

Report on the CCP5 Annual Conference: Computer Modelling of New Materials

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The CCP5 Annual Meeting this year took place in Bristol in January (4th-6th) and was organised by Dr. M.P. Allen of the University of Bristol. The meeting was jointly supported by CCP9, the sister project of CCP5 concerned with electronic structure calculations in solid materials. The subject of the meeting was "Computer Modelling of New Materials" which was intended to demonstrate the importance of simulation and modelling methods at the cutting edge of research in technologically important materials. The subject areas covered included polymers, ionic materials and semiconductors. A strong interest naturally arose in the re-invigorated science of high temperature superconductors, which have been treated by all the computational techniques available.

The meeting started with E.A. Colbourne of ICI Wilton, who spoke on the subject of "Molecular Modelling for Advanced Materials". Dr. Colbourne outlined the interest within ICI in the computer modelling of polymers. The motivation is the understanding of the molecular basis for the preparation and processing of polymers in an industrial context. ICI has an interest in both synthetic polymers and biopolymers, the former in the plastics industry and the latter in pharmaceutical development. These two kinds of polymer have some features in common, but largely the kinds of system being modelled, and the objectives of the work are different. The synthetic polymers are studied to understand their bulk properties and the biopolymers to gain insight into biological activity. Dr. Colbourne concentrated on synthetic polymers, with specific examples made of the polymers polyarylether-ether-ketone (PEEK) and polyethylene terephthalate (PET).

The objective of the work on PEEK was to obtain an adequate description of the crystalline form using molecular mechanics methods. The difficulty here was obtaining a suitably accurate model potential, for which simple site-site pair potentials were used

and tested by prediction of the lattice parameters. Several other possible structures were described, the key differences between them being expressed in terms of the disposition of the ketone and ether groups in adjacent polymer chains (referred to as the *register* of the two kinds of groups). Six structures were modelled by molecular mechanics and their relative thermodynamic stability (in terms of lattice energy) obtained. The energetics of different structures was important in the understanding of the mechanical properties of the polymer.

The study of PET was intended to discover the reasons for the improvement in the properties of this important plastic material as a result of mechanical processing (known as orientation). The normal extruded material is brittle, but becomes more flexible if stretched in the forward and transverse directions. The study, which included molecular orbital calculations, established that the stretching operation reduced the intramolecular stability of the chains, but that this was compensated for by intermolecular interactions. The calculations thus provided important clues to the observed properties of the material. In future studies, ICI intend to make use of molecular dynamics methods, which will provide methods of calculating stress-strain relationships and temperature and time dependent effects etc. They are however mindful of the greater expense implicit in this approach.

The second speaker, G. Goldbeck-Wood of Bristol University, also spoke on the subject of the polymer PEEK. His concern was to simulate the growth and melting behaviour of the crystalline solid using a simple two dimensional model for the crystal growth process, due to Sadler and Gilmer, in which a slab of material grows along the top or side edges in a manner resembling a roughening transition. The preliminary results explain the isothermal growth rates, melting temperature and lamellar thickness of the crystal using parameters estimated from the enthalpy of fusion. The model has been extended to account for transient phenomena such as isothermal annealing.

T.K.H. Barron of Bristol University reported on studies of thermal expansion in idealised models of polyethylene. The underlying theory regards the thermal expansion as an elastic response to thermal stresses. A quasi-harmonic approximation is used in the first instance and the stresses are obtained from a perturbation calculation. A central force model is used for the interactions, which admits three distinct mechanisms for the thermal expansion. Firstly there is bond stretching due to asymmetry of the pair potential functions about the minimum. Secondly, there is contraction along bonds due to tension induced by transverse vibration. Thirdly there is bond rotation due to tension induced by both kinds of vibration. All of these are present to some degree in polymeric systems.

The different idealised models of polyethylene were described. All were contained within an orthorhombic unit cell. The most basic model consisted of parallel, straight flexible polymer chains, which underwent thermal contraction along the chain direction and expansion in the perpendicular direction. Zig-zag polymers (with a 90 degree bend at the carbon sites) showed the largest expansion perpendicular to the ribbon length. The effect was repeated

in non-rectangular zig-zag chains, which were modelled by inclusion of second-neighbour interactions within the chains. A more realistic model of polyethylene, including explicit hydrogen atoms gave good agreement with experiment (X-ray diffraction) up to about 100 K; describing well the anisotropy of the vibration perpendicular to the chain direction, but gave large vibration magnitudes at higher temperatures.

