



ELSEVIER

Computational Materials Science 2 (1994) 279–286

COMPUTATIONAL
MATERIALS
SCIENCE

Systematic analysis of local atomic structure combined with 3D computer graphics

Daniel Faken, Hannes Jónsson *

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195, USA

(Received 30 July 1993; accepted 1 September 1993)

Abstract

The implementation of a method for systematic analysis of local atomic structure in combination with 3D computer graphics is described. The method, Common Neighbor Analysis, is a decomposition of the radial distribution function according to the local environment of the pairs of atoms and can provide direct interpretation of various features of the radial distribution function in terms of atomic structure. It can also be used to identify atoms in particular environment, such as FCC, HCP, BCC or icosahedral. We describe an application of this program to a study of crystal nucleation in a molten Cu slab. While the majority of atoms in the resulting crystals are classified as being FCC, stacking faults are observed and can be traced back to the near-critical nuclei.

1. Introduction

The computational power of modern day computers has made it feasible to carry out detailed simulations of large and complex atomic systems. However, the numerical output from large scale calculations and computer simulations is not very illuminating by itself. In analysing atomic structure, one is faced with the problem of extracting some relevant information from an enormous set of numerical coordinates. Complex ordering phenomena can be very difficult or even impossible to identify by extracting a few numbers (such as coordination number) or scalar functions of one or two variables (e.g., the radial distribution function). Visualization alone, even on the fastest 3D graphics computers, is also not the solution to the

problem. For example, it is very tedious, if at all possible, to identify small crystal nuclei in a liquid configuration by simply looking at an image of the atoms.

A powerful approach to this problem is a systematic analysis of the local atomic structure combined with 3D graphics visualization. We describe here an implementation of such an approach. This computer program allows selective rendering of atoms according to their local environment. This can make it relatively easy to identify phenomena which otherwise would remain buried in the mass of numerical data. The program will be made available via anonymous ftp #.

* To whom correspondence should be addressed. E-mail: hannes@u.washington.edu.

The program Glman will be available starting in October 1993 via the internet. To obtain a copy of the program, FTP to mammoth.chem.washington.edu (IP address: 128.95.172.220) as user 'anonymous' and retrieve the file /pub/glman.tar.Z.

To illustrate the functionality of the program, we briefly describe a study of crystal nucleation in a molten Cu slab.

2. Common Neighbor analysis of structure

The method we use, Common Neighbor (CN) analysis, can be thought of as a decomposition of the RDF according to the environment of the pairs. The first peak of the RDF represents the nearest neighbours. Defining the first peak to be at $r < r_c$ where r_c is the position of the first minimum of the RDF, and referring to those as ‘bonded’ pairs, each pair of atoms is classified in the following way: A set of three indices, $ijkl$, specify the local environment of the pair. The first index, j , is the number of neighbours common to both atoms. The second index, k , is the number of bonds between these common neighbours. The third index, l , is the number of bonds in the longest continuous chain formed by the k bonds between common neighbours (see Fig. 1). After each pair has been assigned one of the $ijkl$ types, the distribution of distances can be calculated in the usual way and a radial distribution function for each type of pairs obtained, $g_{ijkl}(r)$. These will be referred to as the CN components of the RDF function and are normalized in such a way that the RDF can then be written as

$$g(r) = \sum_{ijkl} g_{ijkl}(r).$$

This method can be used to interpret various features in the RDF.

In a two component system, a cutoff r_c is found for each of the partial distribution functions, $g_{AA}(r)$, $g_{BB}(r)$ and $g_{AB}(r)$, and the CN components labeled g_{AAijkl} , g_{BBijkl} and g_{ABijkl} .

