

Simulating Clusters and Interfaces
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INVITED TALKS

Energy Landscapes of Clusters, Biomolecules and Solids

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The energy landscape approach to structure, dynamics and thermodynamics appears to hold the key to resolving both the Levinthal and Kauzmann paradoxes. For small clusters it is possible to find all the important minima and the pathways that link them. Hence for water clusters one can determine the appropriate molecular symmetry group with which to characterise the energy levels of these non-rigid systems.

To treat larger systems the superposition approximation may be used to calculate approximate thermodynamics and the master equation may be used to study relaxation dynamics. Clusters provide examples of both efficient relaxation to the global minimum and of trapping.

Disconnectivity graphs enable us to visualise a high dimensionality potential energy surface. To some extent the dynamics and thermodynamics of the system can be deduced simply by inspecting its disconnectivity graph. Examples are provided by the annealing of C60 to buckminsterfullerene, the folding of a model polypeptide and the freezing of a "nanodroplet" of water.

The insight gained from studies of clusters and abstract energy landscapes led to the "basin-hopping" approach to global optimisation. This algorithm produced the best results in the literature for Lennard-Jones clusters and has since been applied to a range of atomic and molecular clusters.

Metal Clusters: Structures, Mixing, Phases, Reactivity, and all that *

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Results of dynamical and statistical simulation studies of metal clusters of different materials and sizes will be reviewed and discussed. The simulations are based on either first principles or semiempirical many-body potentials. The discussion will encompass structural issues, mixing vs.

segregation in two-component alloy clusters, thermal properties (including composition-dependent peculiarities), electronic features, and interactions of clusters with molecules.

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Extending Atomistic Simulation time scales

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A significant problem in the atomistic simulation of materials is the time scale limitation of the molecular dynamics method. While molecular dynamics can easily access nanoseconds with empirical potentials, many of the most interesting diffusive events occur on time scales of microseconds and longer. If the transition state (i.e., the saddle point) for a given reaction pathway is known, transition state theory can be applied to compute a rate constant directly. If all possible events are known for a given system, these rate constants can be employed in a kinetic Monte Carlo algorithm to evolve the system from state to state over long time scales. Unfortunately, for realistic systems, the transition states are often hard to find. Moreover, it is often the case that our intuition about how the system will behave breaks down, so that key events are missing from the kinetic Monte Carlo treatment. This situation is typical in metallic surface growth, where complicated exchange events prevail, and in many other physically important processes, such as annealing after radiation damage, or diffusion at a grain boundary.

I will discuss some new methods for treating this problem of complex, infrequent-event processes. The idea is to directly accelerate the molecular dynamics simulation to achieve longer times, rather than trying to specify in advance what the available mechanisms are. These new methods, hyperdynamics, parallel replica dynamics, and temperature extrapolated dynamics, can be used individually, or in combination, to extend the molecular dynamics simulation time by orders of magnitude, thus making much closer contact with experimental conditions. I will discuss the relative merits of the different methods and present results demonstrating the power of this general type of approach. Examples will include growth of a copper surface from vapor deposition and from ionized physical vapor deposition.

Theory modelling and simulation of surfactant self-assembly processes

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One major challenge for modelling and simulation is linking microscopic to macroscopic properties, particularly in non-equilibrium situations. Amphiphilic fluids provide an example of the general problem: the macroscopic behaviour is determined by microscopic and mesoscopic features, yet the timescales for most micellar and interfacial self-assembly processes are too long to be accessible by conventional molecular dynamics methods. In this talk, we shall describe some recent very large scale (massively) parallel MD simulations of amphiphilic self-assembly, and compare and contrast the information available from such atomistic approaches with more coarse-grained but much faster mesoscale (lattice gas, lattice-Boltzmann and dissipative particle dynamics) methods, as well as kinetic theories based on the Becker-Doering cluster aggregation/fragmentation equations.

CONTRIBUTED TALKS

The Dynamics of Protonated Rare Gas Clusters: Quantum and Classical *ab initio* Simulation

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The presence of the “naked” proton or, more realistically, the presence of protonated molecular species has always played a major role in the understanding of a large class of chemical processes. The possible understanding of the microscopic mechanisms which preside over the formation of such species, therefore, is of marked importance in many areas of chemical physics. In the last few years we have undertaken a systematic study of the possible stable structures of H^+ inserted in small He and Ar clusters by analysing the ionic chromophores in both systems using *ab initio* quantum methods [1,2,3]. We have further extended the study to the possible dynamics of cluster growth and cluster break up by using *ab initio* molecular dynamics simulations and simulated annealing methods [4,5,6].

