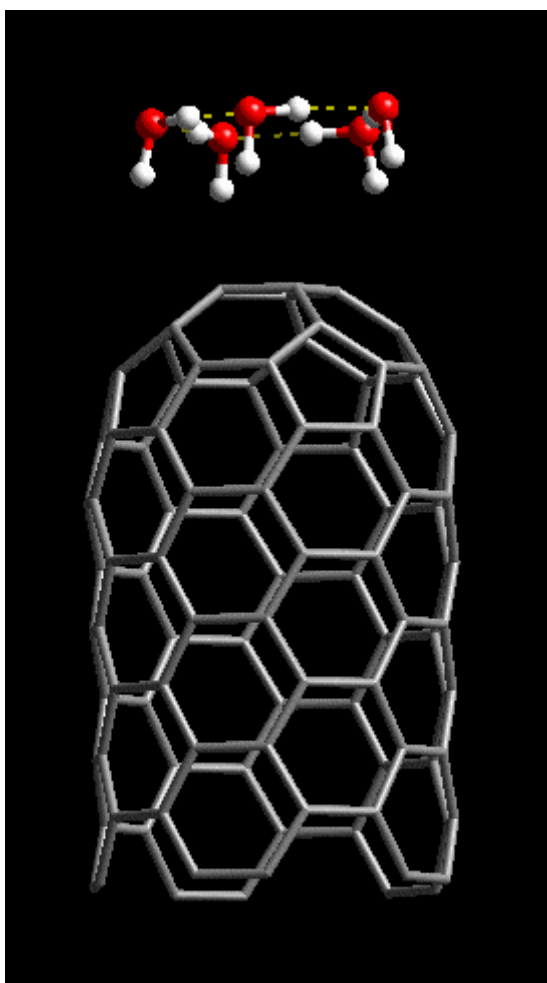


*H-Bonded water cluster on a close-capped (5, 5) nanotube stabilized under field emission conditions. The cluster is found to lower the Ionization Potential of the tube by almost 0.5 eV.*

Of the various potential application areas of carbon nanotubes, Field-Emission-based Flat Panel display is the closest to realizing the first commercial application. A practical challenge to make an efficient display is to reduce the operating voltage. One way to achieve this is to introduce adsorbates that might effectively lower the Ionization Potential (IP) and facilitate the extraction of electrons from the tube tip. Important experiments in this context were recently performed at Motorola, showing that the presence of water significantly enhances the field emission current from carbon nanotubes.

In order to gain an atomistic understanding, scientists at Accelrys and Motorola have investigated the interaction of water with the nanotube tip using Accelrys' DFT code DMol$^3$ [1]. It was found that the interaction is weak in the absence of any voltage.

However, under field emission conditions, large electric fields present at the tube tip are found to: (1) increase the binding energy significantly, thereby stabilizing the adsorbate; and (2) lower the IP, thereby making it easier to extract electrons. Net binding and IP lowering are both enhanced by an increase in the number of water molecules adsorbed on the tip. In contrast, molecules with small or zero dipole moments are found to interact weakly with tube-tip even in large electric fields, and should not affect the field emission behavior, as is observed experimentally.

The above idea of IP reduction in carbon nanotubes was re-confirmed by DMol$^3$ calculations from the group of M. Grujicic (Clemson University) who also investigated additional polar molecules like HCl, HCN, and LiH [2]

### References

[1] A. Maiti, J. Andzelm, N. Tanpipat, and P. von Allmen, *Phys. Rev. Lett.*, 2001, **87**, 155502.
[2] M. Grujicic *et al.*, *Appl. Surf. Sci.*, 2003, **206**, 167.

## Doping: Manipulation of Carbon Nanotubes using Nitrogen Impurities

http://www.accelrys.com/cases/nanotubes4.html

### Industry sectors

**Electronics – General**
**Nanotechnology – Nanodevices**

### Organization

**Cavendish Laboratory, University of Cambridge, UK**

Researchers have used MS Modeling's CASTEP to study the effect of nitrogen substitutional impurities on the electronic properties of single-wall carbon nanotubes.

Such an understanding will enable the electronic properties of carbon nanotubes to be fine tuned. This should lead to the design of better electronic devices, leading to the use of carbon nanotubes in many nanotechnologies and molecular electronics.Carbon nanotubes are long, thin cylinders of bound carbon atoms, about 10 000 times thinner than a human hair, and can be single- or multi-walled. They have remarkable electronic and mechanical properties that depend on atomic structure and more precisely on the manner in which the graphene sheet is wrapped to form a nanotube (chirality). They can vary from being metallic to semiconducting.

Carbon nanotubes are a hot research area, fuelled by experimental breakthroughs that have led to realistic possibilities of using them in a host of commercial applications: field emission-based flat panel displays, novel semiconducting devices in microelectronics, hydrogen storage devices, chemical sensors, and most recently in ultra-sensitive electromechanical sensors. As a result they represent a real-life application of nanotechnology.

However, two major challenges remain an obstacle to the full commercialization of nanotube-based nanotechnologies and molecular electronic devices:

- The manipulation of individual tubes is difficult owing to their size, and

- The ability to manipulate nanotube properties to suit the application has to be achieved.

Reporting in *Physical Review Letters* (2003, **91(10)**, 105502), Professor Michael Payne and team at the Cavendish Laboratory, University of Cambridge, UK, used MS Modeling's CASTEP to study the effect of introducing nitrogen impurities in semiconducting zigzag and metallic armchair single-walled nanotubes.

In semiconducting nanotubes, introducing impurities, a process known as doping, is the main method of tuning properties to make electronic devices. Doping is also a way of creating chemically active impurity sites.

Using CASTEP, the researchers found that, at low concentrations of nitrogen impurity (less than 1 atom%), the impurity site becomes chemically and electronically active. In addition, the team found that an inter-tube covalent bond can form between neighboring nanotubes with impurity sites facing each other.
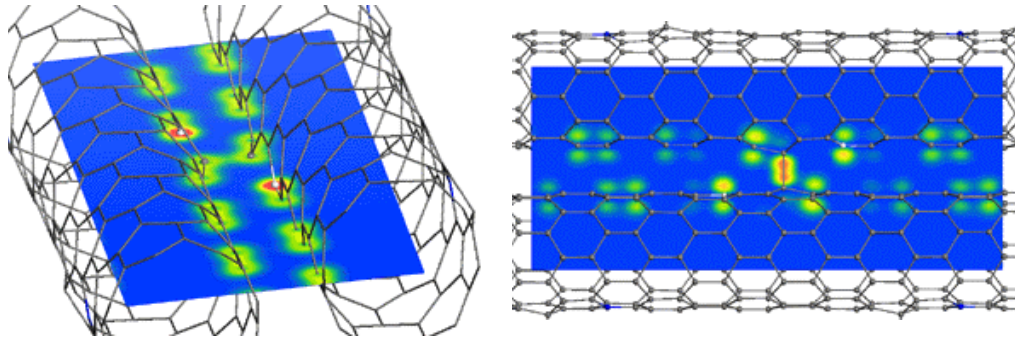


**The effect of nitrogen doping in two zigzag nanotubes. The left image shows the charge density, the right image shows the density of the HOMO orbital (red the highest density, blue the lowest). The chemical bond is formed between the two carbon atoms that have the maximum spin density (red).**

These findings open the door to the possibility of nanotube manipulation via the formation of tunnel junctions between suitably doped nanotubes. Nanotube properties could also be controlled by selective functionalization through ligand docking at the impurity sites.

Professor Michael Payne says, "CASTEP enabled us to treat a system of several hundred atoms, necessary in order to study the intertube covalent bond and the isolated impurity, whose electronic state decays very slowly."

"Treating the system at the ab initio level also allowed us to predict experimental observables which will help in synthesizing this structure," added Professor Payne. "In the future, we hope to study applications of the doped nanotubes, such as the tunnel junction or an enhanced gas sensor. This will require computing non-equilibrium electronic structures, which is at the cutting edge of current quantum mechanical modeling."

## *Drug Delivery*

Nanotechnology is impacting on the design and development potential new drug delivery systems in many ways. In particular, researchers are studying nanoscopic carrier systems such as dendrimers and block-copolymers which 'self-assemble' to nanoscale structures that have many advantageous properties, such as increased circulation time, potential to pass the blood-brain barrier and can be functionalized for targeted delivery.

Mesoscale modeling tools are particularly useful in the study of such nanoscale large objects such as micelles, vesicles, and colloids. To obtain thermodynamic and kinetic information on such systems e.g. their phase morphology and release behavior, it is unpractical to retain all atomistic detail. Rather one wants to retain just sufficient knowledge of the system to make the information obtained from the model meaningful.

DPD and MesoDyn in MS Modeling do exactly this. Using mean-field interaction parameters obtained either from experiment or from fully atomistic systems, and coarse graining the scales (many atoms become a single bead, time steps can be made larger since these units are soft) we are able to study the whole system dynamically.

The case study below shows the application of MesoDyn to modeling micelle drug carriers.

## Simulation of Nanoscale Drug Delivery Devices

**Industry sectors**

> **Pharma – Drug Delivery**
> **Nanotechnology – Nanodevices**

**Organizations**

> **University of Cambridge**
> **Nanyang Technological University,**
> **Accelrys**

Scientists at the University of Cambridge and Accelrys have used mesoscale simulation methods to study self-assembled drug delivery devices.

Novel drug delivery systems based on molecular self assembly at the nanoscale are receiving increasing attention as a means of improving issues of drug solubility, passing the blood-brain barrier, and targeted drug delivery. Amphiphilic block-copolymers are being studied extensively for this purpose, as they spontaneously form nanoparticles known as micelles in an aqueous medium. These micelles are characterised by a hydrophobic core surrounded by a hydrophilic corona. The core region can act as a container for hydrophobic or otherwise purely soluble drugs, which in this way can be transported through the bloodstream.