When the distribution itself is not of interest, the total number of pairs corresponding to each peak in the RDF is an efficient measure of the structure. Pairs corresponding to the first peak in the RDF are denoted $\alpha ijkl$ and their number, $N_{\alpha ijkl}$, is given by

$$N_{\alpha ijkl} = \frac{4\pi N}{V} \int_0^{r_c} r^2 g_{ijkl}(r) dr.$$

Common-neighbour-analysis indices:

j : Number of shared nearest-neighbours

k : Number of bonds between shared neighbours

l : Number of bonds in longest bond-chain formed by shared neighbours

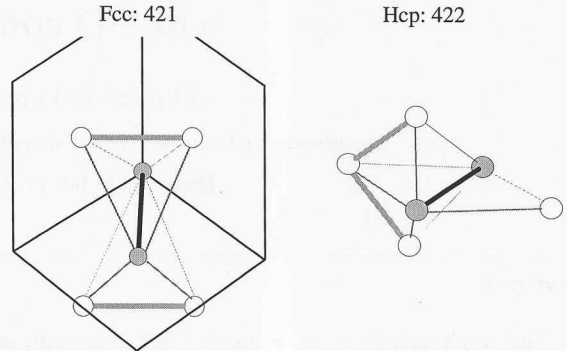


Fig. 1. Illustration of the classification of pairs of atoms according to their local environment, which in CN analysis is characterized by the three indices $ijkl$. The atoms in the pair are colored gray, and the common near neighbors are white.

Similarly, pairs corresponding to the second peak, between r_c and the second minimum in RDF, are denoted by $\beta ijkl$. An earlier and simpler version of this kind of structure analysis was used by E. Blaisten-Barojas [1] to analyse three-body contributions to the energy of small clusters. Honeycutt and Andersen [2] extended the method and used it to analyse the structure of various stable configurations of one-component L–J clusters. Jónsson and Andersen [3] used the method to identify structural relaxations in one- and two-component L–J liquids [4]. Clarke and Jónsson [5] analysed the structural changes during densification of hard sphere packings using CN analysis.

This method has several advantages over other methods we are aware of. It has a simple interpretation, the number of types of features is manageable and yet it is powerful enough to clearly distinguish between various local structures, in particular FCC, HCP, BCC, and icosahedral environments. Different types of pairs are associated with different types of local order. For