Finally, we have investigated the role of quantum effects by constructing the smaller clusters using stochastic methods and quantum diffusion Montecarlo techniques [7]. The combination of all the above methods turns out to provide a rather detailed picture of the microscopic phenomena and to yield specific, and realistic answers for the many questions related to the modelling of microsolvation with small rare gas clusters.

The most recent results will therefore be reported at the meeting and discussed under the above global analysis of our simulations.

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Optimisation of cluster geometries for single and multi-component systems using a genetic algorithm

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Applications of Genetic Algorithms for optimisation of atomic and molecular clusters are reported. It is shown that the genetic algorithms are very useful tools for determining the minimum energy structures of clusters of atoms described by many-body interatomic potential functions containing up to a few hundred atoms. The algorithm generally outperforms other optimisation methods for this task. A number of applications are given including covalent carbon and silicon clusters, close-packed structures such as argon and silver and the two-component C-H system.

Large Structural and Electronic Properties of Small Gold Clusters

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We have investigated the structural properties of several small ordered and disordered gold clusters by computer simulation molecular dynamics using a Gupta n-body model potential. A common-neighbour analysis was implemented in order to characterize the degree of order. Distorted multilayer icosahedral order was found to be most representative of the disordered clusters with the lowest energies. At higher energies the amorphous structures are characterized by the presence of distorted local icosahedral order. We discuss the origin of the stability in both ordered and disordered gold clusters, and present the total density of states (TDOS) calculated by the extended Hückel method for both ordered and disordered gold clusters.

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From Clusters to Colloids: Modelling the Structures of Gold Nanoparticles

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Metal nanoclusters promise to be of significant technological importance. There is particular interest in clusters and colloids of gold (indeed colloidal gold has been known since Egyptian times). Unfortunately, it is often difficult to determine the structures of these nanoparticles directly, which is why theory continues to play an important role in cluster science. This presentation will describe the application of a many-body potential to predict structural motifs and stabilities of gold clusters in the nanometer size range.

Theory of the Island and Capture Zone Size Distributions in Thin Film Growth

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A striking characteristic of the early stages of thin film deposition, where the deposited monomers cluster together into islands, is the scaling property of the island size distribution observed both experimentally and in simulations. The origin of this phenomenon has recently been explained through identifying Voronoi-type capture zones with the island growth rates for the broad range of systems where island development is controlled by the surface diffusion of the monomers. However a gap in the full understanding of the islands' scaling properties remains, because the ongoing nucleation of islands during the deposition process continually changes the network of capture zones and leads to non-trivial broadening of the island sizes. In this presentation we show how this gap is closed by modelling the evolution of the joint probability distribution of island and capture zone sizes, taking into account both island nucleation and growth throughout the film deposition. Furthermore our analysis reveals that the joint probability has robust scaling for spontaneous nucleation (e.g. islands nucleating through the interaction of monomers with the substrate) and a weak coverage- dependence only for systems where it takes two monomers to nucleate an island. The solutions to our model equations correspond well to the joint probability distributions found in thin film deposition simulations. We also find quantitative predictions for the island size distributions that agree well with simulations and experiments for the first time. The work is of importance for many technological systems where the understanding and control of the island sizes and their spatial arrangements is crucial.

Simulation of Colloidal Particles at Fluid Interfaces

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Colloidal particles are relevant in different areas of practical interest such as the petrochemical industry, foam science and also, more recently, in the synthesis and characterisation of nanomaterials. These nanomaterials are often prepared as thin films at fluid interfaces. In this talk we will describe the behaviour of a single colloidal particle, with size of a few nanometers, at liquid-vapour and liquid-liquid interfaces. Molecular dynamics simulations of this model allows us to study the factors that influence the stability of spherical substrates at interfaces. In particular our work has provided information on the role and size of the line tension in determining the contact angle the fluid makes with the colloidal particle.

We also consider a monolayer of colloidal particles at a liquid-liquid interface. This monolayer is compressed emulating a real Langmuir-trough experiment. These studies give insight into the response of the monolayer to compression and are also helpful to assess the validity of thermodynamic analyses, which are the basis for interpretation of the Langmuir-trough experiments.

During this talk we will discuss also the validity of macroscopic approaches such as Young's equation. We consider wetting in systems involving nanometer curved surfaces, such as the colloidal particle considered above, and also liquid lenses at interfaces, which exhibit the interesting phenomena of spreading.

