

CCP5 Annual Meeting 1997

Materials, Microstructures and Simulation

Lecture Abstracts

Metal oxides containing *d* and *f* electrons: a new challenge in surface science

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Many of the transition metal oxides (i.e. oxide materials where metal ions contain *d*-electrons) exhibit high catalytic activity and are widely used in industrial applications. A recent discovery of the possibility of using U_3O_8 for the catalytic destruction of a range of environment pollutants has stimulated research aimed at investigating the connection between the catalytic activity of transition metal and actinide oxides and the electronic structures of their surfaces. It was shown experimentally at the Department of Materials, University of Oxford, that many of the oxide materials, which are room temperature insulators, can be imaged in a scanning tunnelling microscope at an elevated temperature [1]. Theoretical study of electronic structure and STM images [2],[3] based on the LSDA+U approach have led to the conclusion that strong *d-d* and *f-f* electron correlations are responsible for unusual electronic properties of a number of transition metal and actinide oxides. The contents of the talk will cover both experimental and theoretical aspects of this work.

References

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Temperature Dependence of Surface Energies of Oxides

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Virtually all calculations of the surface energies of ionic crystals have been restricted to the static limit. Here we present results for the energies of different surfaces of a range of oxides over a wide range of temperature, calculated by direct minimisation of the free energy via quasiharmonic lattice dynamics. The use of lattice dynamics is particularly useful below the Debye temperature where classical Monte Carlo and molecular dynamics fail due to neglect of quantum effects.

Molecular Dynamics Simulation of Metallic Zirconium

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Molecular dynamics simulations using a many-body potential for metallic zirconium are presented. The high temperature phase of this material is body centred cubic, which has a phase transition to hexagonal close packed via a softening of an N-point phonon coupled to a tetragonal shear. Softening of another zone boundary phonon corresponding to the ω phase is also observed. At the transition, twins of hcp material are formed to absorb the transformation strain, their orientation corresponding to the parent bcc structure. Eventually, a laminated microstructure evolves.

Cohesive Energies and Order-Disorder Transitions in Alloys

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This talk reports a range of Monte Carlo studies of the order-disorder transition in Cu-Au. Results for heat capacities and lattice parameters are reported. An approximate, parameterised Hamiltonian is not used. The Monte Carlo steps include both trial displacements of the atoms and trial interchanges of Cu and Au atoms. Calculations with and without interchanges allow us to determine the difference in the heat capacities of the ordered and disordered states. We are able to explain the tetragonal distortion of ordered CuAu, which is not possible using a mean-field approach.

Self-lubrication in Scanning Force Microscope Image Formation on Ionic Surfaces

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The mechanisms of and conditions required for true atomic resolution remain the focus of Scanning Force Microscopy (SFM). We present a theoretical model of SFM using a molecular dynamics method for the calculation of the interaction between a crystalline sample and a tip nanoasperity, combined with a semiempirical treatment of the mesoscopic van der Waals attraction between tip and surface, and the macroscopic parameter of cantilever deflection. The main features of the SFM experiment were modelled, including force vs. distance curves at various tip positions on the surface, and scanning of a perfect LiF surface in contact regime with repulsive force of 1 - 2 nN. It is shown that tip contamination due to adhesion to the surface atoms may promote periodic SFM imaging, if the adsorbed surface material makes stable structures on the tip. We demonstrate that the adsorbed cluster can adjust itself to conditions of scanning by exchanging atoms with the surface and changing its structure. We believe that this dynamic “self-organisation” of the surface material on the tip during scanning could be a general effect which may explain why periodic surface images are often obtained using a variety of tips and large tip loads. We discuss the implications of these results with respect to friction between tips and surfaces and the possibility to observe point defects at ionic surfaces with atomic resolution.