D.A. Dunmur presented the first talk on the subject of liquid crystals under the provocative title of "Structure - Property Relationships in Liquid Crystals: Can Modelling do Better than Empiricism?". His primary concern was to determine the effect of molecular structure on the formation of liquid crystal (LC) phases, since it is well known that the LC phases are a small perturbation of the liquid state and minor molecular changes can have a substantial effect. He began with a brief description of the phenomenology of liquid crystals and the order parameters used to describe their anisotropic properties (i.e. the s , g_1 and g_2 parameters).

A general structure for molecules that give rise to the nematic/isotropic transition was outlined. It consisted of two ring systems with a bridging "link" group, terminal alkyl and other groups and laterally substituted groups. Various empirical "rules" have evolved, which indicate the favourability of the formation of a nematic phase. For example in the case of the ring system, the order: bicyclo-octane > cyclohexane > benzene is observed. Similar rules arise in regard to the linkage groups and the terminal alkyl group length (where an even/odd effect is also apparent). The importance of dipoles was also discussed: interestingly, no nematic dipole phases have yet been observed.

Professor Dunmur and his colleagues have investigated the subtle effects of molecular structure in these systems with the aid of molecular mechanics modelling. The MM2 force field was used to define the intramolecular effects and site-site forces used to describe the intermolecular effects. In addition a "nematic potential", which was a function of the LC order parameter, was introduced to incorporate the aligning effects of a very large system of molecules. The majority of the calculations dealt with a system of two molecules, for which the minimum energy of the dimer was sought, from many starting orientations. The objective was to find the favoured mode of alignment for the dimer as a precursor to liquid crystal formation. Several typical molecular structures were investigated, including dipolar species, disc-like and rod-like molecules, and molecules possessing chiral centres (such molecules give rise to chiral nematics, with a twist orientation). Overall the method shed some light on the formation of liquid crystals, with some disappointments, such as failure to predict stability trends in experimentally studied systems. However the model was admittedly basic in some respects and offered some hope for the future.

M.P. Allen of Bristol University described his simulations of liquid crystal films based on the Lebwohl-Lasher model, which is a lattice model incorporating nearest-neighbour interactions in the form of orientational coupling. The system had been studied by Fabbri and Zanoni and latterly by Luckhurst, Sluckin and Zewdie. The objective in Dr. Allen's work

was to perform the necessarily long simulations to locate the nematic-isotropic phase transition in films of varying molecular thicknesses. The adaptation of the simulation (Monte Carlo) algorithm to suit the DAP massively parallel processor was described. This was an important aspect given the length of the simulation runs required. (It was estimated that an equivalent MD simulation for a non-lattice model, would require a complete microsecond simulation!.)

The location of the transition temperature (T_{NI}) was achieved by calculating the energy distribution function near the phase transition. For simulations at precisely T_{NI} two peaks should appear, at above or below this temperature the relative sizes of the peaks changes in favour of one of the structures. These considerations enable the accurate determination of the transition temperature (at the expense of very long runs). In these simulations it was found that the nematic/isotropic phase transition ceases to be of first order when the thickness of film reduced to 6 to 8 layers. Below this margin, it was not possible to separate out two peaks in the distribution function.

Dr. Allen went on to describe further work on the orientational wetting that occurs when the film is placed between fixed walls.

The first speaker on the second day was Dr. A.P. Sutton, of Oxford University, who spoke on the subject "Modelling Extended Defects in Silicon". He began by describing the "tight-binding" method that was used to calculate the electronic structure of silicon. In this prescription the bonding energy is written as sum of several terms: the covalent bond energy; the promotion energy (required to promote s^2p^2 occupancy to s^1p^3 prior to hybridisation); the change in electrostatic energy; the exchange and correlation energy and a correction term for the approximations employed. Each of these contributions are written in terms of the electron density matrix $\rho_{i,j}$ and empirical parameters are obtained from the literature or fitted to satisfy the bulk volume of silicon. The recursion method that is central to this treatment was described in detail.