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Car-Parrinello Simulation of H₂O on Rutile

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Titanium implants are widely used because they exhibit both high biocompatibility and favorable mechanical properties. In practice the surface of metallic titanium reacts with ambient oxygen to form an TiO₂ layer which is covered by physi- and chemisorbed water. The adhesion of amino acids on this hydroxylated titanium oxide governs the biocompatibility, but only a few studies are dealing

with the mechanism of this process, reporting both physisorption [1] and bonding of the carbonyl group to dehydroxylated surface Ti [2].

Progress in this field at first affords a good understanding of the hydroxylation of TiO_2 . It was shown by thermal desorption that the (110) surface is not very reactive as compared to (100) [3]. Recently a complicated mechanism for the dissociation of water on oxygen vacancies in the (110) surface was proposed [4]. First principles molecular dynamics gives direct access to reactions mechanisms on oxides [5]. A CASTEP simulation [6] resulted in spontaneous dissociation of adsorbed H_2O on rutile (110). A more detailed study by the same authors [7] revealed that at higher coverages molecular rather than dissociative adsorption occurs and that the energy gain of the dissociation process itself is only 0.04 eV which is well below kT .

Here first results of a calculation using the Car Parrinello method with ultrasoft Vanderbilt pseudopotentials and gradient correction are presented. Simulation cells for both (110) and (100) consist of three layers with four Ti and eight O atoms each. During short molecular dynamics runs the temperature was stepwise increased by rescaling velocities. Then the trajectories for free dynamics were recorded for some thousand time steps (0.17 fs). Neither on (110) nor on (100) clean surfaces spontaneous dissociation of adsorbed water was observed. As this could be due to an unfavourable starting position of the water molecule, the dynamics of dissociated water molecules was simulated. This resulted in recombination within less than one ps implying that hydroxylation does not occur via water adsorption on regular surfaces. In contrast to that water molecules readily dissociated after insertion into an oxygen vacancy on the (100) surface.

Addition of further hydrogen resulted in a very stable fully hydroxylated (100) surface, which is used as basis for the adsorption of amino acids. In a first calculation the carboxyl group of a cystein molecule formed hydrogen bonds with the surface hydroxyl groups indicating that their structure is essential for the adsorption process. Work in this field is in progress.

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Modelling the Effect of Inhibitors on the Growth of Wax Crystals

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The deposition of wax from hydrocarbons is a significant problem for the oil industry, as the deposited wax tends to block pipelines and restricts the flow of oil. Research into effective inhibitors, which reduce the deposition rate to an acceptable level, is in progress. Such inhibitors generally have a dramatic effect on the morphology of deposited wax crystals.

We have used computer modelling techniques to study the interaction between inhibitor molecules and a number of wax crystal surfaces. It was found that the polymer tails of the inhibitor tend to align with the C chains and the inhibitor molecules interact strongly with the wax surface. Two low energy configurations were found, one with the polymer tails pointing in the same direction (closed) and the other with the polymer tails pointing in opposite directions (open). The strong interaction between the molecule and the wax crystal is suggestive of an inhibitor mechanism that involves the incorporation of the additive into the growing crystal, resulting in a weaker, defective crystal.

A model of crystal growth has been developed in which the wax molecules are deposited in a low energy configuration on a surface, using a molecular dynamics technique. The resulting surface is annealed to reduce the density of defects. Three different growth simulations were performed for the (010) surface: one using a clean surface, one with an adsorbed inhibitor molecule in the closed configuration and one with an adsorbed inhibitor molecule in the open configuration. The same number of molecules was deposited in each case. The configuration and energy of the deposited molecules were examined and compared for the three cases. The inhibitor molecules were found to be a source of defects in the growing crystal. These defects weaken the crystal structure and modify the surface energy, and consequently the shape, of the crystal.

The effect of corrosion inhibitor films on deposition of wax to metal oxide surfaces

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There are some processes such as corrosion, scale deposition, wax deposition and clathrate hydrate formation which reduce the efficiency of the transport processes in the oil and gas pipelines. The interaction between these effects is significant. There have been some theoretical and experimental studies in order to understand the separate processes and develop inhibitors to protect the pipelines from them, however there is little information about the interplay between the different processes. The pipelines made of mild steel lead to an oxide film on the iron surface, which mostly presents a hematite structure. To protect this surface from the corrosion it is common to add specific molecules that form protective films and thereby inhibit the process [1,2] Nevertheless, it has been observed that the use of these compounds can induce the wax deposition. In this work, by using molecular dynamics techniques we have studied the deposition processes of the most common alkane chains and their crystal growth on the hematite surface. Adsorption of oleic imidazoline molecules used as corrosion inhibitors has also been modelled. Finally, we have simulated the behaviour of wax molecules in presence of the adsorbed corrosion inhibitor. It has been observed according to the experimental evidences that the inhibitor favours the wax deposition.

