Dynamics of orientationally disordered crystals

M T Dove*, D Fincham** and R E Hubbard†

*Department of Theoretical Chemistry, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK
**Department of Chemistry, University of York, Heslington, York YO1 5DD, UK
†Department of Chemistry and Computing Service, University of York, Heslington, York, YO1 5DD, UK

Techniques in molecular graphics have been combined with computer simulations of orientationally disordered crystals to produce short films. This has enabled the study of the dynamics of molecular crystals at a microscopic level in a new way, giving good qualitative information that cannot easily be obtained by other means.

The study of disorder in condensed media is one of the more rapidly growing areas of condensed matter physics. One class of disordered systems is orientationally disordered (OD) crystals, or plastic crystals[1]. These systems are usually composed of small highly-symmetrical molecules, and are characterized by the spatial positions of the molecules being ordered on a (usually cubic) lattice with the orientations being disordered. Thus these systems can be said to be intermediate between a true liquid (with neither positional nor orientational order) and a true crystalline solid (with both positional and orientational order). The disorder is similar to paramagnetic disorder, but often more complex, and different types of disorder can be identified. Often the molecular symmetry is lower than that of the site, as for a tetrahedral molecule (or molecular ion) in an octahedral site. In the limit of strong crystal field, as experienced by a NH_4^+ ion in an ammonium halide crystal, the molecular ion will take only certain discrete orientations with frequent jumps between different possible orientations. On the other hand, if the crystal field is weak in comparison to the magnitude of the fluctuations, as in CBr_4, the molecule is freer to take on a whole range of continuously changing orientations, giving the phenomena of rotational diffusion, and in the limit of complete isotropy the molecules are able to rotate freely. An example of free rotation is methane. Another type of disorder can be found when the molecular and site symmetries are identical, if a balance exists between two or more competing interactions. An example is SF_6[2,3].

One of the problems in the study of OD crystals is that conventional experimental techniques (e.g. neutron scattering) are often unable to give definitive information about the disorder. This is primarily because the disorder smears out any structure in a response function, or susceptibility, being measured. For this reason computer simulations can have an important role to play in the study of OD crystals. The authors use the technique of molecular dynamics simulation, in which the continuous classical equations of motion for an ensemble of molecules are solved numerically, and the forces are calculated using a representative model intermolecular potential function[4]. Such techniques have been used, for example, in the analysis of inelastic neutron scattering data[5].

Furthermore, there does not yet exist a full theoretical description of OD crystals that reproduces many of the features. It would clearly be of great advantage if it were possible to actually see the dynamical behaviour of these systems at a molecular level in order to be able to qualitatively identify the important elements. This possibility can now be partly obtained by combining computer simulations with techniques in molecular graphics to produce short films that show the motions of the molecules. Here we present the results of such studies on two systems, SF_6 and CBr_4. Both have cubic structures (*bcc* and *fcc* respectively), but SF_6 is representative of the case where the molecular and site symmetries are identical, and CBr_4 of where the molecular symmetry is lower than that of the site and the crystal field is small.

TECHNICAL DETAILS

The simulations were performed on the ICL Distributed Array Processors at Edinburgh University and Queen Mary College, University of London, UK. The simulated system contained 4096 molecules, within periodic boundaries, and each molecule was treated as a rigid body when integrating the equations of motion. Configurations consisting of positional and orientational coordinates of three sets of 25 molecules, representing portions of the (100), (110) and (111) crystal planes, were saved every 0.1 ps. The resulting files were transmitted over the academic network to an ICL Perq at York University, which has an attached Metheus Omega 400 raster graphics device.

The pictures were produced using the program Hydra[6]. Among many other features this program allows files containing dynamical trajectories to be examined and displayed in a number of ways. One of several raster representations has been used in which atoms are dis-

played as shaded colour spheres. Although a full depth-buffer algorithm, allowing correct intersections between spheres to be calculated, is an available option, it is too slow on the Perq for film making. A representation was therefore adopted in which the non-central atoms in a molecule are shown as spheres which just touch; the central atoms are not displayed. The molecular pictures can then be built up by the well-known technique of sorting the atom centres on z before drawing a sphere for each atom. The shaded spheres are created as a series of overlapping concentric circles using a primitive circles-drawing command of the Metheus. Different coloured spheres are used for each atom in a molecule to facilitate viewing of reorientational processes. In the case of SF_6 the fluorine atom positions and radii in our representation correspond quite closely with those of the potential model used in the simulation; in the case of CBr_4 the atoms are somewhat smaller and farther apart than in the potential model.

The films were made by photographing the monitor screen with a 16 mm camera using a simple photoelectric triggering device; with double-framing, a 30 s film can be made in an overnight run.