A condition implicit in this treatment is "local charge neutrality", which is thought to be necessary to enable the interionic forces to be calculated with a degree of accuracy. To ensure this the on-site energy terms (H_{ij}) are adjusted accordingly. In Dr. Sutton's work the method was tested by calculating the structural stability of silicon as a function of volume. The method gave good account of cubic phases but was significantly incorrect for the close packed fcc and bcc phases.

The method was then applied to several systems. The first was a stacking fault in crystalline tin. The method correctly indicated a wurtzite-like structure for the atoms at the defect. The next application was the 112 grain boundary in germanium, which structure was found to be graphite-like in the defect region with a significant peak in the band gap of the density of states - indicating "dangling bonds". In studies of silicon it was noted that the band gap contained little structure. The experiments indicate otherwise, but are probably contaminated with oxygen, which gives the band gap structure. In silicon it was

believed that defects were likely to arise in preference to dangling bonds. A feature of the silicon 110 surface was the tilting of the atoms to remove degeneracy. This introduces strain in the system, but this was thought necessary to reduce the electronic energy. At this stage Dr. Sutton questioned the assumed need for local charge neutrality, since calculations without this ingredient gave equivalent results.

Finally, the tight-binding model was compared with the atomistic model potentials of Stillinger/Weber and Baskes. Both potential models failed to describe surface tilting, as expected in view of its quantum mechanical origin. However the Stillinger/Weber potential seemed to be adequate at describing a 112 interface within the bulk structure.

The application of the tight-binding method was further discussed by L. Goodwin of Imperial College in his talk entitled "Improved Tight Binding Parameters for Silicon". The tight-binding method was known to possess some significant failings, notably the incorrect energy-volume properties of the close packed crystal structures. An improved set of parameters were obtained by rescaling the tight-binding energy functional. The scaling procedure adopted was described. The new parameters were obtained by comparing the results with Yin and Cohen's density functional theory results for the diamond lattice structure. The transferability of the parameters was tested by application to silicon atomic clusters of 2-10 atoms (local charge neutrality was very important here!). The method gave satisfactory account of the bondlengths and structures of these clusters, including the intriguing deviation from octahedral symmetry of the 6-atom cluster.

The final talk on the tight-binding method was given by R. Davies of Imperial College and was on "An Efficient Algorithm for the Calculation of Interatomic Forces in the Tight-Binding Model". The central theme of this talk was a pronounced inconsistency between the analytical forces and the numerical derivatives of the energy within the tight-binding model. This is due to incompleteness in the recursion basis employed in the tight-binding method, which gives rise to an effective force (the Pulay force). This effect was examined in hcp and fcc transition metal atomic clusters of various sizes. It was found that the convergence of the forces and structural energy differences with cluster size, was poor at zero temperature. The problem with the convergence could be dramatically reduced if the discontinuity at the Fermi surface was thermally smoothed with the aid of the Fermi-Dirac function. This reduced the long ranged Friedel oscillations that caused the convergence difficulties.

Dr M. C. Payne (Cambridge) discussed the total energy pseudopotential technique of Car and Parrinello. This method is formulated in the language of molecular dynamics. Dr. Payne addressed the question of the extent to which the electronic degrees of freedom should be regarded as classical degrees of freedom. He stressed that the electronic degrees of freedom are heavily damped. If the ion positions are not evolved then the method is just an iterative matrix diagonalisation. Dr. Payne then considered the case where the ion positions move. Moving the ions feeds energy into the electronic degrees of freedom

which then evolve as the energy is damped. The electronic degrees of freedom have 10^4 times the energy of the ions, so they act as a heat bath. However, they will be continually out of equilibrium with the ions which suggests that the ion dynamics will not be correct. Dr. Payne then went on to show that the errors in the Hellman-Feynman forces are self-cancelling. This introduces a constant error in the dynamics of the ions.

Dr Jordan (Birmingham) then described some of the experimental work which was currently being undertaken to look for new areas of common interest with the work of CCP5 and CCP9. He described the angle-resolved photoemission technique and discussed recent advances in the density functional theory which provide a test of the theory.

