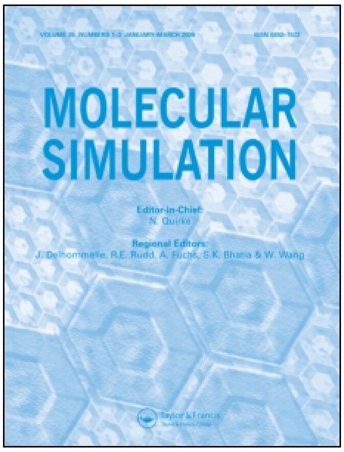

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Atomistic Computer Modelling in Advanced Materials R & D

Malcolm Heggie[a]
[a] Department of Physics, Exeter University, Exeter, Devon, UK

To cite this Article Heggie, Malcolm(1989) 'Atomistic Computer Modelling in Advanced Materials R & D', Molecular Simulation, 3: 1, 183 — 186
To link to this Article: DOI: 10.1080/08927028908034627
URL: http://dx.doi.org/10.1080/08927028908034627

Molecular Simulation, 1989, Vol. 3, pp. 183–186
Reprints available directly from the publisher
Photocopying permitted by license only

Preliminary Communication

ATOMISTIC COMPUTER MODELLING IN ADVANCED MATERIALS R & D

MALCOLM HEGGIE

Department of Physics, Exeter University, Stocker Road, Exeter, Devon, EX4 4QL, UK

(*Received January, 1988; in final form July, 1988*)

One way to model the behaviour of advanced materials is to use *ab initio* total energy calculations. Because these are normally limited in practice to 20–100 atoms either a small supercell or a small fragment of the solid is used. We have chosen a small fragment of silicon with a hydrogenated surface (comprising 26 atoms) to evaluate the formation energy of an ideal vacancy and the activation energy for concerted exchange of atoms. The preliminary results reported here are in reasonable agreement with solid state calculations.

KEY WORDS: Advanced Materials, defect energies, Silicon

INTRODUCTION

Materials subject to extremely demanding specifications, such as ceramics, carbon fibres, nuclear reactor materials and semiconductors, need to be well understood for safety assurance and for performance improvements. Atomistic computer modelling offers fundamental understanding of mechanical, thermal and chemical properties and *ab initio* methods, above all, have proved themselves to be reliable in calculating many material properties with no more input than atomic numbers and atomic masses [1–8]. The predictive power of these methods is amply illustrated by their application to the internal strain parameter in silicon, which had an accepted experimental value of 0.72 [9] for twenty years, but which calculation showed [7], and detailed experiment later verified [10], should be 0.53.

At Exeter we apply these *ab initio* methods to advanced materials (e.g. graphite, silicon, gallium arsenide) using a real space method that does not restrict the geometries we can treat. This sort of approach has been very useful in our previous work on dislocations [11,12]. The surfaces of the fragments we use are hydrogenated to remove dangling bonds and thus to reduce defect-surface interactions. We intend to use the defect energies from these calculations in a database of fitting points for a classical interatomic potential. We are in the process of testing this approach by calculating some defect energies for molecules and showing they are close to the solid state values, prior to fitting the interatomic potential. In the next section I shall describe the first steps we have made in applying the *ab initio* calculation of total energy to molecular fragments of diamond structure silicon.

AB INITIO ESTIMATION OF DEFECT ENERGIES

We have taken two defects relevant to diffusion in silicon as test cases. They both give rise to gap states, which would be expected to lower their energy in the solid state by delocalization, which is not possible in a small molecule. As the molecule size increases we expect to approach the solid state defect energy from above. Neutral defects were considered and we used an *ab initio* total energy program developed by R. Jones [13] at Exeter employing norm-conserving pseudopotentials [3], the local density approximation and a Gaussian basis for orbitals and for the fitted charge density. Typically 4 to 6 sets of s and p Gaussians per silicon site are used plus 1 to 2 sets per bond centre site. This has already been shown to give a good phonon spectrum for silicon when a simple interatomic potential is fitted to various distortions of the diamond-like molecule Si_5H_{12} [14], whose surface is saturated with hydrogen atoms.

Classically the two easiest mechanisms for diffusion are interstitial-interstitialcy diffusion and vacancy diffusion. Two atoms exchanging places (concerted exchange) has usually been excluded on energy grounds. However, recent *ab initio* supercell calculations by Pandey [15] have shown that concerted exchange of neutral atoms is viable, with an activation energy (4.6 eV) comparable to that of self-diffusion in silicon. The ideal vacancy (a vacant atom site with no relaxation of its neighbours) and ideal concerted exchange (two atoms rotating about their mutual bond centre, maintaining their mutual bond length and keeping all other atoms fixed) are the tests we have chosen because of the availability of *ab initio* solid state total energy calculations for comparison.