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Molecular Dynamics Studies of Nucleation and Critical Nuclei in the Freezing of Molecular Liquids

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We report the behavior of large liquid clusters subjected to deep supercooling. Several features distinguish our work from that of virtually all prior MD studies of nucleation. First, we investigate clusters instead of bulk-like systems to avoid effects of periodic boundary conditions, and our subjects are polyatomic molecules, not atoms. In addition, we observe spontaneous nucleation (i.e., nucleation unaided by biasing potentials or the implantation into the liquid of preformed nuclei). Our critical nuclei do not much resemble the idealized nuclei often envisaged by theorists. Our most striking result is that the nucleation rate decreases with increasing cluster size even after the effect of Laplace pressure is taken into account. This is because nuclei preferentially form at or near the surface.

The Riddle of Resorcinol Crystal Growth Revisited: Molecular Dynamics Simulations of α -Resorcinol Crystal - Water Interface

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The mechanism by which solvent exerts its effect during the process of crystallisation is poorly understood. An important and ongoing problem is the uneven growth of the faces $\{0\ 1\ 1\}$ and $\{0\ \bar{1}\ \bar{1}\}$ of α -resorcinol in water. Growth occurs mainly at the $\{0\ \bar{1}\ \bar{1}\}$ surface. In an attempt to determine the mechanism, molecular-dynamics simulations have been carried out of the two surfaces in contact with water. The dynamical properties of the water close to the surface as well as the overall interaction energies of the water with the respective faces have been calculated. The strongest water-binding sites have also been determined and energetically characterised. The data indicate that the adsorption of water molecules is stronger at the slower growing $\{0\ 1\ 1\}$ face, with the strongest binding occurring at specific sites on this face. The motion of the water molecules in the surface layer at this face is also more localised and restricted compared with that at the faster growing $\{0\ \bar{1}\ \bar{1}\}$ face. The binding sites at the $\{0\ 1\ 1\}$ surface are not within the grooves that are present at this surface but are located above the outermost part of the crystal surface. The water molecules form strong hydrogen bonds with the limited number of hydroxyl oxygens of the resorcinol molecules protruding from the surface. The overall inference is that the stronger binding of the water molecules at the $\{0\ 1\ 1\}$ surface serves to retard crystal growth, rather than enhancing it as predicted by the surface roughening theory.

The Simulation of Osmosis and Semi-Permeable Membranes.

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The first computer simulation of osmosis using tolerably realistic semi-permeable membranes was performed in 1993 [1]. This topic has developed rapidly and there are now some twenty papers treating both statics and dynamics of osmosis, reverse osmosis and electro-osmosis. The "experiments", the membranes and the mixtures are becoming rapidly even more realistic and more useful. This has led to a better understanding of the osmosis mechanism especially as regards the dynamics of the process and will surely lead to better, and better-designed, membranes.

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Modelling Meso-Scale Diffusion Processes in Stochastic Fluid Bio-membranes

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The space-time dynamics of rigid inhomogeneities (inclusions) free to move in a randomly fluctuating fluid bio-membrane is derived and numerically simulated as a function of the membrane shape changes. Both vertically placed (embedded) inclusions and horizontally placed (surface) inclusions are considered. The energetics of the membrane, as a two-dimensional (2D) meso-scale continuum sheet, is described by the Canham-Helfrich Hamiltonian, with the membrane height function treated as a stochastic process. The diffusion parameter of this process acts as the link coupling the membrane shape fluctuations to the kinematics of the inclusions. The latter is described via Ito stochastic differential equation. In addition to stochastic forces, the inclusions also experience membrane-induced deterministic forces. Our aim is to simulate the diffusion-driven aggregation of inclusions and show how the external inclusions arrive at the sites of the embedded inclusions. The model has potential use in such emerging fields as designing a targeted drug delivery system.

Growth mechanisms in calcite

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Molecular dynamics simulations were used to model two stepped $\{10\bar{1}4\}$ surfaces of the calcium carbonate polymorph, calcite. The acute monatomic steps were found to be more stable than the obtuse monatomic steps. Using potential parameters which reproduce the experimental enthalpies of growth of the calcite crystal, the formation of the double kinks on the obtuse step is shown to cost less energy than growth onto the acute step, probably due to the lower stability of the obtuse surface. The simulations suggest that formation of the kink sites on the growing edge of the obtuse step of calcite is the rate-determining step and this edge is predicted to grow preferentially, which is in agreement with experimental findings of calcite growth under aqueous conditions.