Dr Jones (Exeter) described some applications of Local Density Functional methods to calculations on solids. He described methods of evaluating the Hartree and exchange-correlation energies and potentials in such systems and introduced an approximation which had an n^3 dependence rather than n^4 . Dr. Jones has used the method to study 5:3 semiconductors with the diamond structure. He has worked with cluster sizes of 56, 86 and 110 atoms terminated with hydrogen; for the 56 atom cluster there are approximately 200 orbitals and 150 basis functions to consider. Dr. Jones described defects in gallium arsenide. The defects were substitutional silicon or beryllium with hydrogen in the lattice. The pure GaAs was simulated with bond lengths correct to within 2% and a band gap of 3.5 eV compared with the experimental value of 1.5. A Ga atom was then replaced by Si and the structure relaxed. H was inserted in two trial positions. When bound to just the Si, the Si As bond length increased from 2.38\AA to 2.73\AA . The donor level dropped to the top of the valence band. With the H in the bond centered configuration, the Si As bond length increased to 3.4\AA . This configuration did not passivate the defect in the same way as the first. The energy of this configuration was higher than the other, suggesting the first configuration as the correct one. Further confirmation came from the prediction of the vibration frequencies of the defect which are known experimentally. Some further work was described on the Beryllium defect, where the bond centered configuration is energetically preferred.

J. den Ouden described some work on the simulation of zeolites. He reviewed the importance of these materials in industrial processes. Zeolites contain Si, Al and O together with exchangeable cations. They need to be selective for the shape of molecules which may be reactants, products or a transition state. He has been looking at Ni^{2+} in the two zeolites mordenite and silicalite. These have been modelled by distributing the aluminium randomly and investigating the preferred positions of the Ni^{2+} . The lowest energy configurations are those where the Ni^{2+} is bound to two Al^{3+} which have exactly one framework Si ion between them.

D. Heyes (Royal Holloway and Bedford New College) described some simulation work using Brownian dynamics on the electrorheological effect. This is the effect on the flow rate and viscous forces due to an electric field and has applications to the manufacture of

clutches and damping devices. He considered 125μ glass spheres in an insulating oil. When an electric field is applied between two plates immersed in this fluid the spheres tend to align in strings between the plates. The strings oppose motion of the fluid when a shear is applied. He simulated this using standard Brownian dynamics but with a dipolar term on the spheres to reproduce the effect of the electric field.

Dr. W. Mackrodt (ICI) described some simulations of High T_c Materials. The techniques used were lattice statics and lattice dynamics using two-body potentials derived from the electron gas method. The shell model was used to simulate the polarizability of the ions. He stressed that this type of modelling should focus on the materials aspects of these compounds rather than attempting to answer detailed questions about mechanism. Using these potentials the structure of La_2CuO_4 may be simulated to within 1%. The orthorhombic phase is more stable than the tetragonal with a calculated transition temperature of $250K$. Dr. Mackrodt then suggested some other materials which may be worth investigation. Nd_2CuO_4 has CuO planes but does not have the same structure as La_2CuO_4 . On the other hand, calcium and strontium cuprates have just 1 dimensional chains. Dr. Mackrodt had also calculated the phonon density of states of a number of these materials. In many cases a 10 meV peak is seen in the density of states. However the material $\text{La}_2\text{SrCu}_2\text{O}_6$ is not a superconductor and lacks the 10 meV peak. He then continued to suggest the effect of changing the oxidation state of the copper. Materials intermediate between La_2CuO_4 and LaCuO_3 could be investigated. One such compound is $\text{La}_3\text{Cu}_2\text{O}_7$ which is predicted to have the 10meV absorption. Some work has also been done on surface properties of these materials and on electronic defects.

Professor Catlow (Keele) then described some powder diffraction work performed on samples under pressure using the synchrotron at Daresbury. The material studied was La_2CuO_4 . He found a 4 – 5% reduction in a, b and c when the pressure was increased to 150 kbar and no evidence of a phase change. The predicted change in cell volume from the band structure calculations agrees well with the experiment.