Experimental investigation of the formation and structure of these nanoscale aqueous systems is very difficult, requiring complex and time-consuming preparation techniques. Accelrys' mesoscale simulation methods MesoDyn and DPD have been developed specifically for investigating nanostructure formation in complex fluids.

Researchers at the University of Cambridge, UK, and Accelrys have used MesoDyn to simulate micelles formed from ethylene oxide – propylene oxide block copolymers in aqueous solution [1,2]. They compared the simulation with direct observation of real micelles by cryo-transmission electron microscopy [3]. Good agreement was found for different formulations, and the simulations could be used to map out the effects of varying the polymer molecular weight, aqueous concentration, and drug loading on the nanostructure.
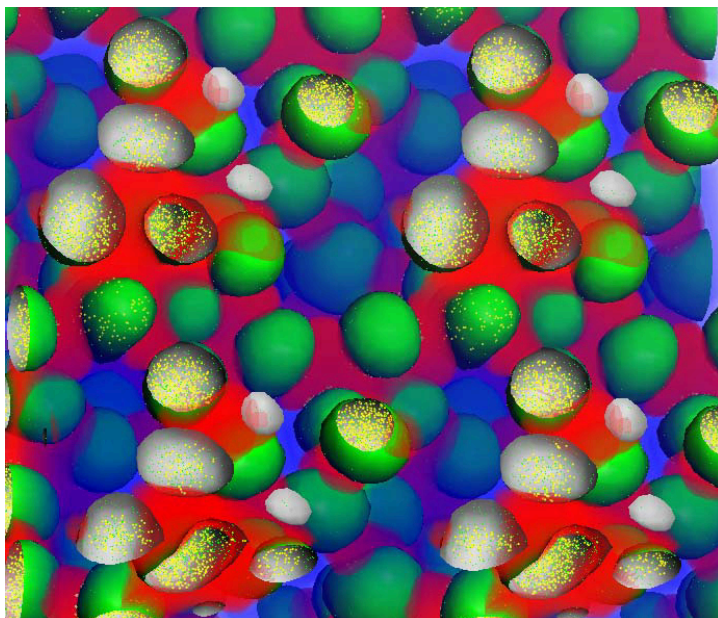


The nanoscale structure of an aqueous solution of amphiphilic block-copolymer with haloperidol drug at 1% concentration. The polymer formes micelles with a hydrophobic core and a hydrophilic corona. In the image the interface between core and corona is shown as green surface (cut through by the front plane of the image in some cases). The corona is shown as a red field, and the water as a blue field. The drug concentration field is depicted by yellow dots, showing that the drug mostly resides in the core of the micelles. Size scale of the image is about 35 nm

In particular, the simulations revealed that the drug tends to be located in the interface region for low loadings and become more aggregated in the core for higher loadings. The micelle shape is distorted towards a rod-like structure at higher drug loading.

### References

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[2] Y.M. Lam, G. Goldbeck-Wood, and C. Boothroyd, *Mol. Sim.*, accepted for Nanotech2003 Special Edition, 2003.
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## *Manufacturing*

## CVD: Atomistic Modeling of Chemical Vapor Deposition (CVD): Silicon Oxynitride

http://www.accelrys.com/cases/SiNO.html

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[2]Semiconductor Product Sector, Motorola, Inc., MD M360, Mesa, AZ 85202

### Industry sectors

**Semiconductors, Chemicals**

### Organizations

**Motorola Inc, USA**
**Accelrys, USA**

Scientists from Motorola and Accelrys have used Accelrys' DMol$^3$ software to study the deposition of NO on a Si(100) surface. This work is a significant move towards being able to model the processes involved in chemical vapor deposition.

### Introduction

Chemical vapor deposition (CVD) is a method of choice to produce thin and high quality films with precise chemical composition and structural uniformity. The optimization of the CVD process conditions (eg. pressure, temperature, precursors and reactor configuration) for better control of the film growth rate, uniformity and composition can be achieved using reactor scale models. Such models in turn require detailed understanding of the deposition chemistry, which can be achieved experimentally. However, experiments with silicon wafers are expensive and time consuming. Thus the theoretical modeling offers an attractive alternative to obtain the input parameters for reactor scale models.

The understanding of gas phase chemistry by far exceeds that of the surface reaction mechanisms. The problem is more complicated from the experimental and theoretical perspectives alike. The topography and the catalytic properties of semiconductor surfaces greatly add to the complexity of the problem. A comprehensive theoretical framework describing the surface deposition is yet to be written.

**Reaction mechanism for NO on Si(100)**

Silicon oxynitride appears in several electronics applications. Oxide-nitride-oxide structures are widely used in the DRAM and EEPROM devices. The interfacial region in such structures is silicon oxynitride. Amorphous silicon nitride is a potential gate dielectric material (the dielectric constant is more than twice that of silicone dioxide). However, the quality of the interface with the SiN films grown directly on Si is not very high.

The deposition of NO on Si(100) surface followed by the oxynitride growth is chosen as a model in this computational investigation. The goal is to obtain a quantitative and qualitative description of the initial NO deposition on Si(100) surface and the silicon oxynitride film growth. This study will further an understanding of the oxynitride film structure, energetics and physical properties.

In this work, we present a theoretical study of initial reaction between nitric oxide, NO and Si(100)(2x1) surface. Two types of the Si models have been investigated - molecular clusters and infinite silicon slabs terminated by hydrogen atoms.
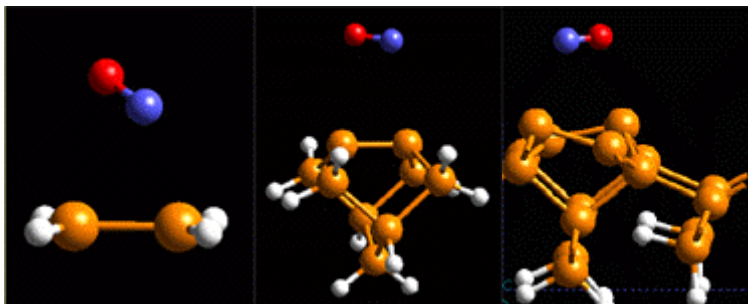


(I) The most simplified cluster model is represented by the $Si_2H_4$+NO system and only includes a silicon double bond as an 'active' reaction center on the surface.

(II) The second cluster contains nine silicon atoms and twelve hydrogen atoms to represent both the surface Si-Si double bond, its immediate chemical environment in the crystal and structural restrains imposed by a body of the bulk material

(III) The most sophisticated model, the infinite silicon slab terminated by hydrogen atoms, contains 16 silicon and 8 hydrogen atoms in a periodic unit cell to reproduce both surface and underlying silicon layers.

We have investigated different structures relevant to the mechanism of the reaction between NO and silicon surface using the above three different models. The cluster models (I and II) have been studied using the B3LYP/6-31G* and BP/DNP & PWC/DNP approach, while the periodic system has been investigated using the BP/DNP & PWC/DNP method. For the validation purpose the simplest model (I) has been also investigated using *ab initio* couple cluster and second order perturbation theories.

For a further case study in this area, Predicting the Thermochemistry and Kinetics of Chemical Vapor Deposition, see http://www.accelrys.com/cases/CVD2.html

## 'Directed Self-assembly': Morphology Formation and the Effect of Process Conditions for Specific Polymer Surfactant Solutions

http://www.accelrys.com/cases/specific.html

http://www.accelrys.com/cases/proccond.html

**Industry sector**

    **Chemicals**

**Organization**

    **University of Groningen, Netherlands**

The MesoDyn code has been applied to the microphase separation dynamics of aqueous Pluronic solutions. All four different phases were reproduced in MesoDyn simulations, in excellent agreement with experiments. Furthermore, to the global ordering under simple steady shear has been investigated.
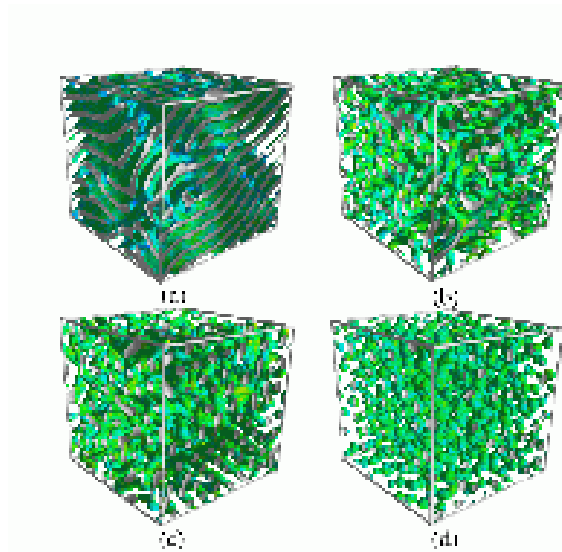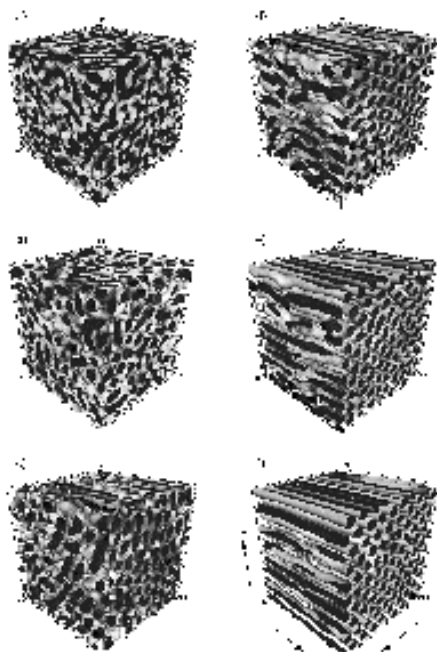
Morphology of Pluronic L64 solutions at 70% (a), 60% (b), 55% (c), and 50% (d) concentration. In exact agreement with experiment, the morphologies are seen to be lamellar, bicontinuous, hexagonal and micellar, respectively.