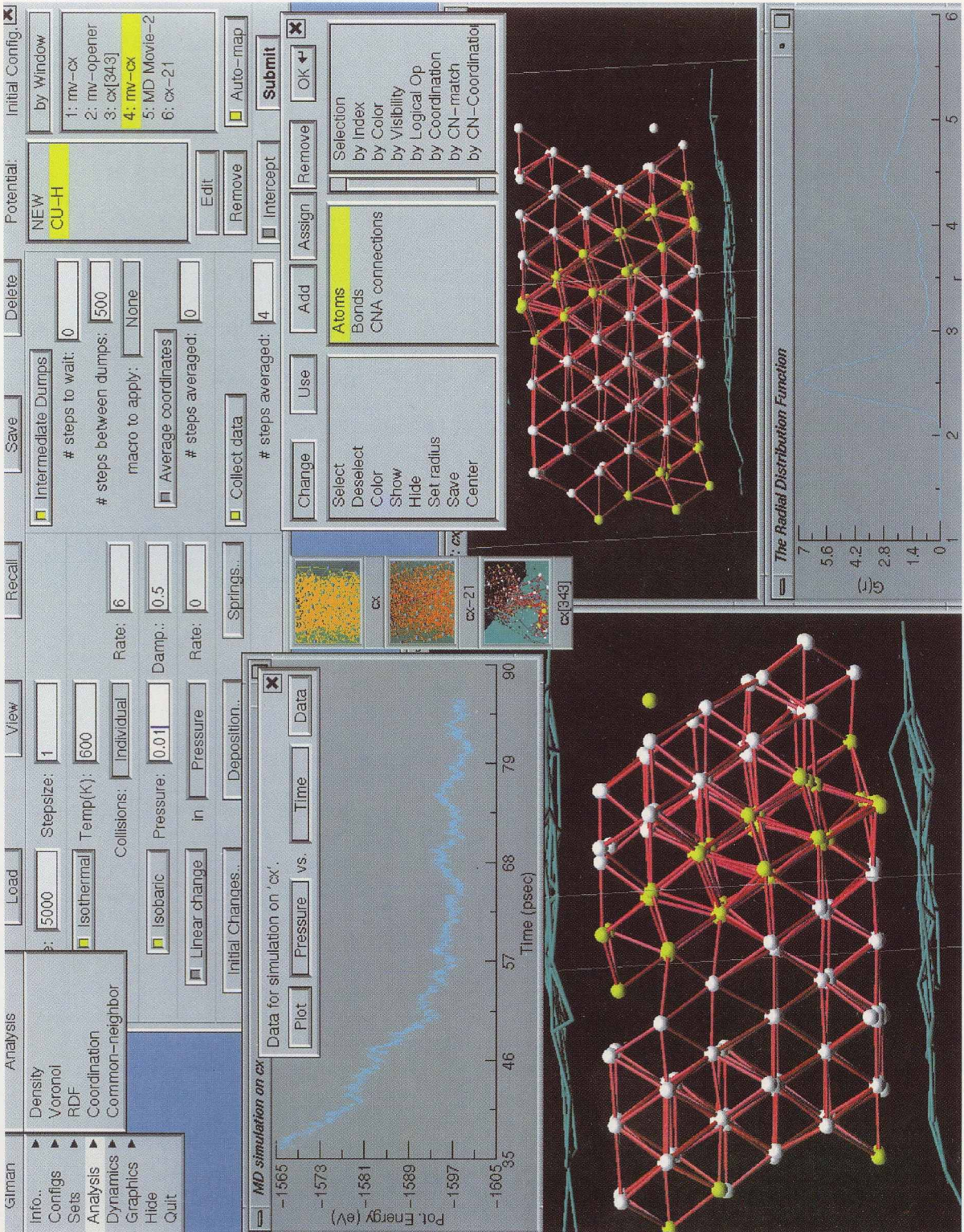


Fig. 2. An image of the entire screen during a Gilman session. The graphics windows show two configurations obtained by cooling a molten slab. Atoms which are locally in an FCC environment are colored white and those in HCP environment are colored yellow. Other atoms are hidden. The graphics images clearly show a stacking fault in the otherwise FCC crystal. The 'grid' above and below the visible atoms are actually surface bonds used to delimit the slab thickness.

example, bonded pairs of type 555 are characteristic of icosahedral order, whereas 421 and 422 pairs are characteristic of FCC and HCP order. The only bonded pairs in the FCC crystal are 421 while the HCP crystal has equal numbers of 421 and 422. The difference between the two pairs is the topological arrangement of the two bonds between the four neighbours. In 421 each of the neighbours forms one of those bonds, in 422 one of the neighbours forms two, two neighbours form one, and the fourth neighbour does not participate in either of the two bonds (see Fig. 1).

The CN analysis is quite insensitive to small displacements of the atoms and in that respect is easier to interpret than Voronoi analysis. Highly symmetric crystalline packings can cause singularities in the Voronoi construction and minor perturbations in the coordinates dramatically change the Voronoi polyhedra. This is particularly a problem in identifying FCC and HCP atoms, as has been discussed by Hsu and Rahman [6]. The problem was demonstrated clearly by Swope and Andersen [7] when they heated a 500 atom FCC crystal (subject to periodic boundary conditions) to 3/4 of the melting temperature, and subsequent application of Voronoi analysis failed to identify any of the atoms as FCC. Remedies have been devised to overcome this problem [6,7]. The simulations presented below illustrate that CN analysis can easily detect atoms in crystalline environment when applied directly to snapshots of crystalline systems as well as systems where early crystal nucleation is taking place.

3. The computer program “Glman”

The program Glman integrates structure analysis tools – in particular CN analysis – with 3D graphics, and thereby enhances both components. The most important features of the program are as follows:

- (1) Realistic, interactive 3D graphics.
- (2) A front end for Molecular Dynamics programs.
- (3) A powerful set-manipulator.
- (4) CN analysis and environment matching.
- (5) Graphing of the $G(r)$, density slices, and other data.

The visualization graphics are written with SGI's GL library and the menus with the FORMS library. If the computer is equipped with graphics hardware such as a z-buffer, the 3D graphics are fast enough to allow interactive inspection (via rotation, translation, zooming, etc.) of the shaded atoms and bonds. One can control rendering aspects such as lighting and colouration to produce striking and informative images.

The front end for Molecular Dynamics programs allows one to set parameters for the simulation, submit a job (possibly to a remote machine), and watch the evolution of the system as the simulation passes the data back to the main program. The program can be set up to preprocess the atomic configurations, e.g. to display only atoms in a certain environment (such as FCC or HCP). The sequences can be stored and later reanalysed and reanimated.