Molecular Dynamics Simulation of the Crystalline Phases of Polyethylene

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Crystalline polyethylene is being studied at a range of temperatures and pressures using molecular dynamics (MD) and x-ray diffraction. The long term aim of the project is to study a proposed transient mobile phase of crystalline polyethylene that may occur under ambient conditions, as part of the process of crystal growth. To establish the required background for this study, the ambient orthorhombic structure and the high pressure pseudo-hexagonal (or “rotator”) phase are being investigated using MD techniques, supported by data from x-ray diffraction. Preliminary simulations have been carried out for small systems, of $2 \times 3 \times 12$ and $2 \times 3 \times 24$ unit cells, of crystalline polyethylene using periodic boundary conditions (PBC) and infinite chains. Larger simulations, of $3 \times 5 \times 48$ unit cells, also with PBC but with finite chains, allowing the formation of *gauche* defects and a fuller range of motion, are in progress. Data will be presented for the unit cell parameters, chain dynamics and chain conformations. This will be compared to the available experimental results for a range of temperatures at ambient pressure. Initial simulations of the high pressure mobile phases will also be discussed.

Young’s modulus for individual carbon nanotubes and a monoatomic graphite sheet: comparing theory to observations.

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A simple theory presented demonstrates how Young's modulus of an individual carbon nanotube depends on characteristics of the interatomic interaction, the external and internal radii of a tube, and on the energy expense of bending a graphitic sheet into a seamless cylinder. The theory qualitatively reproduces the first direct measurements of Young's modulus for 11 individual carbon nanotubes published recently [1]. The extreme stiffness of single walled and thick tubules relates mainly to the absence of defects in a perfect graphitic network . The Young's modulus of perfect tubules is very close to that for defectless graphitic monolayer. The theory also predicts that multilayered defectless tubes might have the Young's modulus in a range of several terapascals.

References

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Misfit strains simulation in heterostructures: HTSC and semiconductors

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The misfit strains is one of the dislocation reasons, which leads to physical features degradation of heterostructures and, sometimes, to destruction of a film. Thus, investigation of formation of the misfit strains is a quite an important research objective.

An approach to simulation of the misfit strains is based on the information on tension module (Young modulus and Poisson ratio) and variation of crystal lattice parameter **A** in the intermediate layer.

A number of ultrasound measurements has been performed to calculate a variation of tension module in HTSC and in $A^{2(4)}B^6$ semiconductor heterostructures. Electronic spectroscopy has been used to determine the variation of **A**. Three-dimension pictures of the misfit strains were obtained for $A^{2(4)}B^6$ films, and isotropic approximation has been used to obtain a two-dimension plot of the misfit strains in HTSC ones. These computer simulations can be used for quality control of heterostructures.

We are comparing two reasons that cause dislocation: misfit strains and discrepancy of heat expansion coefficient. We have identified that even for films and layers which are in close agreement in the **A** parameter, the misfit strains dominate over second mechanism due to interdiffusion of

the chemical elements.

Keywords: heterostructure, misfit strains, computer simulation, ultrasound, tension module.

CVD Diamond: From Atomistics to Microstructure

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Diamond films are routinely grown via chemical vapor deposition (CVD) techniques in which a precursor gas containing a small amount of hydrocarbon (usually CH₄) in H₂ is heated by a hot filament, microwaves, or DC arc jet, dissociating some of the H₂ into atomic H and creating many different hydrocarbon. Atomic H helps stabilize the diamond phase by terminating the diamond lattice with C-H bonds (i.e., passivating the surface), converting sp²-bonded C into sp³-bonded diamond, and etching sp²-bonded C from the surface. We present an atomic-scale, kinetic Monte Carlo model of diamond growth that includes a wide range of surface chemical reactions and allows us to simulate in excess of 10⁹ reaction events corresponding to reactor times of up to one hour and hundreds of 10⁴ atom monolayers. We employ this method to predict diamond growth rate as a function of surface crystallographic orientation, gas phase composition and temperature, in excellent agreement with experiment. The resultant structures are analyzed to understand nucleation and growth on the surface, surface roughness and faceting. Using these growth rates determined from the atomistic simulations, we develop a front-tracking model of microstructural evolution on a much coarser scale. This model is used to predict the evolution of crystallographic texture, surface roughness, and grain size and to understand the growth competition between grains that leads to the development of columnar films.