Surfactant molecules can assume a bewildering variety of structures, and end material properties can be enormously dependent on these. One such example is in drug delivery using nonionic surfactants such as BASF's Pluronics, where delivery rates can vary enormously depending on whether the system is micellar, hexagonal, lamellar, or one of the bicontinuous morphologies.

The MesoDyn code has been applied at the University of Groningen to the microphase separation dynamics of aqueous Pluronic solutions, which are also used as emulsifiers, stabilisers, and wetting agents.

For the Pluronic L64, four different mesophase morphologies exist in a small 50-70% surfactant concentration interval. All four different phases (micellar, hexagonal, bicontinuous and lamellar) including their defects and time development are reproduced in MesoDyn simulations, which is in excellent agreement with experiments. In a further study, using the same parameters, the known phase behaviour of the Pluronic 25R4 was equally well reproduced.

The MesoDyn code provides a flexible way to account for changes in molecule properties, such as changes in the block lengths and the chemical dissimilarity between blocks.



Evolving morphology of a 55% Pluronic L64 solutions in water under steady shear. In agreement with experiment, the hexagonal lattice forms with one lattice vector perpendicular to the plane of shear.

Scientists have known for centuries that material properties depend just as much on processing conditions as on chemical composition. Now Accelrys' MesoDyn code provides a method to predict micro-phase separation in complex liquids in externally applied flow fields. The strong effect of the applied flow on structure is demostrated in a study by researchers at University of Groningen who used the MesoDyn mesoscale modeling code to calculate the global ordering effects in polymer melts and solutions under simple steady shear. Both for a model system of A-B diblock copolymers and for the hexagonal phase of the specific Pluronic L64-water system, the experimentally observed most stable phase was found.

For further case study on directed self-assembly, looking at reactive blending, see http://www.accelrys.com/cases/mesoblend.html

For a case study on copolymer phase separation pathways, see http://www.accelrys.com/cases/copolymer.html

## In Situ Intercalative Polymerization: Formation of Clay-Polymer Nanocomposites

http://www.accelrys.com/cases/nanocomposites2.html

**Industry sectors**

> **Automobile, Electronics, Furnishing**

**Organizations**

> **Queen Mary, University of London**
> **Universite Paris Sud**

Researchers at Queen Mary, University of London and the Universite Paris Sud have used Accelrys' density functional theory (DFT) code CASTEP to study the formation of clay-polymer nanocomposite materials by self-catalyzed *in situ* intercalative polymerization.
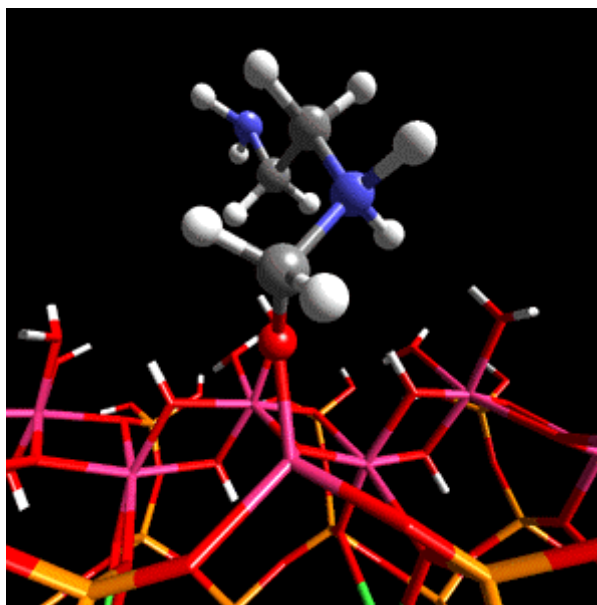


**Methanal coordinated to aluminium in the tetradral layer of montmorillonite is activated towards nucleophilic attack by ethylenediamine**

Clay-Polymer nanocomposite materials have recently attracted a great deal of attention as they offer enhanced mechanical and thermal properties as compared to conventional materials. Because of these enhanced properties they find application in the electronics, automobile, and furnishing industries.

One preparation of clay-polymer nanocomposites is *in situ* intercalative polymerization. This process involves mechanical mixing of the clay mineral with the required monomer. The monomer then intercalates within the interlayer and promotes delamination. Polymerization follows, initiated by a number of ways, to yield linear or cross linked polymer matrices. Often the clay mineral needs to be dispersed by a preswelling step of long-chain alkylammonium ion intercalation to aid exfoliation.

A recently discovered preparation [1], called 'self-catalyzed *in situ* intercalative polymerization' , is similar to *in situ* intercalative polymerization, but differs in the fact that no pretreatment of the clay is required.

Reporting in the *Journal of the American Chemical Society* [2], Stephen Stackhouse and Peter Coveney of Queen Mary, University of London, and Eric Sandre of Universite Paris Sud, describe how they used Accelrys' CASTEP to provide theoretical insight in to the mechanism of this novel process by determining the role played by the clay matrix.

The researchers first describe the work done on a specific example, that of methanal with ethylenediamine within a sodium montmorillonite interlayer, and then discuss the role that the clay structure may play in catalysis and the potential sources of Bronsted and Lewis acidity in sodium montmorillonite. The scientists then discuss previous *in silico* work done on clay minerals which leads to their reasoning behind their use of DFT - the fact that this method is particluarly suited to the study of crystalline materials (*e.g.* clays and zeolites) when used in conjunction with periodic boundary conditions and a plane-wave basis set.

Using CASTEP as the optimization method on periodic model systems from Cerius$^2$ 4.2's structural database, Coveney and team showed that the proximity to isomorphic substitution sites within the silicate layers has a marked effect on the Bronsted acidity of the hydroxy groups.The hydroxy groups being further from the sites of the magnesium-for-aluminium substitution being more Bronsted acidic, although it was shown that it was energetically favorable for the to be nearer the substitution sites. The simulations also revealed that the monomer catalysis occurs at the mineral lattice edge. Here exposed $Al^{3+}$ ions and hydroxy groups act as Lewis and Bronsted acid sites, respectively.

### References

[1] P. V. Coveney, J. L. W. Griffin, M. Watkinson, A. Whiting, and E. S. Boek, *Mol. Sim.*, 2002.
[2] S. Stackhouse, P. V. Coveney, and E. Sandre, *J. Am. Chem. Soc.,* 2001, **123**, 11764.

## *Analytical*

## Combining HRTEM and ab initio Simulation to Reveal Grain Boundary Structure and Segregation Mechanisms

http://www.accelrys.com/cases/grain.html

### Industry sectors
Electronics, aerospace, automotive, and metallurgical industries
### Organization
Oak Ridge National Laboratory

Scientists at Oak Ridge National Laboratory have used a combination of high-resolution transmission electron microscope (HRTEM) and the Accelrys QM code CASTEP to gain an atomic level understanding of grain boundaries which can help to design materials with more desired macroscopic properties.

Grain boundaries are internal interfaces between perfect crystalline regions (grains). They control a number of important macroscopic properties of materials: mechanical, electrical, doping, microstructural, and diffusional transport, to name a few. An atomic level understanding of grain boundaries helps design materials with more desired macroscopic properties.

Scientists at Oak Ridge National Laboratory have used a combination of high-resolution transmission electron microscope (HRTEM) and the Accelrys QM code CASTEP to obtain a number of new and important results, including:

A novel segregation mechanism of n-type dopants (As, P) at Si (Ge) grain boundaries in the form of dimers and chains of dimers, with each dopant atom threefold-coordinated [1, 2]. Threefold coordination explains experimentally observed large segregation energies of n-type dopants in poly-silicon. They also provide deep electronic trap states that can significantly alter performance of poly-silicon based electronic devices. CASTEP-predicted Arsenic dimers were subsequently observed in HRTEM images [3].
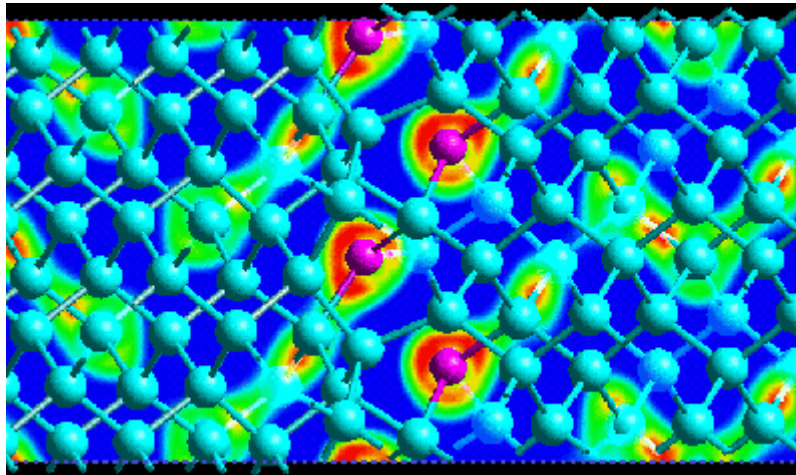


**Figure 1 Chain of As-dimers in a Σ = 5 {310} <001> tilt boundary of Si. Optimized structure and charge density slice were computed by CASTEP. CASTEP-predicted dimers were subsequently observed in HRTEM images**

Structural transformation in MgO grain boundaries induced by Calcium segregation [4]. The presence of Calcium was detected by careful EELS measurements only after a disagreement was discovered between the HRTEM image of the MgO boundary and the CASTEP-predicted structure of a 'pure' boundary. Segregation-induced grain boundary transformation opens the door for altering certain structural and mechanical properties of materials in a controlled way.

Possibility of grain boundary reconstruction in a class of technologically important oxide ceramics, including $SrTiO_3$ [5].

The understanding gained from atomistic simulations of grain boundaries is directly relevant to materials processing and quality management, and is particularly important in electronics, aerospace, automotive, and metallurgical industries.