Fig. 2 shows an image of the entire screen during a Glman session, in order to give an impression of the controls used to operate the program. Clockwise from the top-left are: The main menu, the molecular-dynamics controls, the set-manipulation panel, a graphics window with a configuration obtained by crystallization of supercooled liquid slab, the $G(r)$ averaged over several configurations in the simulation, another graphics window with a configuration from an earlier point in the simulation, a plot of the pressure vs. time step for the cooling run, and a small panel which controls plotting of the simulation data (such as the pressure). There are many additional control panels not shown in the figure.

The set-manipulator allows one to form sets of atoms, bonds, or CN pairs, and either modify the characteristics of the items in the set, or perform data analysis on the items. For example, one may wish to find what CN pairs a particular atom on the screen forms. To this end, one could select the atom on the screen (by clicking with the mouse), and then use the data-analysis action ‘CN statistics’ on the objects of type ‘Atom’ with the attribute ‘Selected’. One can store the sets, and do further refinement on their members by boolean algebra (e.g. the blue atoms AND the icosahedral atoms) and other operations which define a set relative to other sets. This allows a

large number of ways to specify a particular group of atoms while using relatively few primary attribute definitions. For example, instead of writing a new function to ‘show neighbours of FCC atoms’, one can apply the action ‘display’ to the atoms with the attribute ‘neighbour’ relative to another set: atoms with the attribute ‘FCC environment’.

The CN analysis component of the program takes nearest-neighbour cutoffs and generates a list showing the number of pairs formed for each pair-type. One can render lines connecting the pairs of a given type, and manipulate the lines and atoms relative to one another via the set-manipulation mechanism described above. The environment matching allows one to enter ‘patterns’ in terms of coordination(s) and the types and numbers of CN-pairs formed. Sets of atoms are generated by these patterns, and can be used as above. For example, one might specify an ‘HCP’ atom to have twelve nearest-neighbours, form six ‘alpha’ 421 pairs, and six ‘alpha’ 422 pairs. One could also perform an approximate BCC match by specifying ten to sixteen neighbours, four to eight 666 pairs, and four to twelve

444 pairs (an atom in an ideal BCC crystal has 14 near neighbors, forms six 666 pairs and eight 444 pairs).

In the graphics windows shown in Fig. 2 (and later figures), the set-manipulation menu and CN analysis have been used to colour FCC atoms white, and HCP atoms yellow. Other atoms are hidden. The ‘grid’ above and below the visible atoms are actually surface bonds used to delimit the slab thickness (the box is much longer than the slab is thick) – surface atoms (identified via the ‘sets’ facility above by looking for bonds of atoms with less than ten neighbours) can never be in FCC or HCP environments.

The graphing tool handles data such as the $G(r)$, and will provide an easy way to decompose the $G(r)$ in terms of sets of pairs (such as the set of 555 CN connections, to obtain $g_{555}(r)$).

All data analysis and ‘set’ operations can be done on sequences as well as individual configurations, so that, e.g., one’s $G(r)$ can be averaged across an entire run (or not), and cutoffs specified for CN-analysis can be used for a group of configurations. To form new sequences, one may simply pick configurations (or sequences) out of a