Bond Order Interatomic Potentials for Modelling of CVD Diamond Growth

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A basic understanding of surface chemical reactions which take place during CVD diamond growth can only be achieved by reliable atomistic modelling of the reaction pathways and activation barriers. Ab-initio methods are restricted to simulating very small systems, therefore, the development of semi-empirical interatomic potentials which allow us to model much larger systems for longer times is the focus of current theoretical efforts.

We develop analytical bond order potentials (BOPs) for hydrocarbon systems based on the two-center tight-binding (TB) approximation to the electronic structure. In the BOPs the electronic degrees of freedom are no longer treated explicitly but their influence is captured through

the functional form of the BOP which is devised by a well-defined set of approximations to the TB Hamiltonian, thereby avoiding the many ad hoc parameters and functional forms that enter empirical potentials. We demonstrate that the first term of the BOP expansion, which corresponds to a Tersoff type potentials, is unable to account correctly for the relative stability of different structures such as graphite, diamond simple cubic and FCC. Accurate structural predictions require inclusion of the second term of the BOP expansion which guarantees that the fourth moment of density of states is included exactly. This property of the analytical BOP is of paramount importance for the covalent systems with band gaps such as silicon and carbon.

The remarkable feature of the novel BOP is that it predicts the environmentally dependent angular functions of the interatomic potentials which were recently introduced by inversion of ab-initio binding energy curves (M.Z. Bazant and E. Kaxiras, Phys Rev Let, 77, 4370 (1996)). As a result, analytical BOP gives the right ordering of different crystal structures and cohesive energies for open structures (diamond and graphite). We validate the analytical BOP against experiment and ab-initio predictions.

Dynamic Scaling in Simulations of Island Growth and Coalescence on Substrate Steps

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Monte Carlo simulations of island growth on substrate steps have been performed, whereby monomers are randomly deposited on a bare substrate and diffuse to substrate steps where they can nucleate $D = 2$ dimensional islands of critical size $i = 1$. In this work the dynamics of the cluster density during the nucleation, growth, coalescence and final percolation of the islands has been studied. It is usual to treat the growth and coalescence regimes separately, because the physical processes appear to be distinct in each. However we have found that our data display dynamic scaling for the whole evolution. In other words the density variation over time for simulations performed at different deposition rates collapse well to a universal curve under appropriately scaled time-density axes. The reason for this is that the pertinent length scale for the maximum island density is also that for the percolation regime where the clusters all join to form complete coverage of the step. In this work we show how this length scale is determined by the diffusion equation of the monomers attached to the steps, and derive explicitly the scaling exponents observed. Furthermore this treatment is generalised to the case of D -dimensional islands with critical island size i , yielding explicit predictions for the dependencies of the maximum island density and percolation regime on the deposition rate. This extension to the theory is important because i and D are accessible to experimental tests through choice of materials and control of substrate temperature.

Comparison of Initial stages of Ni-Electrodeposition with Electroless Ni deposition on Si(100) substrate.

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Electrodeposition and electroless deposition processes provide a continuous buildup of metal coating on a substrate from suitable aqueous solutions. Both these methods are very useful for the fabrication of a high density and uniform metallisation of complementary metal oxide semiconductor devices in Ultra-Large Scale Integration. (ULSI) metallisation and in the formation of thin metal etch marks for deep ultra-violet lithography.

In this study, we have compared the electroless deposition of nickel from NH_4F solution with electrodeposition of nickel from HF solution. The initial stages of deposition by both the techniques are compared and studied using several surface analytical techniques. Each technique has been used according to its characteristics to study the parameters that can influence the metal deposition process. In both these metal deposition processes pH can be adjusted to thermodynamically facilitate the deposition (at greater pH) or a H-terminated silicon substrate (at lower pH). Evidence for (metal) deposition-induced etching of the substrate has been reported. The substrate influence (p- and n-silicon) on the deposition process has also been investigated.