The Ideal Vacancy

A small fragment of the two closely spaced (111) planes of silicon, comprising six atoms plus one atom from the distant plane below, was used. All surface dangling bonds were saturated with hydrogen (Si–H bond length 1.635 Å, the bare proton potential was used instead of the H pseudopotential) giving a molecule Si_7H_{16}. Two structures were employed (depicted schematically in figures 1a and 1b) one (a) where each silicon atom is four-fold coordinated, only one silicon atom being surrounded by four silicon atoms and the other (b) where that atom is removed to a surface site. The energy of formation of an ideal vacancy in this molecule is thus the total energy

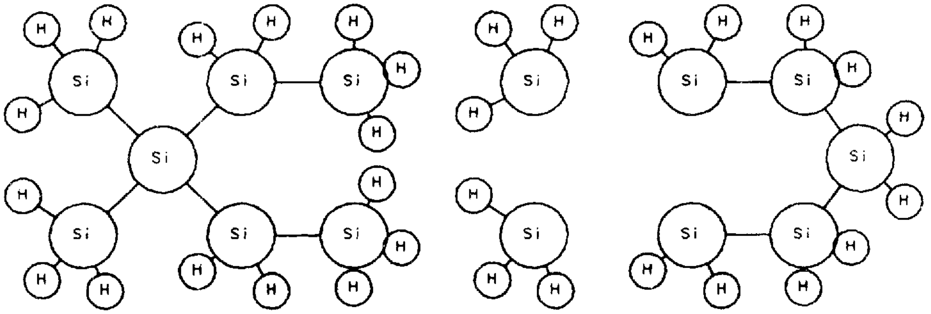

Figure 1 Schematic (flattened) representation of the molecules used for ideal vacancy formation: (a) perfect diamond structure (b) ideal vacancy.

of molecule (a) minus the total energy of molecule (b), *i.e.* 5.2 eV, with two reservations. First, there is a correction of +0.67 eV to the formation energy due to the interaction of two close hydrogen atoms in molecule (a) – this was calculated from the interaction of two close silane molecules. Second, it must be borne in mind that although the number of silicon atoms and hydrogen atoms and Si–H bonds is the same for both molecules, the second neighbour relationships are not equivalent. The approximate value for the formation energy of an ideal vacancy is then 5.9 eV. For comparison, the result of a Greens function *ab initio* calculation for the solid state was 4.5 eV [1] for the relaxed neutral vacancy and a previous estimate of the Jahn-Teller relaxation energy by the same authors was 0.8 eV [16] giving an ideal vacancy formation energy of 5.3 eV. This agreement, within about ten percent, is better than might have been expected.

Ideal Concerted Exchange

The molecule used for concerted exchange comprised two silicon atoms each bonded to the other and to three other silicon atoms, with all surface dangling bonds saturated with hydrogen. We followed the ideal concerted exchange path given by Pandey [15] involving a rotation about the mid-point of the mutual bond from $\theta=0°$ to 180°, combined with a rotation about the initial bond direction. Figure 2 shows how our molecular calculation compares with Pandey's supercell calculation. As expected Pandey's results are lower than ours by between 20 and 25 percent. Although it seems obvious that a molecular calculation would over-estimate the actual energy of the process in the solid state, it should be mentioned that the supercell used by Pandey was rather small (54 atoms) and there may have been some energy-lowering interaction between the defect and its images in neighbouring cells.

CONCLUSION:

The use of molecular fragments combined with a classical interatomic potential should provide an acceptable and efficient alternative to empirical potentials. Al-

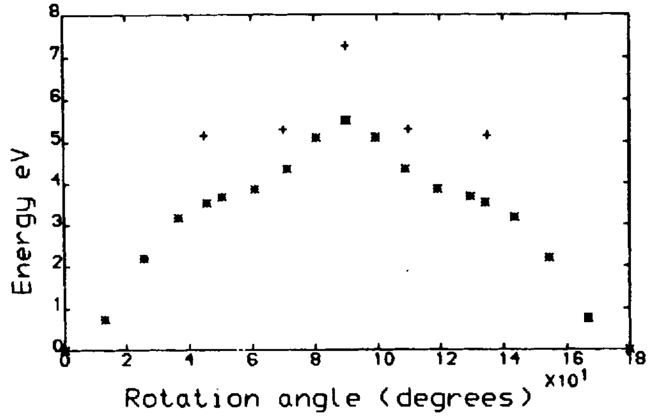

Figure 2 Variation of energy as a function of rotation angle, θ, for ideal concerted exchange. Asterisks – calculation due to Pandey [15], crosses – present calculation.