Growth of magnesium ions onto the growing calcite steps is an exothermic process on both acute and obtuse edges, indicating that incorporation of magnesium into the calcite crystal is a straightforward process on energetic grounds. These results agree with the fact that large amounts of magnesium are found in calcite crystals. Subsequent growth of calcium ions onto the magnesium terminated edges is endo-thermic which indicates that precipitation of magnesium onto the edges inhibits calcite growth, again in agreement with experimental findings.

Methane Hydrate: Memory and Melting

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We present the results of a long timescale molecular dynamics simulation of a methane hydrate / methane gas interface formed along the [0 0 1] hydrate surface. The simulations were performed at 15 - 20°C above the stable hydrate temperature so that we were able to observe melting under conditions that were sufficiently gentle to allow any residual order associated with the memory effect for hydrate nucleation to be identified. The simulations have been analysed using a set of novel order parameters designed specifically to quantify the microscopic molecular structure associated with the different phases of water. The simulations do show an enhanced level of ice- and clathrate-structure in the liquid water that forms when the hydrate decomposes, but there is no evidence of significant clusters of the ordered water.

Monopoles, Dipoles and Quadrupoles, A Chemist's Perspective

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The usefulness of the partial atomic charge approximation and its definitions are discussed. This leads on to the definition and use of the higher moments. In the world of modern computational density functional theory is any of this any use by comparison with the full density?

Notwithstanding that for a thousand pounds one can buy as much computing power in a supermarket as was in the national computer centre 20 years ago some calculations which can be done on the back of an envelope are presented. Such calculations often make use of the archaic concept of electronegativity, used continually in chemical discussion, but not so useful where $\Delta\chi$ is small. Concepts such as the chemical potential of a single molecule are however fully and precisely definable in density functional theory.

Very often in the real world we have an inverse problem of the problem we can really answer. "Give me a molecular system which has properties A, B, C, and not D, which costs less than

E dollars per kilogram and can be safely buried in the garden when we have done with it.” Often our only answer is: “give me the geometry of a candidate and I will give you the values of A-D to within a fifth of an order of magnitude”. The crude way to invert this problem is to generate and screen all plausibilities with a fast algorithm. Regrettably it appears to be desirable that the same person must be able to do both supercomputer and back of the envelope calculations in order to be able to interpret, explain and predict the properties of matter, tough!

Large Molecular Dynamics Simulations of Nanocolloidal Liquids

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Nanocolloids are at the forefront of technology as small-scale devices are starting to feature nanocolloids and nanocolloidal technology *e.g.*, in the area of data storage and ‘defect-free’ ceramics. Nanoparticles are also ‘primary’ particles that are the initial stages of precipitation of inorganic and polymers from solution. Overbased detergent (surfactant-coated calcium carbonate particles) are nanoparticles added to automotive and marine engine lubricants to neutralise the acidic by-products of combustion which would otherwise corrode the engine.

In this talk I will review our ongoing simulation studies of nanocolloids and nanocolloidal liquids [1]-[11]. Molecular Dynamics, MD, simulations have been used to calculate the translational and rotational relaxation dynamics of model atomistically rough spherical nanocolloidal particles in solution at infinite dilution by immersing a single Lennard-Jones cluster in a molecularly discrete solvent. The effects of the relative solvent and colloidal particle mass density, and colloid size on the translational and rotational self-diffusion coefficients were investigated. At liquid-like number densities ($\rho_s = N\sigma_s^3/V \simeq 0.9$) the translational, D , and rotational, D_{rot} , self-diffusion coefficients for the nanocolloids of all sizes were statistically independent of the ratio of colloidal to solvent particle mass density up to the value of ca. 20.0 explored.

Key timescales characterising colloidal particle dynamical relaxation were computed from time correlation functions. For translational motion these were τ_v , the colloidal velocity relaxation time, τ_f , the hydrodynamic relaxation time and the timescale for significant particle displacement, τ_d . We show that $\tau_v \simeq \tau_f$ when the relative mass density of the colloidal particle divided by the bulk density of the solvent is *ca.* $\rho^* = 20$, in agreement with theoretical predictions. Preliminary evidence from the velocity autocorrelation functions, VACF, of the nanocolloidal particle also supports the theoretical treatments that the transition from the Liouville to Fokker-Planck description (evident by exponential decay in the VACF) is determined by both the colloidal particle mass **and** size.

We calculated the relaxation times for angular velocity relaxation, τ_ω and reorientation, τ_u and found them to scale reasonably well with the relaxation time for the free rotor, for size dependence but not so well for mass dependence. The angular velocity correlation function of 13 atom clusters departed from Langevin (exponential) relaxation also for $\rho^* < 20$. The rotational self-diffusion coefficient was also non-classical in this range.