The first speaker on the final day was Dr W. Temmerman of Daresbury Laboratory, who spoke on the subject “Computational Methods and Electronic Structure calculations for High T_c Materials”. He began by describing the principal method he and his collaborators have used in this study, which is the LMTO-ASA or “Linear Muffin-Tin Orbitals in the Atomic Sphere Approximation”. In this method, the atoms in the crystal are described by spherically symmetric potential fields in which the radial Schrödinger equation is solved. Use is made of the local density approximation to account for the electron exchange and correlation. The method is a self-consistent-field (SCF) method, in which the electron density is iterated until the lowest electronic energy is found in accordance with the Variation Principle. An important aspect of these calculations is the evaluation of the integrals in the Brillouin zone, which was described in detail. To stabilise the convergence of the SCF cycle, care is taken to produce a reliable progression to the energy minimum.

This in practice amounts to mixing the electron densities of the previous two cycles at each cycle. In a typical application of the method (La_2CuO_9), the unit cell contains 14 atoms, giving rise to matrices 154x154 in size. 15 iterations are required for convergence and 150 k-points are obtained. On the Cray XMP/48 about 5 hours of cpu time are required.

The method has been applied to a number of crystal structures relevant to the study of high T_c superconductors. The electronic energy of the La_2CuO_4 structure was obtained as a function of volume and found to agree very well with experiment. However the method failed to explain that the structure is an antiferromagnetic insulator. Some light was shed on this problem in a study of La_2NiO_4 . This material became metallic or insulating according to the ratio of the axial and planar $Cu - O$ bondlengths in the nominally octahedral structure. The generally good description of the electronic and bonding properties in this case suggests that an antiferromagnetic state in La_2CuO_4 may lie close to the groundstate.

Dr. D. Nicholaides of the University of Bristol described current progress in a "Molecular Dynamics Study of a 2D Gauge Glass". This work is in progress on the AMT DAP, which is employed in simulation studies at Bristol. The model is an idealisation of conduction through a random arrangement of superconducting grains, where each grain is assumed to have four nearest neighbours (to map onto the DAP architecture). The density of electron "Cooper Pairs" on each grain is assumed to be the same and the grains interact via the Josephson effect. An important feature of "glassy" models is the phenomenon called "critical slowing down", which implies the existence of long-lived metastable states and hence a costly simulation. Dr Nicholaides described his approach to this problem with a dynamical analogy of a many-particle system. The treatment required the introduction of a "mass matrix", the off-diagonal elements of which are dependent on the interaction terms in the system and are scaled by a control parameter. As this control parameter is reduced to zero, the eigenvalues of the mass matrix become the conventional system masses and normal dynamics applies. At nonzero values the eigenvalues may be very different from the natural masses and consequently the dynamics is different. This property may be used to alter the equations of motion to speed up the dynamics in regions where critical slowing down occurs. The method is currently undergoing development.

Professor Cormack (New York State College of Ceramics) described some of the pitfalls in using static simulation methods to model new materials. He defined new materials as ones whose properties fulfill a technological requirement. They are usually less ionic and have more complex structures than those which have been studied traditionally. The main difficulty in simulating these materials is to decide how transferrable the potentials are. Often materials of interest are ternary oxides where the potentials need to be transferred from binary oxides. In this case the short-range part of the potential transfers well but the shell model parameters do not.

Professor Cormack then gave some examples. The materials $MA_{12}O_{19}$ ($M = Sr, \dots$) and $LnMA_{11}O_{19}$ ($M = Mg, Mn, \dots$) are of interest as hosts for laser ions, as substrates for

ferroelectric devices and in radioactive waste disposal. Simulation work on these materials is at an early stage, but the relaxed structures agrees well with experiment. Work is in progress on the point defect properties which are technologically important. Another example was $\text{Gd}_2\text{Zr}_2\text{O}_7$, which has a fluorite superlattice. A simulation using transferred binary oxide potentials failed because the shells polarized excessively. The remedy is to ensure that the shell model parameters are consistent with both the binary and ternary oxides.

Drs. Kenway and Parker (Bath) described some calculations on the segregation of Ca and Mg ions to the surface of Al_2O_3 . Two surfaces have been considered; a basal surface terminated by cations which contracts on relaxation and a prism surface which has ruffled Al – –O – –Al planes. Some calculations were presented on the segregation energies of defects at these surfaces.