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For further case studies on the modeling of HRTEM images, see:

http://www.accelrys.com/cases/clusters.html

http://www.accelrys.com/cases/HRTEM1.html


# Diffraction: Structure Solution of Inorganic Crystals from Powder Data

http://www.accelrys.com/cases/an_inorganics.html

Reflex Plus has been successfully applied to inorganic materials of different complexity including framework structures like zeolites and layered aluminophosphates.

Single crystal x-ray diffraction is the ideal technique to solve crystal structures. However, materials are often only available as polycrystalline powders. In such cases, successful structure solution from powder diffraction data becomes essential. Reflex Plus, Accelrys' leading technology for structure solution from x-ray (or neutron) diffraction data, has proved successful [1] for a wide range of organic molecules, including salts and organometallics. Recent applications also include inorganic crystals.

The procedure comprises several steps, which are accounted for by different tools in Reflex Plus, namely, Powder Indexing, Powder Refinement and Powder Solve. The indexing of the powder pattern is followed by the determination of the space group and the refinement of the cell parameters, peak shape and background parameters by a modified Pawley method. Then, a global optimization algorithm, either Monte Carlo Simulating Annealing or parallel tempering, is used to generate trial structures in direct space finding the solution that maximizes the agreement between the simulated and experimental powder diffraction pattern. Such agreement is measured by a full-profile comparison using the $R_{wp}$ factor. During the search phase, promising structures are automatically subjected to rigid body Rietveld refinement in the search parameter space to locate the local minimum.

The information contained in a powder diffraction pattern is limited. In fact, whereas the number of observations in a single crystal diffraction pattern is greater than the number of variables, the structure solution from powder diffraction data is an underdetermined problem. In order to limit the number of variables, structure solution methods of organic crystals typically make use of molecular topology constrains like bond lengths and angles as well as space group symmetry constraints. In inorganic crystal structures, molecular topology restrictions cannot be so generally applied. On the other hand, the presence of strongly scattering elements can help the search.

Making use of the space group constrains reduces the search space to the asymmetric unit. However, it implies added difficulties when atoms occupy special positions, which is common in inorganic crystals. One of the recent improvements of Powder Solve is the ability to deal with special positions. If the position is unequivocally defined, placing the atom (or fragment) on this position reduces the number of degrees of freedom. If the position is not unambiguously defined, Powder Solve will be able to deal with it provided that the atomic occupancies are assigned according to the Wyckoff position multiplicity. In such cases, the solutions found would contain overlaid copies of the low occupancy atoms.

As an initial validation project on inorganic crystals, six structures of different complexity were studied [2]: $LaB_6$, $Y_2O_3$, AK-100, FIN-31, the zeolite SAPO-56 and the layered aluminophosphate KOK-282. The rate of success for $LaB_6$, $Y_2O_3$, AK-100, FIN-31, SAPO-56 was 100% for 5 independent runs. The number of required steps per degree of freedom is in general smaller than in organic cases due to the efficiency of the rigid body Rietveld refinement.
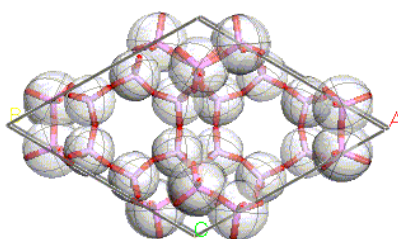
In the case of FIN-31 the set-up consisted in a tetrahedral $PO_4$ motion group and atomic motion groups for Ca and F.

The cell contents deduced from the cell volume and the experimental density, $Ca_{10}F_2P_6O_{24}$, indicated that all the motion groups occupied special positions in the P $6_3$/m cell. The atomic occupancies were set-up accordingly. Six degrees of freedom were explored in the Simulating Annealing search. The structure could be found within 6 minutes.
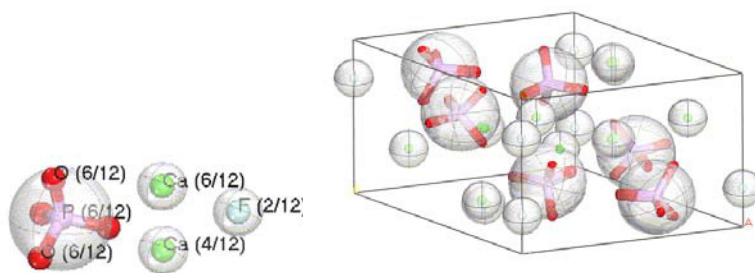
**Motion group and occupancies set-up and structure solution of FIN31**

When dealing with framework structures, structural restrictions can be used to facilitate the search. In the case of the zeolite SAPO-56, for instance, two motion groups consisting of tetrahedral $PO_4$ and $AlO_4$ were set up. Since every oxygen atom had to be shared by two tetrahedra to build up the framework, their occupancies were halved. The cell content deduced from the experimental density was $Al_{24}P_{24}O_{96}$. Thus, 24 copies of each motion group were required, which is the multiplicity of the general position in the previously determined space group (P $6_3$/m m c). Therefore, the search could be limited to the rotation and translation of a tetrahedral $PO_4$ and a tetrahedral $AlO_4$ within the asymmetric unit, resulting in a total of twelve degrees of freedom. The number of SA steps needed to solve the structure varied from 37187 to 702572 (1.02 to 18.84 minutes in a PC, 256Mb, PII 400MHz running NT).



**Structure solution of SAPO-56**

In the case of KOK-282, the search set-up consisted of a tetrahedral $PO_4$ motion group and atomic motion groups for Al, F and the water oxygen. The organic molecule, ethylenediamine, was included in another motion group with fixed bond distances and angles. The content of $PO_4$, Al, F and water in the unit cell was compatible with the multiplicity of the general position; thus, their occupancies were set to 1. For ehylenediamine, the cell contents indicated that it lied on the inversion center. Placing it on the special position reduced the degrees of freedom to the tree rotations. The SA search was trapped in a deep local minimum but the parallel tempering algorithm found the global minimum in 214503 steps [3].
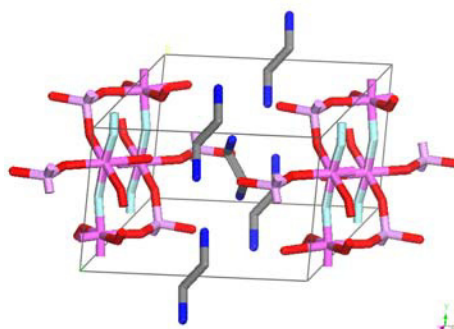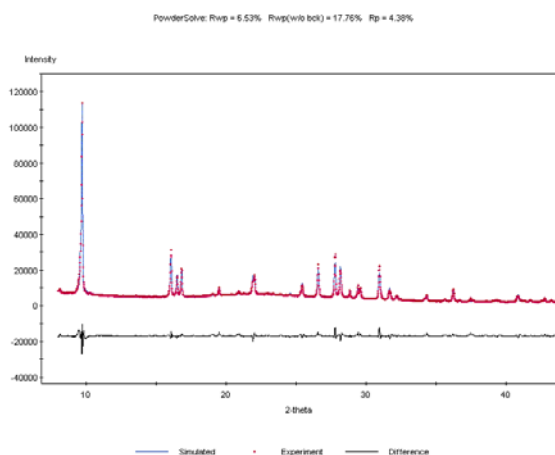


**Structure solution of layered aluminophosphate KOK-282.**

In summary, Powder Solve can be successfully applied to inorganic materials of different complexity including framework structures like zeolites and layered aluminophosphates. The input requirements are an indexable powder pattern and the experimental density.

## References

[1] G.E. Engel, S. Wilke, O. König, K.D.M. Harris, and F.J.J. Leusen, *J. Appl. Crystallogr.*, 1999, **32**,1169-1179.
[2] Data kindly provided by R. W. Broach (UOP, Illinois), K. P. Lillerud (University of Oslo) and Peter Ramminger (University of Innsbruck).
[3] K. P. Lillerud and C. Conesa-Moratilla, manuscript in preparation.

**For a general overview of the methodology, see:**

http://www.accelrys.com/cases/psolve.html

## Scanning Probe Microscopy Combined with Mesoscale Simulations: Block Copolymers Phase Behavior in Thin Films Revealed

**Industry Sectors**

> **Nanotechnology – Nanomaterials**
> **Chemicals - Coatings and Additives**

**Organizations**

> **Bayreuth University, Germany**
> **Leiden University, The Netherlands**

MS Modeling has been used to model the phase behavior of cylinder-forming block copolymers in thin films.

Using a combination of mesoscale simulations and scanning force microscopy experiments, the studies revealed that the phase behavior in such systems is dominated by surface reconstructions.

This finding will help to understand and control thin film structures in ordered fluids, including surfactant based systems.

The work demonstrates that mesoscale simulations and scanning force microscopy are a powerful complimentary approach to tackle complex nanostructured materials.

At the mesoscale (10-1000 nm), ordered fluids, for example amphiphilic block copolymers, are interesting as they show a crystal like order. At the same time they exhibit a fluid-like disorder on the molecular scale and behave on macroscopic length scales like fluids. At interfaces and in thin films further order is induced as one component usually has a lower interfacial energy than the other and tends to accumulate at the interface.

Near surfaces and in thin films a number of interesting phenomena have been observed such as the existence of wetting layers, spherical microdomains, perforated lamella, and cylinders with necks.

Despite numerous experimental and computational studies, the origins of these phenomena remain unclear.

In order to clarify matters, researchers at Bayreuth University (Germany) and Leiden University (The Netherlands) used the MesoDyn mesoscale tool to model the phase behavior of cylinder-forming polystyrene-*block*-polybutadien-*block*-polystyrene (SBS) triblock copolymer in thin films.