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POSTER ABSTRACTS

Ab initio density-functional calculations of the geometries, electronic structures and magnetic moments of Ni-Al clusters

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We report *ab initio* molecular dynamics simulations of Ni₂, Al₂, Ni₁₃, Al₁₃ and Ni₁₂Al clusters using SIESTA [1], a fully self-consistent density-functional method that employs linear combinations of atomic orbitals as basis sets, standard norm-conserving pseudopotentials and a generalized-gradient approximation to exchange and correlation (see Ref. [2]). Our results for the pure Ni and Al clusters, which are compared with those obtained by other recent *ab initio* calculations [3,4], are in good agreement with available experimental data. For the binary cluster Ni₁₂Al our calculations show that a distorted icosahedral configuration with the Al atom at the cluster surface is more stable than that with the Al atom located at the central site, a result which clarifies discrepancies between the results of different semiempirical treatments [5,6].

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Computer Modelling of Metal Carboxylates

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A key feature of this work has been the development of a working potential model for metal carboxylates, and an assessment of its transferability to related molecular systems. The structures of these organic salts depend on a combination of strong ionic forces and weak van der Waals forces. This system exhibits mixtures of bonded and non-bonded interactions which need to be considered in the potential model.

The aim of this work was to establish a set of potentials that could describe the structure and properties of the short chain metal carboxylates, sodium and lithium acetate.

Empirical potential fitting was used to obtain potentials for lithium acetate dihydrate and anhydrous sodium acetate. The results showed good agreement with the experimental crystal structure.

Computer Modelling of Crystal Morphology

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During the last 10 years the growth in computer power, both hardware and software has meant that computers are no longer used solely for the reproduction and analysis of experimental data, but can be used as a predictive tool in the determination of crystal morphology.

The technique of lattice energy minimisation, using the GULP (General Utility Lattice Program) code has been used to model the calcite phase of calcium carbonate. The original potential model [1] has been modified in light of recent work carried out on modelling solids containing molecular ions [2,3]. Results are presented of the calculated bulk structure.

The next stage of the project has involved the use of the MARVIN program to calculate surface and attachment energies, and hence predict the morphology of calcite. Results are presented of the calculated surface and attachment energies of calcite.

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The effect of ion localization on cluster size. MD simulations of $\text{Cl}(\text{H}_2\text{O})_n$ ($n=10, 25, 50, 100, 200, 400, 800$) clusters

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MD simulations on $\text{Cl}(\text{H}_2\text{O})_n$ ($n=10, 25, 50, 100, 200, 400, 800$) clusters have been performed in order to study the effect of the location of the Cl^- ion in the water clusters. A new augmented NEMO potential has been used for the $\text{H}_2\text{O}-\text{H}_2\text{O}$ and $\text{H}_2\text{O}-\text{Cl}^-$ interactions. It was found that the ion prefers to locate at the surface of the cluster for all the cluster sizes above. It was also found that the ratio polarizability/size of the ion plays an important role for the location of the ion in the clusters. An energy transfer from the internal degrees of freedom to the total rotation and translation degrees of freedom was observed during the simulation. The problem is related to the velocity rescaling in order to keep the temperature constant. The internal motion will slow down and the cluster will be internally cooled. To get rid of this phenomena one has to periodically remove the net translation and rotation of the center of mass of the clusters.

Structural and dynamical properties of fulleren - rare gas clusters

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Using molecular dynamics (MD) simulation technique we have studied the fullerene - argon mixture cluster $\text{C}_{60}\text{Ar}_{46}$. The temperature evolution of the radial distribution function, mean square displacement, velocity correlation function and diffusion coefficient were calculated for argon. The substantial differences between the dynamics of argon in pure Ar_{46} and mixture $\text{C}_{60}\text{Ar}_{46}$ clusters have been observed, both in solid and liquid state.

Embedded atom model calculations of the ground-state configurations of Fe and Fe-Al clusters

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Using the noncentral embedded atom model potential recently proposed by Besson and Morillo [1] for $\text{Fe}_{1-y}\text{Al}_y$ bulk alloys ($y \leq 0.5$), we performed computer simulations to predict the ground-state configurations of Fe_n and $\text{Fe}_{n-x}\text{Al}_x$ clusters ($n \leq 19$) [2]. The computed structures of Fe_n clusters are in general agreement with such theoretical results as have been obtained by density functional calculations (i.e. for $n \leq 7$; [3,4]). The results for Fe-rich $\text{Fe}_{n-x}\text{Al}_x$ clusters show surface segregation of Al, which is in keeping with the findings of a previous study of $\text{Ni}_{n-x}\text{Al}_x$ clusters [5].