Tapping mode atomic force microscopy (TMAFM) was used to characterise their main features towards atomic level deposition. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) allow us in some cases to identify the chemical nature of the observed features. The results obtained throughout this study support further demonstration on detailed mechanism.

Modelling Non-epitaxial Growth of Metallic Clusters

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We model the growth of metallic clusters on graphite substrates using Molecular Dynamics techniques. The metal/metal interactions are modelled using the Sutton Chen potentials. The validity of these potentials for small clusters was verified by comparing the binding energies and equilibrium atomic separations with the corresponding values from density functional calculations.

The metal/graphite potentials were calculated using density functional theory. The interaction energy of an isolated metal atom with a cluster of 7 carbon rings, passivated with hydrogen, was calculated for various separations and the results fitted to a modified Lennard Jones potential. A similar calculation for an atom over a carbon bond enables the structure of the graphite substrate to be included in the model.

Using *ab initio* calculations, we have demonstrated a strong variation in the metal/substrate interaction with metal cluster size. This many body effect will have a significant influence on growth processes, therefore it is necessary to include it in the model. We have derived a many

body term which has the effect of reducing the metal/substrate of a metal atom as the number of neighbours increases, similar to the many body term in the Sutton Chen potential.

The calculated potentials for Ni and Cu are used in a Molecular Dynamics simulation to model growth of these metals on a graphite substrate. We find that Ni exhibits layer-by-layer (Frank van der Merve) growth whereas Cu exhibits island (Volmer Weber) growth. Similar growth modes are found experimentally for these metals on amorphous carbon.

Modelling Polyethylene: Path Integral Monte Carlo, Molecular Dynamics and Lattice Monte Carlo

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When one models dense polymer systems by means of computer simulation methods, one is immediately faced with the broad range of length scales (from the bond length of $\approx 1 \text{ \AA}$ to the radius of gyration of $\approx 100 \text{ \AA}$) and time scales (from bond length vibrations of $\approx 10^{-15}$ sec to renewal of the overall chain conformation in the ns to μ s range for short chains) that characterize these molecules. No single simulation method or model can cover all these scales. The most promising approach is therefore to use models containing the specific level of atomistic detail required in the simulation and devise interfaces between the models on different scales.

I will present a classical and path integral monte carlo study of the orthorhombic polyethylene crystal using an all or explicit atom force field. For some quantities quantum effects will be seen to play a role even at room temperature. From there we will move on to a united atom description of a short chain polyethylene melt. This model will be validated by a comparison of molecular dynamics simulation results to various experiments at one high temperature. This will show that our model is able to reproduce the experimental findings quantitatively. Finally we will map this united atom model onto the bond fluctuation lattice model of polymers and use the monte carlo method to study large scale conformational and dynamic properties over a broad temperature range in the melt.

A degenerate Rosenbluth Monte Carlo scheme for cluster counting and lattice animal enumeration

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We describe a new algorithm for the Monte Carlo enumeration of clusters and lattice animals. The method may be used to calculate associated properties such as moments or perimeter multiplicities of the clusters. The scheme is an adaptation of the Rosenbluth method for growing polymer chains and may be used to estimate the number of distinct lattice animals on any lattice topology. The

method is validated against exact and Monte Carlo enumerations for clusters of size 30, on two and three dimensional simple cubic lattices. The method may be readily adapted to yield Boltzmann weighted averages over clusters. Work is currently being undertaken to extend the method to count clusters of chains.

Dynamical scaling anomaly for a two-dimensional polymer chain in solution

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We report on extensive molecular dynamics simulations of a 2D polymer in solution. An analysis of the structure factor data has revealed anomalous dynamical scaling behaviour currently not predicted by theory. Subsequently, a closer scrutiny of the Zimm model predictions has revealed a breakdown of the preaveraging approximation due to the logarithmic infinite range structure of the 2D Oseen tensor. Numerical studies of the Zimm equations upon introducing the 2D Oseen tensor have yielded results in accord with the simulations in the scaling regime. While this offers some insight into the observed anomaly, our results show that the scaling arguments in 2D are in need of a careful reexamination.