Robert Magerle's team determined experimentally a phase diagram for the SBS triblock copolymer in thin films using well-controlled sample preparation and scanning force microscopy. To gain further insight into the structure formation process, the phase behavior of the system was modeled using MesoDyn.
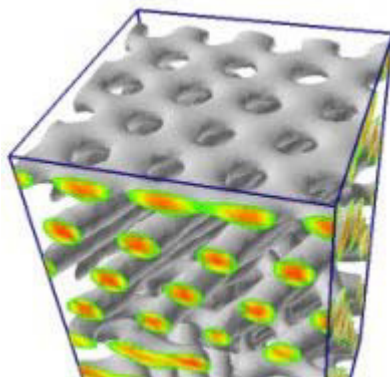


**MesoDyn simulation of a film of cylinder forming triblock copolymer forming a perforated lamella surface reconstruction at the film surface**

The simulations enabled the researchers to identify the underlying fundamentals for structural deviations from the bulk structure, so called surface reconstructions, such as wetting layer, perforated lamella, and lamella, both near surfaces and in thin films of the SBS triblock copolymer.

These findings, taken in context with previous results, support a general mechanism for the phase behavior of block copolymers at interfaces and in thin films. The structure near the surface depends on the strength of the preferential attraction of one of the components to the surface and the deformability of the bulk structure, affecting the orientation of the microdomain structure or causing surface reconstructions to form.

This work could lead to a better understanding and eventually control of thin film structures in a wide-range of ordered fluids, including surfactants and lubricants.

Dr Robert Magerle said, "We expect a large impact on nanotechnology where block copolymers are used as self-organized templates for the synthesis of anorganic nanostructured materials".

**References**

[1] A. Knoll, K. S. Horvat, G. Lyakhova, G. J. A. Krausch, A. V. Sevink, A. V. Zvelindovsky, and R. Magerle, *Phys. Rev. Lett.*, 2002, 89, 035501;

http://www.uni-bayreuth.de/departments/pcii/magerle/index.html

Two follow-up articles:

- A. Knoll, R. Magerle, and G. Krausch, *J. Chem. Phys.*, 2003, in print (Experiments).

- A. Horvat, K. S. Lyakhova, G. J. A. Sevink, A. V. Zvelindovsky, and R. Magerle, *J. Chem. Phys.*, 2003, in print (Simulations).

# Nanotechnology Tools

Accelrys, the leading provider of quantum mechanics, molecular mechanics, and mesoscale simulation software for pharmaceutical, chemical and materials research, offers an extensive suite of tools to support nanotechnology R&D in its MS Modeling software, operated within the Materials Studio PC environment.

To obtain an evaluation copy of Materials Studio, please get in touch with Accelrys via www.accelrys.com/contact/.

Classical molecular mechanics assumes that a molecular system can be described using the laws of classical mechanics. It provides a fast, though approximate, way of studying molecular structure, energetics, and motion. Mesoscale methods introduce a further level of approximation: only the key elements of the molecular structure and interactions are retained, so that larger length and time scales are probed. Quantum mechanics methods are usually more accurate but also much more computationally expensive. Frequently these different approaches complement each other.

A selection of tools appropriate for various aspects of nanotech R&D are introduced below. For further information, visit the Accelrys web site at www.accelrys.com/materials/nanotechnology.html

## Amorphous Cell

**Amorphous Cell** is a suite of computational tools that allow you to construct representative models of complex amorphous systems and to predict key properties. By observing the relation between system structure and properties, you can obtain a more thorough understanding of the important molecular features, allowing you to better design new compounds or new formulations. Among the properties that you can predict and investigate are cohesive energy density, equation-of-state behavior, chain packing, and localized chain motions.

The behavior of amorphous materials is critical to products including plastics, glasses, foods, and chemicals. Researchers studying amorphous polymers, for example, seek to optimize their mechanical behavior, the transport of molecules through the system, and their surface and interface interactions. These properties impact the polymer's performance in applications including separation processes, packaging, and in drug delivery systems.
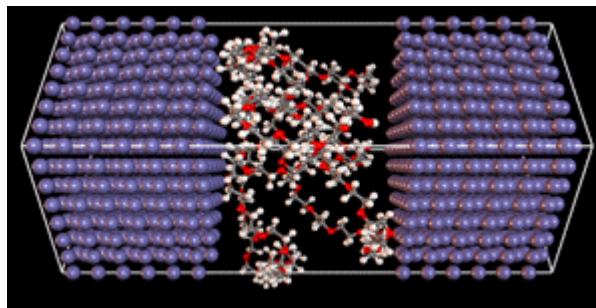


**A polyoxyethylene oligomer confined between two iron surfaces. Such a scenario can be used to study the effect of shear on the polymer structure and properties.**

# CASTEP

**CASTEP** is an ab initio quantum mechanical program employing density functional theory (DFT) to simulate the properties of solids, interfaces, and surfaces for a wide range of materials classes including ceramics, semiconductors, and metals. First principle calculations allow researchers to investigate the nature and origin of the electronic, optical, and structural properties of a system without the need for any experimental input other than the atomic number of mass of the constituent atoms. CASTEP is thus well suited to research problems in solid state physics, materials science, chemistry, and chemical engineering where researchers can employ computer simulations to perform virtual experiments which can lead to tremendous savings in costly experiments and shorter developmental-cycles.
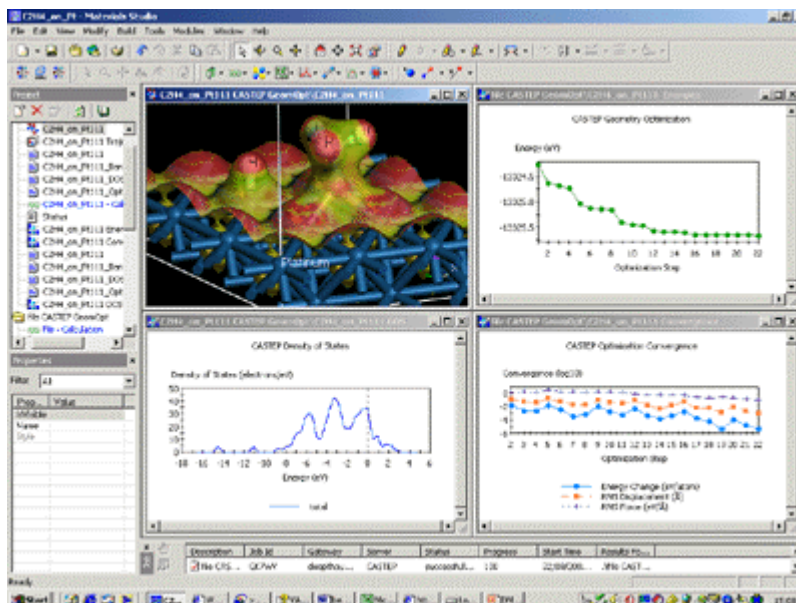


$C_2H_4$ absorption on a Pt(111) surface showing the electrostatic potential projected on the electronic density isosurface. Density of states, energy evolution and energy convergence graphs are also shown.

# COMPASS

**COMPASS** stands for Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies. It is the first ab initio forcefield that has been parameterized and validated using condensed-phase properties in addition to various ab initio and empirical data for molecules in isolation. Consequently, this force field enables accurate and simultaneous prediction of structural, conformational, vibrational, and thermophysical properties for a broad range of molecules in isolation and in condensed phases, and under a wide range of conditions of temperature and pressure.

Currently, the coverage includes the most common organics, inorganic small molecules, polymers, some metal ions, metal oxides and metals. All of the parameters in COMPASS are derived in a consistent manner so that, in principle, one can study very different systems including interfaces and mixtures.
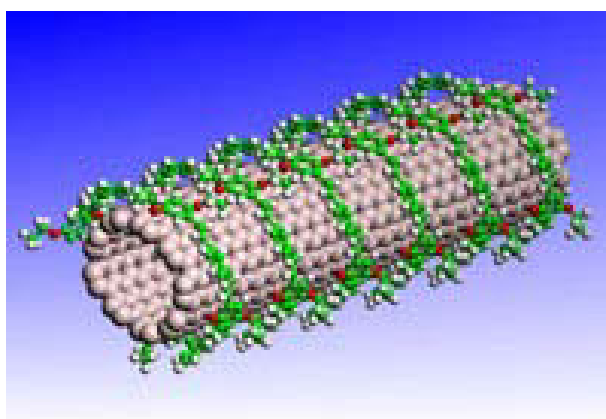


A polymer chain helically wrapping a carbon nanotube. Structure optimized with MS Modeling's Discover and the COMPASS forcefield.

## Discover

**Discover**® is MS Modeling's 'simulation engine'. It incorporates a broad spectrum of molecular mechanics and dynamics methodologies that have demonstrated applicability to molecular design. Using a carefully-derived forcefield as the foundation, minimum energy conformations, as well as families of structures and dynamics trajectories of molecular systems, can be computed with confidence.

Discover provides underlying calculations for products such as Amorphous Cell. It also supports varied simulation strategies. Periodic boundary conditions allow the simulation of solid-state systems, whether crystalline or amorphous, and of solvated systems. Comprehensive analysis features enable the extraction of pertinent results from the simulation.
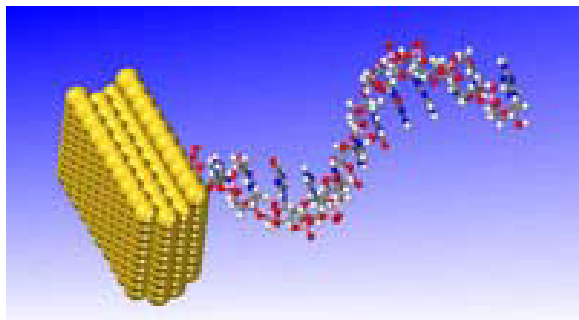


**A single strand of DNA attached to a Gold surface. The system is a simplified prototype of a DNA-chip. Structural and dynamical properties can be studied using MS Modeling's Discover.**

## DMol$^3$

**DMol$^3$** is a premier, robust DFT program with a long track record of successful commercial applications. Owing to its unique approach to electrostatics, and an efficient optimizer, DMol$^3$ has long been one of the fastest methods available for performing molecular DFT calculations, especially for large molecules. It now extends this approach to solid-state problems via a high-performance internal coordinate optimizer that can treat the full range of solid-state state systems. The DMol$^3$ code delivers the first robust, general-purpose internal coordinate optimization scheme for periodic systems. A new transition state search employing a combination of LST/QST algorithms with subsequent conjugate gradient methods greatly facilitates the optimization of the transition state structure. This robust and easy-to-use scheme works for both molecular and periodic systems and offers a significant speed-up as compared to traditional methods. The transition state toolbox contains the powerful transition state confirmation method Nudged Elastic Bands (NEB). NEB enables scientists to verify that the transition states obtained by the LST/QST technique is the one linking the reactants and the products.