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Depolarized light scattering from $\text{C}_{60}\text{Ar}_{46}$ cluster - MD study

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We have calculated (MD simulation) the interaction-induced polarizability correlation functions and spectra of the depolarized light scattering from argon atmosphere surrounded fullerene. The solid and liquid phases of $\text{C}_{60}\text{Ar}_{46}$ have been studied.

Molecular Dynamics Simulations of Overbased Detergent Particles

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Overbased detergents, OD, are sold commercially as additives for automotive and marine engine base oils. They are mixed in with the base oil to neutralise the acidic by-products of fuel combustion and oil degradation, which would otherwise corrode the engine. Chemically the OD are typically a mixture of calcium carbonate (the neutralising agent) closely bound to the calcium salt of a

surfactant. Experimental work (e.g., Low angle neutron and X-ray scattering, and surface pressure determination by Langmuir trough measurements) suggests that the overbased detergent exists in the oil in an inverse micellar state, with the detergent 'coat' surrounding the calcium carbonate core thereby making it oil-soluble (see refs. [1] - [4]).

The results will be described of Molecular Dynamics simulations we have carried out over the last few years with the objective of elucidating the atomistic structure of the OD particles. We have been particularly interested in the effects of surfactant type on the shape and structure of these micellar particles.

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A Highly Vectorized "Link-Cell" FORTRAN Code for DL_POLY Molecular Dynamics Simulation Package

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The highly vectorized fortran subroutines based on the link-cell algorithm for DL_POLY molecular dynamics simulation package are developed. For several specific benchmark systems the efficiency of the proposed codes on Fujitsu VPP700/128E vector computer has been tested. It is shown that in the constructing of neighbour list and calculating of atomic forces our link-cell method is more faster than the original code.

Modelling aluminium clusters with an empirical many-body potential

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An empirical two-plus-three-body atomistic potential, derived by fitting experimental data pertaining to bulk aluminium, has been applied to the study of structures and growth patterns of small aluminium clusters. The high dimensionality of the nuclear configuration space for clusters results in an extremely large number of isomers and local minima on the potential energy hypersurface. Global optimisation (i.e. searching for the lowest energy structure) was carried out using Random Search and Monte Carlo Simulated Annealing methods, for Al_2 to Al_{20} . The results of random searching have been used to put lower bounds on the number of minima for these nuclearities, and the efficiency of the Monte Carlo Simulated Annealing approach has been demonstrated. Comparisons have generally been in good agreement with results of previous calculations using electronic structure and empirical potential methods. While many of the global minima were also global minima for Lennard-Jones or Morse clusters, a number of new structures have been identified for Al_N clusters, notably for $N = 9, 16, 17, 18$ and 20 .

Structure and melting of small Ni clusters on Ni surfaces

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Using the Voter and Chen (VC) version of the embedded atom model (EAM) [1], we performed computer simulations to obtain the structures and binding energies of small Ni clusters on Ni(001), Ni(110) and Ni(111) surfaces [2]. The predicted Ni cluster structures on Ni(001) and Ni(111) generally agree with the results obtained by Liu and Adams [3] using the Foiles, Baskes and Daw (FBD) version of the EAM [4] (the only exception is one structure formed on the Ni(001) surface), but the corresponding binding energies differ significantly. The temperature-dependence of the behaviour of the seven-atom Ni cluster on the Ni(111) surface shows that the predicted cluster melting temperature also depends significantly on which version of the EAM is used. Hence EAM predictions of the properties of supported metal clusters depend crucially on the parameterization of the model, i.e. on the kind of data used in optimizing the embedding function and pair interaction. Although *ab initio* results for Ni clusters on Ni surfaces are not available for comparison, it seems plausible that the EAM description of supported transition metal clusters, like the EAM description of free transition metal clusters, may in general be more accurate if the VC version of the model is used rather than the FBD version since the former uses diatomic data as well as bulk properties in

optimizing the EAM functions, and its parameterization should therefore be more appropriate for the cluster level.

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Molecular Dynamics Simulation of Molecular Ionic Materials

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Molecular ionic materials such as ammonium nitrate play an important role in industry and are challenging materials to model. We present continuing work on ammonium nitrate, showing the simulation of thermal expansion in phase V and a solid/solid phase transformation to phase IV. We also present recent results of work on the thermal expansion of sodium nitrate, and potassium dihydrogen phosphate.