Modelling surface topographical development on solids subjected to bombardment by energetic particle beams

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This paper will show how surface damage as a result of irradiation by energetic particle beams can be modelled. The techniques used in the simulation process will be classical molecular dynamics (MD) to model the effect of single particle impacts but also the effect of large doses will be considered by using continuum and Monte-Carlo models. The MD models will consider the damage on both covalent materials such as graphite and silicon and also metals such as copper or zirconium. Comparison will be made to experimental results using scanning force or scanning tunnelling microscopy. Attempts will be made to relate the development of damage on the atomic scale to micron scale structures which can develop after large doses.

Computer Simulation of Defect Production by Displacement Cascades in Metals

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Molecular Dynamics (MD) techniques have been used to investigate the mechanisms and final state of defect production due to the primary cascade state of radiation damage in metals. This study includes research dealing with the effect on defect formation and clustering of primary knock-on atom (PKA) energy, irradiation temperature and the spatial overlap of cascades. The simulation has confirmed some of the early ideas based on binary-collision concepts and revealed new aspects not anticipated. The defect production efficiency in metals under cascade-producing irradiation with ions and neutrons is approximately one quarter of the NRT value, which is consistent with experimental data. Both interstitial and vacancy clusters are features of displacement cascades. Most interstitial clusters have dislocation character, but a few metastable clusters have been found and are persistent over the period of the MD simulation. Because the timescale of cascades is very short, some experimental results cannot be explained by MD simulation, for example the temperature dependence of matrix hardening, void swelling and the different mechanisms of hardening under electron and neutron irradiation. A possible way for the future development of models of the evolution of damage beyond the stage of the cascade process is discussed.

The Vibrational Anomalies and Polymorphism in Titanium: A Tight-Binding Approach

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The group IV transition metals (titanium, zirconium and hafnium) possess a number of rather remarkable features in their properties attributed to strong anomalies in their phonon spectra. These include crystalline polymorphism, a high temperature saturation of the electrical conductivity, rapid increase of the constant pressure heat capacity at high temperature, and anisotropy in diffusion and thermal properties. The vibrational anomalies manifest themselves by a strong (and sometimes inverse) temperature dependence of the certain phonon frequencies even at the conditions far away from the phase transition. For example, the $[0001]LO$ branch in the low temperature hexagonal close-packed α -phase of Ti and Zr exhibits substantial softening with temperature. The frequencies of the $[001]T_1$ zone-boundary and $[111]L$ ($q = \frac{1}{3}$) phonons in the high temperature bcc-structured β -phase, also decrease dramatically while approaching the $\beta - \alpha$ transition temperature from above. The established large sensitivity of the vibrational and elastic properties of d-metals to the d-band filling, as well as to the details of d-band structure, suggests strong electron-phonon interaction effects. Thus the study of the anharmonicity in such systems requires the method accounting for at least some electron density effects and, at the same time,

allowing for large scale MD simulations, so the dynamics beyond the harmonic approximation can be studied. The various $O(N)$ implementations of the tight-binding approach seem to be adequate compromise for this purpose. Having titanium as the case study, we analyse both anharmonic and electron-phonon coupling effects in different polytypes, by means of bond order potential approximation to tight-binding approach implemented in OXON package. We apply this method for both molecular dynamics and frozen phonon calculations and compare results, where relevant, with the k-space tight-binding calculations. Based on these simulations, we discuss the static and dynamic variations of the electron chemical potential as applied to either the whole system or particular phonons, and the implications of these changes in the thermal frequency shifts and relative phase stability.