The Handy-Tozer functionality enables the simulation of hydrogen bonded systems and accurate molecular structures and thermodynamic data can be obtained.

Using parallel versions of the DMol$^3$ code large problems can be tackled.
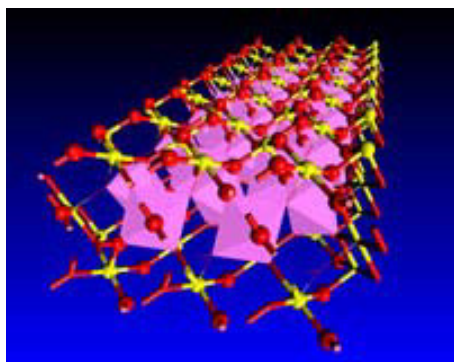


**$SnO_2$ nanoribbon with exposed (10-1) and (010) surfaces. Such a system can be used as ultrasensitive nanosensors for various gases, e.g., $NO_2$, $O_2$, and CO. Calculations performed with MS Modelings's DMol$^3$.**

# DPD

**DPD** is a robust, coarse-grained, dynamics algorithm for simulating soft matter. The basic idea of DPD is that it should be possible to replace 'blobs' or 'droplets' of fluid with individual particles, which interact in such a way as to reproduce Newtonian hydrodynamics of the fluid as a whole. Thus, the contribution of the microscopic details of the system, i.e., the main concern of atomistic simulation methods, is integrated out, allowing access to much larger time and length scales. The underlying chemistry of the system is not lost in the coarse-graining. The resulting 'beads' interact with one another via a pair-potential related to the Flory-Huggins interaction parameter. This parameter can be measured experimentally or obtained from modeling with atomistic detail.

The particles are subject to pair-wise forces, which comprise: soft repulsions, stochastic noise and dissipation (conceptually similar to a viscous drag). Navier-Stokes behavior is obtained with a suitable choice of functional form of these potentials and so the method captures hydrodynamics.

A wide range of properties can be calculated with DPD, including:

- Phase morphology
- End to end distance distribution of any chain molecules
- Stress tensor
- Surface tension
- Critical micellar concentration
- Aggregation and coagulation
- Effect of confinement on miscibility
- Effect of shear on morphology
- Concentration profiles
- Diffusion rates of various species.
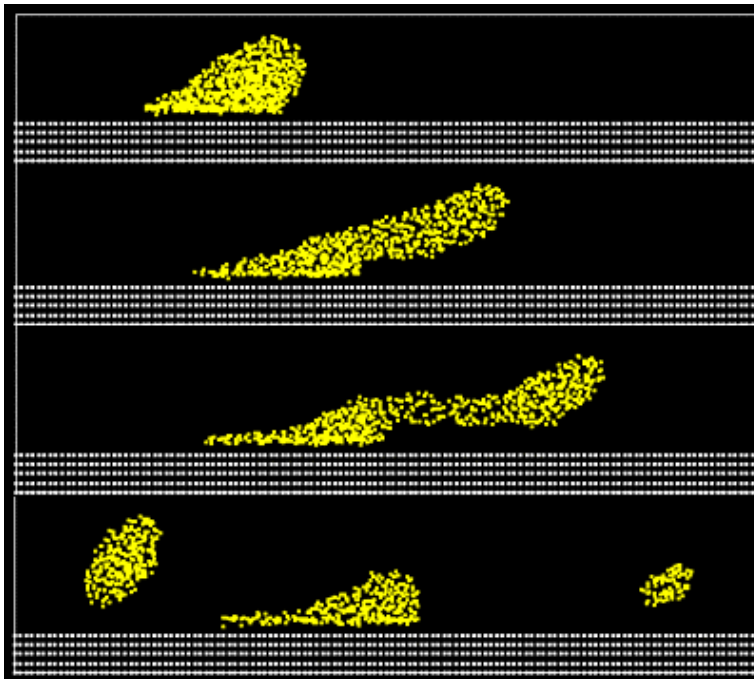


**DPD can be used to probe nanofluidic behaviour, since it operates on the length scale of 100nm. The figure shows the breakup and partial removal of a nano-drop from a surface.**

# *Forcite*

**Forcite** calculates single point energies and performs geometry optimization, i.e. energy minimization, of molecules and periodic systems. For periodic systems, Forcite allows the optimization of the cell parameters simultaneously with the molecular coordinates. In addition, an external hydrostatic pressure may be applied.

During a geometry optimization of a crystal structure, Forcite preserves the symmetry defined by the space group.

Since Forcite is a molecular mechanics tool, its calculations draw upon forcefields, and associated parameters settings. Forcite is designed to work with a wide range of forcefields, and give easy and flexible access to the associated parameter options.

The image below shows hydrogen interaction with a tungsten surface. Geometry optimization with Forcite calculates the physisorption of the hydrogen molecule, which can be used as a starting structure for chemisorption simulations with DMol$^3$ or CASTEP.
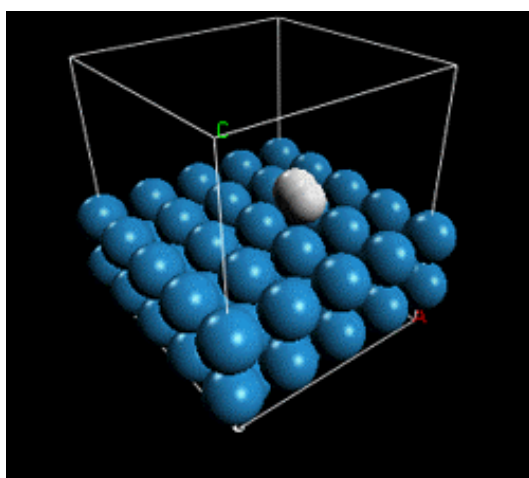


# *Materials Visualizer*

**Materials Visualizer** provides modeling, analysis and visualization tools. Combined with its clear and intuitive graphical user interface, these offer a high-quality environment into which you can plug any MS Modeling product.

Run stand-alone, Materials Visualizer offers a comprehensive modeling and visualization system. You can increase your understanding of materials and improve your communication of chemical information. Visualize and model structures from chemical databases. Build your own molecules and materials with fast, interactive sketching, building, and editing tools. Calculate and display key structural parameters. Display the results of calculations from MS Modeling computations - animated dynamics trajectories, graph data, and molecular models. Annotate models for pictures and diagrams and produce exceptionally high quality hard-copy output.
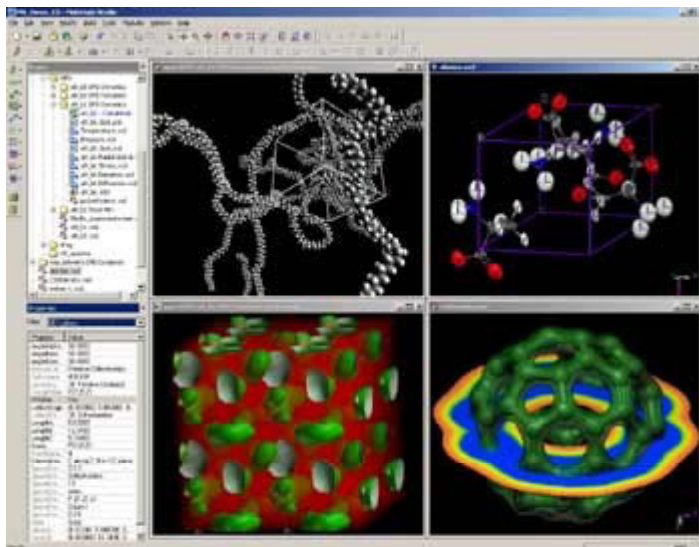
**This is a screenshot of Materials Visualizer, the core MS Modeling product. MS Modeling can display a wide range of materials from bulk amorphous polymers to organic and inorganic crystals. The modules in the MS Modeling suite allow access to tools covering size scales from the quantum to the mesoscale, allowing the calculation of many properties.**

# MesoDyn

**MesoDyn** takes a coarse-grained description of a complex fluid and performs time-evolution dynamics of the density and potential fields of the system. The coarse-graining of the system involves replacing polymer chains by a Gaussian representation with the same response functions and including non-ideality of the system via effective external potentials, the magnitude of which is determined by the Flory-Huggins interaction parameters of the various binary pairs in the system. Electrostatics may be included via the Flory-Huggins parameter, or may be explicitly included for each bead in the system.

The dynamics of the system is described by a set of so-called functional Langevin equations. In simple terms these are diffusion equations in the component densities, which take account of the noise in the system. By means of numerical inversions, the evolution of the component densities is simulated, starting from an initially homogeneous mixture in a cube of typical size 100-1000 nm and with periodic boundary conditions.