Enthalpies of mixing of solid oxides

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We propose a simple method for the calculation of the enthalpy of mixing of binary oxides, based on the use of quasiharmonic lattice dynamics for the efficient evaluation of the free energy of individual configurations. Results are presented for MnO/MgO, CaO/MgO and ZrO₂/CaO.

The effects of oblique incidence and surface steps on energetic silver cluster impacts with graphite

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The energetic impact of Ag clusters on graphite is investigated using classical molecular dynamics simulations with pair interatomic potentials to describe the Ag - C interactions and semi-empirical many-body potentials for Ag - Ag and C - C. The impact of normally incident size-selected silver cluster ions on graphite over the energy range 15-1500 eV has been previously studied [1] by a combination of scanning tunnelling microscopy and molecular dynamics simulations. Here we consider the effects of oblique incidence with silver clusters over the energy range 1 - 3 keV, investigating the dependence on the incidence angle of the cluster penetration into the graphite crystal, the area of the footprint which the cluster creates on the surface and the effect of surface steps. The initial stable configuration of silver clusters of various sizes is obtained by a genetic algorithm. We implement a long-range interatomic potential to model the interaction between different layers of graphite to improve the elastic properties of the material and to enable the modelling of steps on the surface. The simulations show that the clusters reflect from the surface at incidence angles θ in excess of $\approx 75^\circ$ and that up to the reflection angle the depth of the cluster penetration is proportional to $\cos\theta$.

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Clusters and adlayers on NaCl(100) and MgO(100)

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Adsorbed water on ionic crystal surfaces have been extensively studied experimentally and theoretically. The conclusions from these studies are not always in agreement. We have explored structures of small clusters and adlayers of water molecules adsorbed on NaCl(100) and MgO(100). On NaCl there is a conflict between the optimum O \cdots O distance of about 3Å in hydrogen-bonded water and the Na⁺ \cdots Na⁺ distance of 4Å, with the consequence that there are several monolayer structures with similar energies. In the case of MgO the Mg²⁺ \cdots Mg²⁺ distance is 3Å, so which matches the optimum O \cdots O distance, but the square structure of the crystal surface is still in conflict with the preferred hexagonal structure of ice. Monte Carlo calculations suggest that there is considerable disorder in water adlayers on NaCl. Experimental infrared spectroscopy of the adsorbed water at ambient temperatures suggests that two phases coexist on the surface at low

coverage, and our calculations suggest that one of them comprises a relatively ordered monolayer structure and the other, which appears at higher vapour pressure, a more disordered liquid-like phase involving 3 or more water molecules per NaCl unit. The distribution function $g(z)$ of water molecules with respect to height above the surface shows a distinct division into three layers.

Computational investigation into the morphology of solvated crystalline urea

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The prediction of crystal morphology is important for industrial processes. The morphology is controlled by the relative growth rates of the crystal faces. An ability to make valid predictions of the influence impurities and inhibitor molecules have is crucial to understanding how crystal morphologies may be tailored to suit specific requirements. Urea is chosen as a model system for such a study and in particular its morphology is investigated with respect to the influence solvent interactions have on determining morphology. The attachment energies of (001), (110), (101) and (200) faces are considered and morphologies are predicted for urea in vacuo, urea with static solvent interactions and urea with explicit treatment of solvent and solute dynamics, using MARVIN.

Modification of Lattice Phonon Absorption at the Interface Between Diamond and Graphite Nanoclusters.

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The effect of giant enhancement of two-phonon lattice absorption at the interface between a diamond nanocluster and graphite is observed experimentally and is modelled by considering a heterostructure consisting of a semi-infinite conductive media and a semi-infinite dielectric medium. The dielectric medium consists of a material which possesses the phonon lattice absorption. This enhancement of the absorption is considered in terms of excitation of collective electronic oscillations at the interface. It is suggested that the oscillations can be induced by the dynamical dipole momentum of the material. This effect appears when the absorption coefficient of the material exhibits its maximal value. The Born approach is used to derive an analytical expression for the enhancement factor of the absorption. The effect of the influence of spatial confinement of the heterostructures on the enhancement of the absorption is investigated in terms of the effective medium approximation

(EMA) theory. For this purpose the EMA theory is modified to obtain the dielectrical response of a medium constructed with a set of nanoclusters of two different types. The dielectric (diamond) and metallic (doped graphite) clusters are assumed to have the shape of flat ellipsoidal disks and the model takes into account the dielectrical permittivities of both materials from which the clusters are constructed. The conditions for a large increase in the absorption coefficient are given. A comparison between theoretical and experimental data on the giant enhancement of two-phonon absorption of diamond-graphite nanosize heterostructures is presented.