A New Approach to Impurity Scattering in Doped Semiconductors

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There is a clear evidence that mobility data depend on the species of dopants in heavily doped semiconductors. To clarify this still unsolved problem from a physical point of view we adopt a new theoretical approach to discuss the influence of the ionized impurities on the electron mobility in doped semiconductors. We show for the first time that consideration of the charge density of the valence electrons allows not only to distinguish the majority and minority electrons, but also to differentiate between various acceptors and donors. Since the picture of the hydrogenic behavior of shallow impurities can well describe ionization and screening properties, we assume a hydrogen-like exponential electron charge distribution consisting of N electrons while retaining a point-like nucleus of total charge Z (in units of the elementary charge e). The charge distribution of the impurities is described within the Thomas-Fermi theory in the energy functional formulation. By means of a variational principle one obtains a unique charge density for each dopant. The corresponding atomic form factor $F(q)$ of the electron charge distribution in Fourier space is significantly different for various dopants at higher doping concentrations. Taking into account many-particle interactions the total scattering cross section within the Born approximation is derived.

We calculate the electron mobility μ at 300 K employing the derived formulas in a single-particle Monte Carlo procedure using analytic band structure including phonon and plasmon interaction. The Pauli principle is accounted for by a rejection technique. Our results for Si, GaAs, and InP confirm experimental data indicating that ions with higher Z result in lower values of μ .

In conclusion, the present approach to our knowledge is the first physically based model to date which explains the dependence of the majority and minority electron mobility on various species through the atomic number.

Ab Initio Path Integral Molecular Dynamics of Hydrogen Diffusion

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We present here preliminary results for the simulation of hydrogen diffusion on the Si(111) surface. This is a system for which the quantum zero-point motion of the light hydrogen atom has a significant effect on observed properties. We have used an *ab initio* path integral molecular dynamics technique in order to fully simulate the zero point motion whilst at the same time calculating the electronic structure and relaxation of the surface. We highlight those features in our results that can only be explained by a proper treatment of the zero-point motion and hence demonstrate the usefulness of this technique. This is the first time that the *ab initio* path integral molecular dynamics technique has been applied to the properties of surfaces.

Poster Abstracts

FEOS: A Code for Lattice Dynamics and Structure Optimisation of Polar Solids

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This contribution describes FEOS, a program which uses a combination of lattice statics and quasi-harmonic lattice dynamics to calculate *analytically* the free energy of a crystal and its geometrical derivatives, at a given temperature and pressure. These quantities are used to perform efficient fully dynamic structure optimisation of unit cells containing hundreds of ions. High precision is readily obtained. Quasiharmonic lattice dynamics has proved to be a good technique for the calculation of free energies of solids, often even up to quite elevated temperatures. It is much cheaper than Monte Carlo or molecular dynamics. Recent applications include studies of the free energy of defect formation and of ceramics with large negative thermal expansion. The code is now ready for distribution to interested academic groups.

Lattice Modelling of Fracture in Impure Metals.

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The intragranular fracture of steels has been investigated using a two dimensional lattice model. The D_2Q_8 model is based on a square lattice with interactions between neighbouring and next nearest neighbour sites, bond-bending is controlled using a form of Born potential. Plastic behaviour

is incorporated using a reversible two-step potential function. The model has been mapped onto the isotropic continuum to allow parameterisation from experimental data. Bonds are switched to the plastic state or broken using a stochastic technique [1], with a probability determined from the energy of the bond. We present the results of a series of simulations of metal matrices containing single and multiple particulate defects. We demonstrate that by choosing the correct parameterisation, particulates can be made to either debond from the matrix or to undergo brittle fracture.

References

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Thermal and Mechanical Properties of FCC metals and their binary Alloys

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The temperature dependence of thermodynamic and mechanical properties of fcc transition metals (Ni,Cu) and their alloying behavior are studied using molecular dynamics (MD). The structures are described at elevated temperatures by the force fields developed by Sutton and co-workers within the context of tight binding approach. MD algorithms based on extended Hamiltonian formalism from the works of Andersen, Parrinello and Rahman, Nosé, Hoover and Çağın. The SIMULATOR program that we use generates information about various physical properties during the run time along with critical trajectory and stepwise information which need to be analyzed post production. The thermodynamic and mechanical properties are calculated in the temperature range between 300K to 1500K with 200K increments using the statistical fluctuation expressions over the MD trajectories.