A wide range of properties can be calculated with MesoDyn, including:

- Phase morphology
- Aggregation and coagulation
- Effect of confinement on miscibility
- Effect of shear on morphology
- Concentration profiles
- Density histograms
- Free energy and entropy evolution
- Species potential plots (indicating areas of high and low energy)
- Compositional order parameters, giving a direct measure of phase separation.
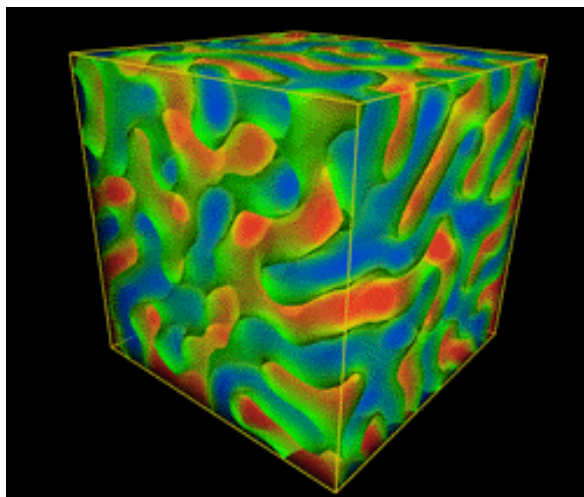
**Image from a MesoDyn simulation of the phase separation of diblock copolymer. The surface links point at the dividing surface between the two phases. The entire volume is color-coded by the density of one of the blocks (red at higher density, blue at low density). This image is a state prior to equilibrium, and the system utimately evolves to a lamellar phase.**

## Reflex Plus

- The Reflex Powder Indexing tool determines the cell parameters and crystal system by indexing the experimental powder diffraction pattern

- The modified Pawley procedure available in the Reflex Powder Refinement module refines the cell parameters, peak shape, and background parameters, and is also a helpful tool to narrow down the list of possible space groups

- The Powder Solve method performs a search of possible arrangements and conformations of the molecular fragments in the unit cell. It finds a structure whose simulated powder pattern matches the experimental one as closely as possible and is also chemically viable

- A final refinement of the proposed solution is performed with the rigid-body Rietveld Refinement functionality available in Reflex.

## VAMP

**VAMP** allows fast and reliable calculations to be performed on large systems utilizing semi-empirical methods. The tasks that can be performed by VAMP range from geometry optimization, transition state search and optimization to the evaluation of many chemical and physical properties. VAMP can optimize monomers and oligomers, calculate input charges for molecular dynamics simulations, for UV/VIS spectra calculations, to calculate potential energy surfaces for force field parameterization, and for IR spectra calculations where force-fields are not applicable.

VAMP implements the Natural Atomic Orbital-Point Charge (NAO-PC) model for molecular electrostatic properties. It gives accurate dipole, quadrupole, and higher moments, and high quality Molecular Electrostatic Potentials (MEPs), many times faster than comparable methods. Molecular quadrupoles calculated with MNDO, AM1, or PM3 agree at least as well with experiment as those calculated using ab initio theory at the MP2/6-31G* level.

VAMP can successfully optimize geometries for which other semi-empirical programs cannot find the minimum. The program also contains two different transition state optimizers: eigenvector following and Powell's method.

Solvent effects are simulated using numerical Self-Consistent Reaction Field (SCRF)[9] calculations for ground and excited states; and COnductor-like Screening MOdel (COSMO) for ground states.

VAMP is the only program that calculates both ESR hydrogen hyperfine coupling constants and ^{13}C chemical shifts using artificial neural nets. Current accuracy (standard deviations from experiment) is about 0.5 Gauss for ESR coupling constants and 6-8 ppm for 13C chemical shifts.

VAMP provides a number of molecular properties such as ionisation potential, multipole moments, accurate molecular polarizabilities, atomic polarizabilites, and optical spectra.
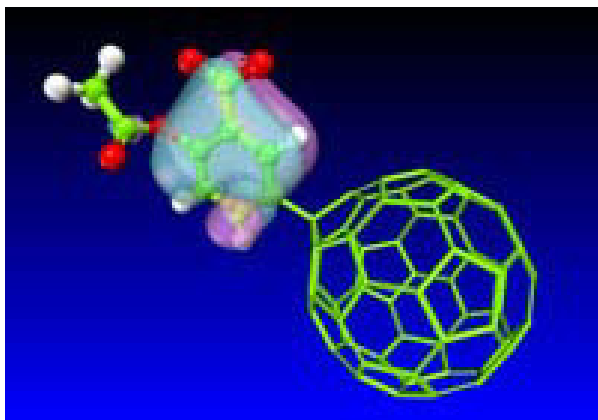


**'Buckyaspirin' - an aspirin molecule attached to a Buckyball. An orbital localized on the phenyl ring is displayed. Calculation performed with MS Modeling's VAMP.**

# An Application Example in MS Modeling

The following example is taken from a tutorial in the MS Modeling 3.0 software:

## *Effect of Water Adsorbates on the Field Emmision from Carbon Nanotubes*

**Purpose**: Provides an introduction on how to use DMol3 in order to compute binding energy of a water cluster to a carbon nanotube under field emmision conditions.

**Modules**: Materials Visualizer, DMol[3]

## Background

Of the various potential application areas of carbon nanotubes, Field-Emission-based Flat Panel display is the closest to realizing the first commercial application. In these devices, electrons are emitted from tips of carbon nanotubes, which have been parallel aligned on a silicon or glass substrate. A practical challenge to make an efficient display is to reduce the operating voltage under which electron emission occurs. One way to achieve this is to introduce adsorbates that might effectively lower the Ionization Potential (IP) and facilitate the extraction of electrons from the tube tip. Important experiments in this context were recently performed at Motorola [1], showing that the presence of water significantly enhances the field emission current from carbon nanotubes.

## Introduction

In this tutorial, you will use first-principles quantum mechanics to compute the binding energy of a water cluster to a nanotube tip under field emission conditions. You will also compute the ionization potential (IP), a measure of the difficulty to extract an electron from the nanotube tip. The MS Modeling module used is DMol[3] [2], a first-principles code based on the density functional theory (DFT). In this code, the electronic wave functions are expanded in an atom-centered basis set defined on a numerical grid.

The cluster of water in this calculation is represented by a H-bonded crown of 5 water molecules. The reason for considering 5 molecules is the fivefold symmetry of the (5,5) nanotube in our simulation, which made it easy to determine a minimum energy structure.

In step 1, you will learn the basics of how a capped nanotube is created, and how you can create a water adsorbate on the top of the capped nanotube. Such structures, once created, need to be optimized with DMol$^3$ in order to obtain accurate binding energies. Since that can take a significantly more time than we can afford here, in step 2, we will perform single point energy calculations on pre-optimized structures.

This tutorial covers:

**1. Sketching a capped carbon nanotube**

Create a (5,5) nanotube stem

Create a stem from a $C_{70}$ molecule

**2. Ab initio calculations**

Computation of the single point energy of the nanotube + water system

Repeat the ebove calculation for the tube.xsd system

Compute the total energy of the water cluster in the absence of any electric field

Compute the binding energy of water to the nanotube

Compute the Ionization Potential (IP)

Note: The most time efficient way for you to carry out this tutorial will be to first just read through Part 1, then carry out Part (2), and while you are waiting for calculation results to complete, attempt to carry out Part 1.

## 1. Sketching a capped carbon nanotube

Create a (5, 5) nanotube stem

First import a model for a 5,5 nanotube in the following way:

On the menubar click on File | Import. Open the folder called Structures | nanotubes, choose 5_5.msi and click Import. On the Menubar click on Build | Symmetry | Supercell. Set the Supercel range A, B, C parameters from 1 1 1 to 1 1 2 and click Create Supercell. In order to create an isolated tube stem, go to Build | Symmetry | Non-periodic Superstructure. Save this structure as stem. The document stem.xsd appears in the Project Explorer.

Note: You could create a longer stem by choosing a longer supercell in the Z-direction.

Create a cap from a $C_{70}$ molecule

Similar to above, import a $C_{70}$ structure document:

File | Import, go to Structures | organics, choose C70.msi, click Import.

Next, locate the equatorial plane passing through only hexagons (this plane is perpendicular to the long axis o f the $C_{70}$ 'ellipsoid'), and orient it horizontally. You should see clearly 30 carbons in the top half, 30 in the bottom and the equator of 10 carbons as indicated:
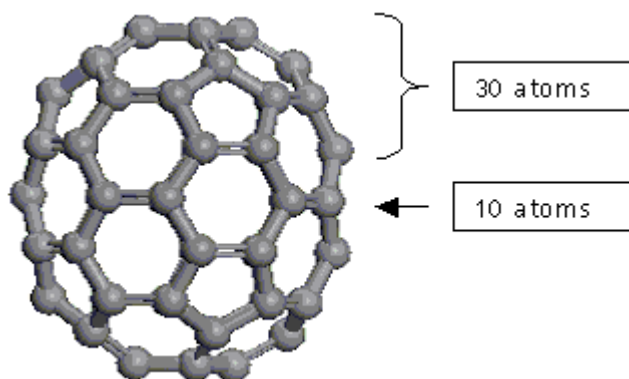
C$_{70}$ structure

Now select and delete the bottom 30 atoms. This can be done in the following way:

Click on the 3D Viewer Selection Mode button [icon] on the toolbar, then click and hold left mouse button and drag a selection box around the bottom 30 atoms. Once the selection is done hit the DELETE key on your keyboard.

You should be left with a 40 atom cap. This is a good representation of a cap for a (5,5) nanotube.

 Save this structure as cap. The document cap.xsd appears in the Project Explorer.

You can now add the stem created in the previous step to the bottom of the cap in order to obtain a capped nanotube. This will require the following steps:

(a) Create a new file by doing: File | New | 3D Atomistic Document. (b) Make the stem.xsd file active. Then copy the structure, Edit | Copy and paste it in the new document: Edit | Paste. Repeat these actions with the cap.xsd file. (c) While the cap structure is selected in the 3D Atomistic Document (in yellow) make the necessary moves (rotations and translations) to bring the cap on the top of the stem in a such configuration that hexagones can be formed between the stem and cap end carbons. (d) Click on [icon] to create the missing bonds. (e) Click on [icon] to 'clean' the structure. Finally, save the document as my_tube.xsd and carry out a Geometry Optimization with the Forcite module: Modules | Forcite | Calculation. Click Run on the Setup tab.