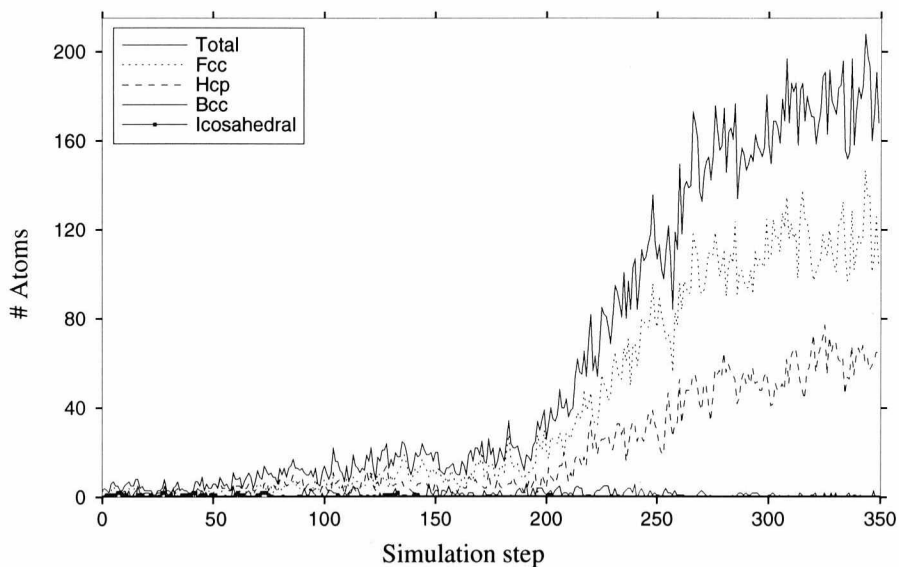
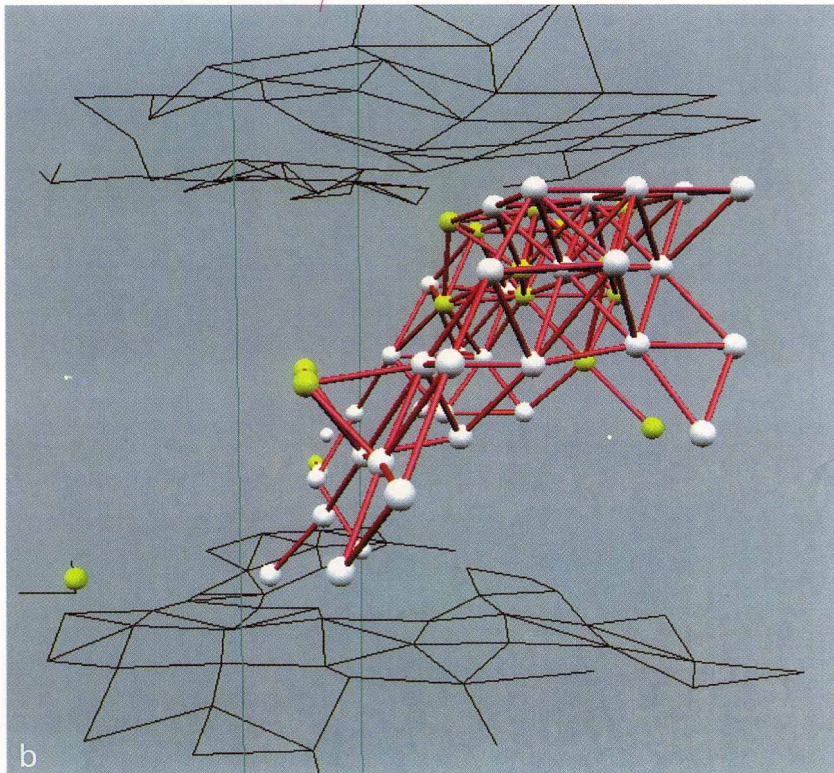
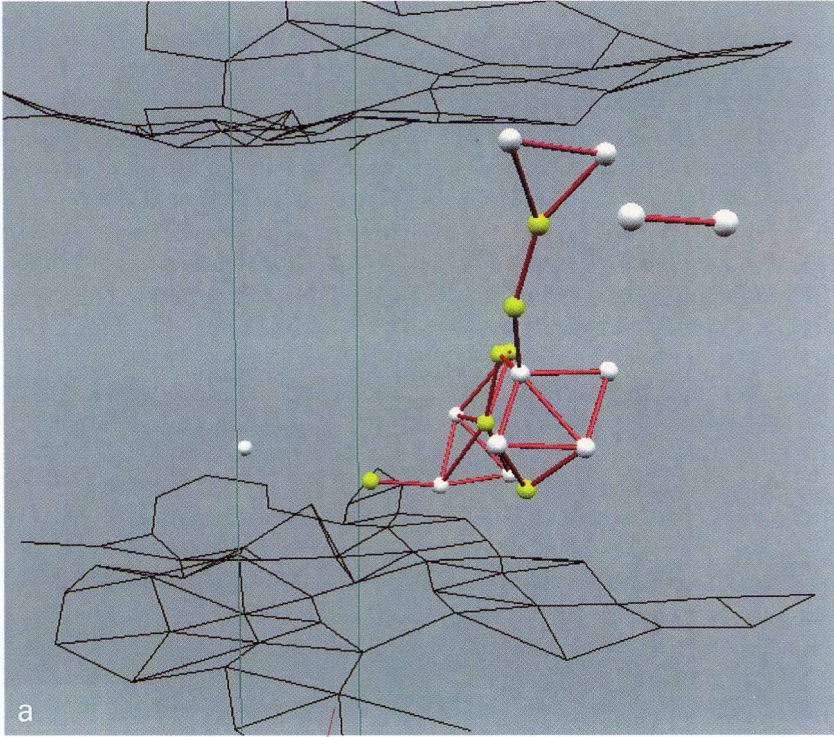
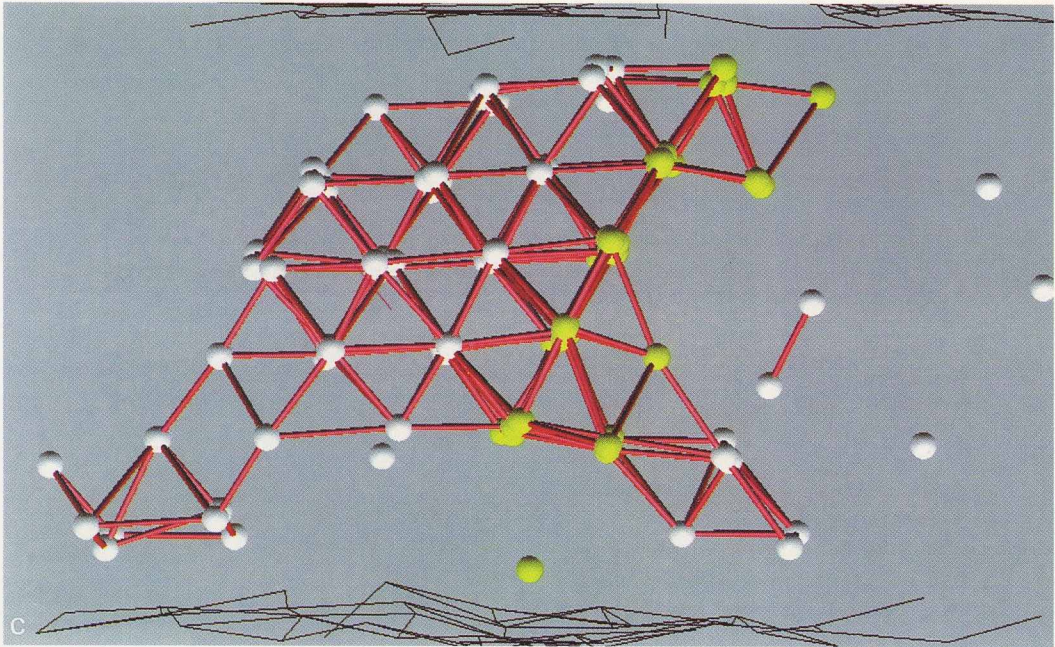