Excited State Dynamics in Nanodots

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Nanodots exhibit special features upon excitation, in particular broader than expected transition widths. Excitation causes a change in the volume of the dot. The consequent dilatational strain shifts the transition energy. Where the excitation does not cause a large redistribution of the charge density, the volume change is essentially independent of the volume of the nanodot. Hence

the shift in transition energy is inversely proportional to the dot volume, broadening transition widths where the system consists of a distribution of dots of various sizes. However, even for single dots, there is an intrinsic broadening due to the finite time taken for the volume relaxation. The volume change takes place over a timescale determined by the radius of the dot and the velocity of sound in the dot, leading to an electronic dephasing time of the order of several hundred fs for dots of radius 10\AA . We have verified the above effects using MD simulations of NaCl nanodots. The finite size of the nanodot also affects phonon relaxation in the system. We conclude with a discussion of the nature and effect of phonon dephasing in nanodots.

The Dynamics of the Nucleation and Coalescence Regimes in Simulations of Island Growth on Substrate Steps

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In an accompanying presentation it has been demonstrated how the dynamics of island growth and coalescence on substrate steps display dynamic scaling. In this work we focus on the detailed evolution of the cluster density in both the early stage nucleation regime and the later coalescence regime, for a simulation using island dimensionality $D = 2$ and critical island size $i = 1$. We show that the inter-island gap size distribution is a scaling property of the growth, which implies a hierarchical self-similarity in the system, and derive an approximate form for this distribution from the monomer diffusion equation. In the nucleation regime we predict that the island density should grow as the fifth power of (ϕ/r) , where ϕ is the number of monolayers deposited on the step and r is the ratio of the monomer diffusion and deposition rates. The simulation data confirm this behaviour, and the constant of proportionality agrees reasonably well with theory given the approximations used. However this low- ϕ behaviour indicates that the dynamic scaling plots cannot be exact in this regime, but instead possess a residual $1/25$ power dependence on r , an observation in agreement with the data. In the later stages we show how it is the smallest islands that coalesce first, which enables accurate calculation of the cluster density evolution in the coalescence regime based upon the gap size distribution derived above. Taken with the dynamic scaling results, this work shows how complete theoretical understanding of the detailed evolution of the simulated growth can be obtained.

A Study of a Steric and Electric Multipole Model of Liquid Crystal Geometry

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Liquid crystals are asymmetric in varying degrees in their molecular shape, charge distribution and polarisability and the problem of relating molecular structure to phase behaviour is complex. We report results [1] from a series of molecular dynamics simulations designed to study the phase behaviour of model rod-like liquid crystal molecules interacting via the Gay Berne Potential. We also report results from a study of quadrupolar single and multi-site Gay Berne molecules.

Following classification of molecular geometry in terms of a multipole expansion of steric asymmetry, two models have been studied in detail: a zigzag model defined as a steric quadrupole and a triangle model defined as a longitudinal steric dipole, and comparison has been made with a cylindrical model. Extensive simulations in the NPT ensemble a delay in the temperature of onset of the smectic B phase, with a lower temperature of onset observed with the steric quadrupole than with the steric dipole. Local anti-parallel steric ordering within a layer was observed with the model steric dipole in the crystal B phase but not with the model steric quadrupole. This structure is in agreement with experimental results and with the prediction of the generalised molecular asymmetry model [2]. The steric quadrupole demonstrated a rippled structure throughout the smectic B phase increasing in amplitude and wavelength sufficient to tilt molecules along a wave with respect to the system director as the system was cooled. This structure was almost absent in the final crystal structure cooled.

Results for the addition of a longitudinal and transverse electric dipole to a cylindrical Gay Berne molecule indicate that both the longitudinal and transverse electric quadrupole raise the temperature of onset of the nematic phase and destabilise the smectic phase. The effect is greater with a transverse electric quadrupole and the trend opposes that of the transverse steric quadrupole. Preliminary results for the addition of an electric quadrupole to a steric quadrupole again indicate a rise in the temperature of onset of the smectic phase compared to the steric quadrupole alone.