After the calculation is finished you close all windows and save the changes in the my_tube.xsd file.

For the next step you need to sketch a water molecule in a new 3D Atomist Document.

Make my_tube.xsd document active. Copy the water molecule and paste it in the my_tube.xsd document. Place the water molecule on the top of the tube. Repeat this action 4 more time. Save this document as my_tube5water.xsd.

The final structure of the system should like:
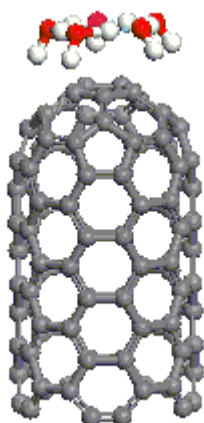
The tip with the water cluster

In an actual research project, the next step would involve performing a geometry optimization using DMol$^3$. However, to save time, we have provided you with the pucture-optimized structures of: (1) the isolated nanotube **tube.xsd**, where only the 40 atoms from the $C_{70}$ has been retained; (2) a H-bonded cluster of 5 water molecules **5water.xsd**; and (3) the nanotube with the water cluster adsorbed on it **tube_5water.xsd**.

In the first two structures, the tube axis is aligned along the negative Z-direction. In order to simulate Field Emission conditions, calculations of systems (1) and (2) are performed in the presence of an electric field oriented along the positive Z-axis, while calculation for system (3) is performed in zero electric field. See ref. [3] for more details.

## 2. Ab initio calculations

Compute the single point energy for the tube + water system

Import the structure documents tube.xsd, tube_5water.xsd, and 5water.xsd. Make tube_5water.xsd the active model. Locate the DMol$^3$ module icon and open the Calculation window. On the Setup tab choose the following settings: Task to Energy; Basis Set to MIN; Functional: GGA, PBE On the Electronic tab set: Integration Accuracy to Coarse, SCF Tolerance to Coarse, Real Space cutoff to 3.5 Angstrom. Click on More, check Use Smearing.

Next you need to save the input deck.

Click on Files at the bottom of the window, then click on Save Files.

Finally, we need to add some advanced information directly into this input deck which you have just saved.

In the Project Explorer, double click open the tube_5water.input file. Add the following lines anywhere in the document and then Save the file.

Symmetry          c1

Electric_Field        0.0 0.0 0.02

The **Symmetry** line is to make sure that DMol3 does not reorient the molecule away from the current alignment along the Z-direction. The electric field units are in Hartree/Bohr, which implies a field of ~ 1 volt/Angstrom parallel to the tube axis directed toward the nanotube cap from above [3].

With the tube_5water.input file still in view,

click on Run Files to start the Calculation. Click on Yes to the dialog asking to save changes in input file. Once the calculation finishes, open the tube_5water.outmol file. Note the total energy Ef toward the end of the file. It should be $E_{tube\_5water}$ = -1901.0883766 Ha.

Repeat the above calculation for tube.xsd system

In order to do this use the same DMol$^3$ settings as above, and make the same changes to the **tube.input** file as for the **tube_water** system. The total energy should be $E_{tube}$ = -1519.579648 Ha.

**Compute the total energy of the water cluster in the absence of any electric field**

Make **5water.xsd** the active model.

Open the DMol$^3$ Calculation panel, and with all settings unchanged, click on Run. After the job finishes, check the total energy. It should be $E_{5water}$ = -381.4085840 Ha.

**Compute the binding energy of water to the nanotube**

It is given by the formula $E_{tube}$ + $E_{5water}$ - $E_{tube\_5water}$ = 0.1001446 Ha = 62.84 kcal/mol. (1Ha = 627.5095 kcal/mol). This large binding energy is in agreement with the stability of water molecules on the nanotube tip to temperatures as high as 900 K [1].

**Compute the ionization potential (IP)**

In order to obtain an insight into the effect of adsorbed water molecules on the field emission current, it is interesting to compute the ionization potential (IP) of an electron from the nanotube tip in the presence and absence of water. The IP is defined as the difference in energy between a system with a +1 charge (i.e., 1 electron removed) and the original system with a net zero charge. Also, the system with the +1 charge has essentially the same atomic geometry as the neutrally charged system, because the resulting "hole" almost immediately recombines with an electron flowing in from the stem side of the nanotube. Thus all we need to perform is a single point energy with the same DMol3 settings as before, except that the charge has to be set to +1.0.

Double click to open the tube_5water.input file, change the Charge from 0.000 to 1.000, click on Files... on the DMol$^3$ Calculation panel, and click Run Files... Note the total energy of the +1 charged system. It should be $E_{tube\_5water\_charged}$ = -1900.7002016 Ha. Repeat the above for tube.input. The total energy of the +1 charged tube chould be $E_{tube\_charged}$ = -1519.1810342 Ha.

The IP for the tube (in absence of water) is therefore $E_{tube\_charged}$ - $E_{tube}$ = - 1519.1810342 + 1519.5796480 = 0.398614 Ha. In the presence of water, the IP becomes $E_{tube\_5water\_charged}$ - $E_{tube\_5water}$ = 1901.0883766 - 1900.7002016 = 0.388175 Ha.

So, the presence of the water cluster lowers the IP by 0.398614 - 0.388175 = 0.01044 Ha = 6.55 kcal/mol, thereby enhancing field emission current at a given voltage.

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3. A. Maiti, J. Andzelm, N. Tanpipat, and P. von Allmen, *Phys. Rev. Lett.*, 2001, **87**, 155502.

# List of Publications in the Different Nanotechnology Areas

The following is a list of some of the many publications in different areas of nanotechnology, using Accelrys' materials modeling software.

## *Carbon Nanotubes*

Accelrys + Motorola: Field Emission & Effect of Adsorbates
A. Maiti *et al.*, *Phys. Rev. Lett.*, 2001, 87, 155502.
Accelrys + NASA Electromechanical Sensors
A. Maiti, A. Svizhenko, and M. P. Anantram, *Phys. Rev. Lett.*, 2002, 88, 126805.
Accelrys + Trinity College, Dublin Polymer-Nanotube Complex
'Selective interaction in a polymer - single wall carbon nanotube composite', M. in het Panhuis *et al.*, *J. Phys. Chem. B*, 2003, 409, 178.
NIST (Tanner Yildirim)
'Pressure-induced interlinking of carbon nanotubes', T. Yildirim *et al.*, *Phys. Rev. B*, 2000, 62, 12648-12651.
'Variable and reversible quantum structures on a single carbon nanotube', Ç. Kiliç *et al.*, *Phys. Rev. B*, 2000, 62, R16345.
Wright Patterson (Ruth Pachter)
'Comparative theoretical study of single-wall carbon and boron-nitride nanotubes', *Phys. Rev. B*, 2003, 67, 245404.
Cambridge Univ. (Michael Payne) Doping
'Manipulation of CNT using N-impurities', *Phys. Rev. Lett.*, 2003, 91, 105502.

## *Chemical Sensors*

**Accelrys + Berkeley + Brookhaven**
'$SnO_2$ Nanoribbons as $NO_2$ sensors', A. Maiti, J. Rodriguez, M. Law, P. Kung, J. McKinney, and P. Yang, *Nano Lett.*, 2003, **3(8)**, 1025.

## *Liquid Crystals*

**Wright Patterson (Ruth Pachter)**
'Polymer-dispersed liquid crystalline system' S. S. Patnaik and R. Pachter, *Polymer*, 1999, **40**, 6507-6519

## *Optoelectronics*

**University of Medan (Marcello Luppi):** Si Nanodots
M. I. Luppi and S. Ossicini, *Phys. Stat. Solidi (A)*, 2003, **197**, 251; N. Daldosso, M. Luppi, S. Ossicini *et al.*, *Phys. Rev. B.*, 2003, **68**, 085327; M. Luppi and S. Ossicini, *J. Appl. Phys.*, 2003, **94**, 2130.

## *Nanocomposites*

**Cornell (E.P. Giannelis)**
R.A. Vaia and E.P. Giannelis. MRS Bulletin, May 2001, Volume 26, No 5; and D.B. Zax, D.-K. Yang, R.A. Santos, H. Hegemann, E.P. Giannelis, and E. Manias, *J. Chem. Phys.*, 2000, **112**, 2945.
**University of London (P. Coveney)**
P. V. Coveney, J. L. W. Griffin, M. Watkinson, A. Whiting, and E. S. Boek, *Mol. Sim.*, 2002; and S. Stackhouse, P. V. Coveney, and E. Sandre, *J. Am. Chem. Soc.*, 2001, **123**, 11764-11774.

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## *Catalysts*

**Brookhaven National Lab** DeNOx/ DeSOx catalysis
http://www.accelrys.com/cases/denox.html

## *Nanostructured Polymer Blends*

**Rhodia**: T. Spyriouni and C. Vergelati, *Macromolecules*, 2001, **34**, 5306.

## *Nanostructured Polymers / 'Soft Nanotechnology'*

**University of Bayreuth and Leiden:** Block copolymers phase behavior in thin films A. Knoll *et al*., Physical Review Letters 89(3), 035501, 2002, see also http://www.uni-bayreuth.de/departments/pcii/magerle/index.html
**University of Leiden:** Model for Pattern Formation in Polymer Surfactant Nanodroplets, J.G.E.M. Fraaije and G.J.A. Sevink, *Macromolecules*, 2003.
**Accelrys, University of Cambridge, Nanyang University Singapore:** Drug Delivery Micellar drug delivery systems. Y.M. Lam, G. Goldbeck-Wood and C. Boothroyd, *Mol. Sim.*, accepted for Nanotech2003 Special Edition, 2004.