Fig. 3. The figure shows the number of atoms identified by CN analysis as being in a crystalline environment at different time steps in the simulation. Atoms in FCC, HCP, BCC, and icosahedral environments were found, but only the first two were present in significant amounts. The atoms identified as being in an HCP environment constitute stacking faults in the FCC crystal.





browser. For example, the images in this paper are of frames in a single sequence which was analysed once, and manipulated only once in order to color certain types of atoms and bonds, hide others, etc.

4. Application to crystal nucleation in molten Cu

We now briefly describe the application of CN analysis and the program Glman to the study of crystal nucleation in molten Cu slab. The purpose is to illustrate the functionality of the program rather than to present definitive results on nucleation. Extensive and informative studies of crystal nucleation by computer simulation have been carried out recently by several groups [7,8].

Presented in Fig. 2 are snapshots from the time-evolution of a seven-layer copper slab. The

system consists of 448 atoms, initially in 7 layers and is subject to periodic boundary conditions in two directions. The system therefore represents an effectively infinite slab with free surface above and below. The edges of the simulation box are drawn in the figure as narrow lines. The Molecular Dynamics were carried out using the velocity Verlet algorithm [9]. The atoms interact via an EAM-type potential [10] adjusted to reproduce various properties of crystalline Cu and Cu dimer [11]. The potential favors FCC over HCP, but only very slightly.

Initially a crystalline slab, the sample was heated above the melting temperature (1350 K) until thoroughly molten, showing no sign of crystalline order (using CN analysis). The sample was then cooled rapidly to 600 K. This was done interactively through Glman, using only menus.