though small molecules lead to overestimates for defect energies it should be possible to use larger molecules, for instance on the CRAY 2, for which the error would be acceptable. In any event, since the *ab initio* calculation can be done for any new geometry, these potentials should not be susceptible to the catastrophic failures characteristic of the empirical potentials. Their reliability combined with their ease of use (especially considering likely improvements in computer power) make them very attractive for industrial research into advanced materials. It should be noted that one company with a vast materials interest and that already undertakes atomistic computer modelling has an involvement in a similar, molecular approach [17].

References

[1] G.A. Baraff and M. Schlüter, "Migration of interstitials in silicon," *Phys. Rev. B* **30** 3460 (1984).

[2] R. Car, P.J. Kelly, A. Oshiyama and S.T. Pantelides, "Microscopic theory of impurity-defect reactions and impurity diffusion in silicon," *Phys. Rev. Lett.*, **54**, 360 (1985).

[3] G.B. Bachelet, D.R. Hamann and M. Schlüter, "Pseudopotentials that work: from H to Pu," *Phys. Rev. B*, **26**, 4199 (1982) and D.R. Hamann, M. Schlüter and C. Chiang, "Norm-conserving pseudopotentials," *Phys. Rev. B*, **43**, 1494 (1979).

[4] M.T. Yin and M.L. Cohen, "Microscopic theory of the phase transformation and lattice dynamics of Si," *Phys. Rev. Lett.*, **45**, 1004 (1980).

[5] R. Biswas, R.M. Martin, R.J. Needs and O.H. Nielsen, "Complex tetrahedral structures of silicon and carbon under pressure," *Phys. Rev. B* **30**, 3210 (1984).

[6] S. Froyen and M.L. Cohen, "Structural properties of NaCl," *Phys. Rev. B*, **29**, 3770 (1984).

[7] O.H. Nielsen and Martin R.M., "First principles calculation of stress," *Phys. Rev. Lett.*, **50**, 697 (1983).

[8] O.H. Nielsen and Martin R.M., "Stresses in semiconductors: *ab initio* calculations on Si, Ge and GaAs," *Phys. Rev. B*, **32**, 3792 (1985).

[9] C.S.G. Cousins, "Internal strain in diamond structure elements: a survey of theoretical approaches," *J. Phys. C: Solid State Phys.*, **15**, 1857 (1982).

[10] C.S.G. Cousins, L. Gerward, J. Staun-Olsen, B. Selsmark and B.J. Sheldon, "Surface effects in uniaxially stressed crystals: the internal-strain parameters of silicon and germanium revised," *J. Phys. C: Solid State Phys.*, **20**, 29 (1987).

[11] M.I. Heggie and R. Jones, "Models of hydrolytic weakening in quartz," *Phil. Mag. A*, **53** L65 (1986).

[12] M.I. Heggie and R. Jones, "Density functional analysis of the hydrolysis of Si–O bonds in disiloxane: Application to the hydrolytic weakening in quartz," *Phil. Mag. Letters*, **55**, 47 (1987).

[13] R. Jones and A. Sayyash, "Approximations in local density calculations for molecules and clusters: applications to C_2 and H_2O" *J. Phys. C: Solid State Phys.*, **19**, L653 (1986).

[14] R. Jones, "*Ab initio* calculation of the phonon frequencies in silicon using small clusters," *J. Phys. C: Solid State Phys.*, **20**, L271 (1987).

[15] K.C. Pandey, "Diffusion without vacancies or interstitials: a new concerted exchange mechanism", *Phys. Rev. Lett.*, **57**, 2287 (1986).

[16] G.A. Baraff, E.O. Kane and M. Schlüter, "Simple parametrized model for Jahn-Teller systems, vacancy in *p*-type silicon," *Phys. Rev. B*, **21**, 3563 (1980).

[17] D.P. Birnie, W.C. Mackrodt and W.D. Kingery, "Studies of defect formation in silicon carbide," *Advances in Ceramics*, **23**, 486 (1987).