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Evolution of microstructure in the bcc-hcp martensitic phase transition in zirconium

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We report molecular dynamics simulations of the martensitic phase transition from bcc to hcp in zirconium. We show the evolution of a laminated twin microstructure, with some plastic deformation occurring to rotate the twins. This rotation is such as to alter the twinning angle from the 60°

between the hcp variants to the 61.5° angle of the low energy ($10\bar{1}1$) twin. The proximity of a low energy twin to the twinning angle is thus identified as a cause of microscopic irreversibility in the transition.

Ordering in Oxides and Silicates

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Cation or anion ordering is often crucial in determining phase stability and in determining thermodynamic, electrical and geochemical properties. The simulation of ionic solids with a finite impurity or defect content, or with extensive disorder, is still problematic. Such systems have largely been studied theoretically either via point defect calculations which refer only to the dilute limit, or via "supercells" in which a periodic superlattice of defects or impurities is introduced extending throughout the macroscopic crystal. These methods have clear limitations.

In this presentation we report the implementation of Monte Carlo techniques specially adapted to allow for the sampling of many configurations and to take *explicit* account of the complex relaxation accompanying the disorder, without resorting to the use of parameterised Hamiltonians. Preliminary results for cation ordering in olivines and for the enthalpies of mixing of simple oxides are presented.

Template-Framework Interactions in Chiral AlPO's

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Self assembly is a major tool in nanotechnologies. Intercalation of organic molecules between the layers of inorganic solids is used to construct pores and channels of controlled size on a nanometer scale.

The materials created by templating have so far been largely achiral. The fabrication of materials with chiral nano-environments will open an important field in nano-technology, where the separation of enantiomerically pure substances is desired, as in biological and medical applications.

Recently, there have been successful attempts to intercalate chiral transition metal complexes into aluminophosphates (AlPO's), forming chiral layered compounds [1]-[4].

We are undertaking Molecular Dynamics simulations to identify the key template host interactions which are the structural determinants. A Molecular Dynamics simulation has been performed to study the structural characteristics of a novel type of chiral aluminophosphate that has been recently synthesized [1]. The force fields for the Al-P-O interactions were obtained from previous work [5]-[9].

For the chiral template a rigid body scheme was used with three different approaches. A simple charged sphere model with nearly hard-sphere interactions was used first. This simple model was able to explain the mechanical stability of the structure in a constant volume simulation, but failed under constant pressure simulations. A more detailed model was then constructed by including the detailed shape of the overlap forces arising from the chiral template. This system gave a good reproduction of the experimental structure vibrational spectrum. The final model was an extension of the second model to incorporate chemical interactions such as hydrogen bonding. solid.

The aim of this study is to evaluate the different degrees of complexity needed to reproduce the features of the system. This will identify the factors needed to stabilise a chiral nanoporous material. In this work we report the optimised structures of the chiral AlPO compared with the X-ray structures, the corresponding energies, and the calculated vibrational spectra.

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Molecular Dynamics Simulation of Homogeneous Nucleation in Vapor Phase

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Molecular dynamics computer simulation was carried out to investigate the dynamics of vapor phase homogeneous nucleation for a Lennard-Jones fluid. To control the system temperature, the 5000 target particles were mixed with 5000 soft-core carrier gas particles. The observed nucleation rate is six orders of magnitude larger than prediction of a classical nucleation theory for Lennard-Jones fluid. The kinetically-defined critical nucleus size, where the growth and decay rates are balanced, is 30–40, as large as the thermodynamically-defined value estimated with the classical theory. Using the cluster concentration expression reversely, the free energy of cluster formation ΔG is estimated. The surface contribution term has a peculiar dependence on the cluster size n as $\propto n^{0.88}$. With this ΔG , the predicted nucleation rate agrees with the simulation result. The temperature dependence of nucleation rate will be presented.