Fig. 3 shows the number of atoms identified by

Fig. 4. Snapshots of the system at various times during the simulation (the time step numbers have arbitrary origin but correspond to the axis on Fig. 3). (a) Time step number 135, a small crystal nucleus has formed, corresponding to a maximum in fig. 3, but a few time steps later it has dissolved. (b) Time step number 214, shortly after the crystallisation has started. A stacking fault is already evident here. (c) Time step number 240, a large portion of the slab is crystallised with a clear stacking fault.

CN analysis as being in a crystalline environment vs. the step in the simulation (only part of the simulation is shown). Atoms in FCC, HCP, BCC, and icosahedral environments were found, but only the first two were present in significant amounts.

Fig. 4(a) shows the crystalline atoms in simulation frame No. 135, which, judging from the plot (Fig. 3) is close to being large enough to serve as a nucleus for crystallisation. However, it dissolves a few timesteps later.

Fig. 4(b) shows frame No. 214, taken shortly after the crystallisation has caught on. One can see that the center of crystallisation has moved from the previous figure's, and seems to be more dense than spread-out, with a triangular lattice already becoming evident.

The last Fig. 4(c), shows frame No. 240, where a large portion of the slab is crystallised, and the close-packed planes are obvious (this view is from an effectively orthogonal field of view, in order to show the regularity of the lattice). Two of the close-packed planes are identified as HCP. This represents a stacking fault in the otherwise FCC crystal. It corresponds to skipping a plane in the FCC stacking: from the right, the stacking is A B C B C (A). A stacking fault is also detectable in Fig. 4(b), but it later disappears and a new stacking fault develops in a different direction. This stacking fault persists through the simulation, as can be seen from the two graphics display-windows in Fig. 2 (frames No. 266 and No. 343).

It has been hypothesized that lattice defects are essential for rapid growth of crystal nuclei, and could explain the preference of FCC over HCP ordering even in systems such as Lennard–Jones, where HCP is energetically slightly favored [12]. GIman is a powerful tool for studying such phenomena.

Another application where GIman has proven very useful is studies of solid interfaces, in particular the interface of two FCC solids with lattice mismatch [13]. The local atomic structure at the interface, the radial distribution within layers

parallel to the interface and the density of atoms perpendicular to the interface can all be analysed quite easily within the program.

5. Acknowledgements

We have had several helpful discussions with Marco Ronchetti and his group, and with John Shelley. This work has been supported in part by NSF grant CHE-9217774 and by the NSF-REU program (DF). Part of the code development was done at Centre Européen De Calcul Atomique et Moléculaire (CECAM) in Orsay, France, with financial support from the institute. The computer program was developed as part of an effort to integrate research level computers and chemistry software into the undergraduate curriculum. For this purpose, a computer teaching laboratory has been established at the University of Washington Chemistry Department, under a grant from the NSF (CHE-9114495).

6. References

- [1] E. Blaisten-Barojas, *Kinam* 6A (1984) 71.
- [2] J.D. Honeycutt, H.C. Andersen, *J. Phys. Chem.* 91 (1987) 4950.
- [3] H. Jónsson and H.C. Andersen, *Phys. Rev. Lett.* 60 (1988) 2295.
- [4] In these earlier studies the last index did not have a systematic definition and the notation for the CN pairs was slightly different.
- [5] A.S. Clarke and H. Jónsson, *Phys. Rev. E* 47 (1993) 3975.
- [6] C.S. Hsu and A. Rahman, *J. Chem. Phys.* 71 (1979) 4974.
- [7] W.C. Swope and H.C. Andersen, *Phys. Rev. B* 41 (1990) 7042.
- [8] J. Yang, H. Gould and W. Klein, *Phys. Rev. Lett.* 60 (1988) 2665.
- [9] H.C. Andersen, *J. Chem. Phys.* 72 (1980) 2384.
- [10] A.F. Voter and S.P. Chen, *Mat. Res. Soc. Symp. Proc.* 82 (1987) 175.
- [11] A. Goldstein and H. Jónsson, unpublished.
- [12] B.W. van de Waal, *Phys. Rev. Lett.* 67 (1991) 3263.
- [13] J. Hoekstra, H. Yan, G. Kalonji and H. Jónsson, manuscript in preparation.