SF₆ SIMULATIONS

The OD phase of SF_6 has been studied in some depth by simulations[2,3,5]. The main results were that the average orientation of the molecules corresponds to the six S–F bonds lying close to the unit cell axes, and that the disorder arises because of a competition between two opposing interactions. The nearest neighbour interactions favour the orientational ordering of molecules, whereas the next nearest neighbour interactions oppose this ordering because it brings two fluorine atoms too close to each other along a unit cell edge. This competition has been called 'orientational frustration'. Thus the molecules take on new orientations in order to relieve this frustration.

The nature of the disorder can be seen in Colour Plate 1, which shows one frame of a film displaying part of a (100) plane. The films show that the disorder is dynamic, with the molecules moving to avoid close F···F contacts. The molecular motions are quite complicated, as would be expected, showing large amplitude librations and vibrations with frequent reorientations, usually about axes close to the crystal 4-fold axes. Some aspects of correlated motions of neighbouring molecules are shown in Colour Plate 2, which shows a series of frames, 1 ps apart, of two next nearest neighbouring molecules. The way the molecules move to avoid close contacts is illustrated; in particular the feature that one S–F bond 'precesses' about another which is approximately stationary was frequently present. This type of motion had been predicted by calculations of appropriate distribution functions[3], its realization was unclear. One interesting type of correlated motion is when two molecules rotate together and become momentarily locked into a cog-wheel type motion. This occurs between 18 ps and 19 ps in Colour Plate 2, and is illustrated in greater time resolution in Colour Plate 3.

The films give the overall impression of the dominance of diffusive collision-induced rotational motions, and have highlighted the nature of molecular reorientations. They have also answered one important question that could not be easily resolved by other means: that of whether part of the disorder was due to the existence of small domains of molecules ordered in a low symmetry structure as precursors of the low-temperature ordered triclinic phase. These small domains would still yield crystal-averaged disordered cubic structures, although the apparent disorder would be static. However, the films conclusively show that such domains do not exist, and that the disorder is purely dynamic.

CBr₄ SIMULATIONS

The case of the OD phase of CBr_4 is more complex than that of SF_6, and the films of CBr_4 have played a significant role in augmenting recent simulation work[7,8]. One frame is shown in Colour Plate 4. The overall impression is that the distribution of orientations is much more uniform than in the case of SF_6. The films have shown that one model for the disorder, in which the orientation of each molecule is one of six possible orientations[7,9], is incorrect. Instead the molecular orientations are continuously changing, and the films show that this occurs in periods of slow rotational diffusion occasionally interrupted by short periods of more rapid spinning in which the molecule is rotating by as much as 1–2 complete turns. The motion of a single molecule is illustrated in Colour Plate 5, which shows a sequence of frames.

The correlation of the motion of a CBr_4 molecule and its neighbour is different from SF_6 as the motions are more complex. The CBr_4 molecules do not have enough free volume to permit unhindered rotation, and the films show clearly how the molecules rotate in order to avoid close Br···Br contacts. The free rotation of a molecule occurs when the neighbouring molecules all move away, expanding the volume and hence allowing unhindered rotation. A few occurrances of correlated cog-wheel type rotations were observed.

DISCUSSION

The value in augmenting computer simulations with molecular graphics to produce films is that this approach can give useful qualitative information about the dynamic nature of OD crystals, particularly as there is as yet no comprehensive guiding theoretical model. The importance of this qualitative information is two-fold: first, in disordered systems it is never clear from the outset what features are interesting and worthy of study, and second it is also often difficult to give a precise mathematical description of such features (e.g. correlated reorientational motions) in order to obtain quantitative data. The results presented above illustrate these points well.

One important point in making films is that the graphic representations should aid the eye as much as possible. For this reason the use of coloured and shaded spheres to represent atoms is preferable to simpler representations such as line drawings, which force the user to concentrate more on following the representations and less on the complex motions under study. The use of the program Hydra with raster graphics has proved to give very good representations of the molecules. The user is able to select colour schemes that suit his purpose, and by using different colours for different atoms the

eye is able to follow the reorientational motions very easily.

Our results demonstrate that the use of films with computer simulations is very useful in the study of OD crystals. The qualitative information given by the films often cannot be readily estimated by other techniques, and is crucial for more quantitative analyses. The authors plan to use this approach for the study of further systems of interest, including the case of strong crystal fields. Part of the success of the use of films is due to the simplifying feature that OD crystals have an underlying lattice, so that the same set of molecules always remain in view. Thus it may be that other disordered systems such as liquids will prove to be too complex for graphics to be of use. However, the study of other disordered systems such as fast-ion conductors would doubtless be considerably aided by the use of graphics.

In addition to producing films, the authors have used an Evans and Sutherland PS300 to experiment with the use of interactive graphics to study the dynamical trajectories. The program Hydra can download short sequences of configurations into the PS300, which can then be scanned in time interactively, in addition to the other transformations possible such as rotation. This is obviously a much more flexible method of studying dynamics. However it suffers from the limitation of only allowing a vector representation, which does not enable events such as correlated motions to be so easily perceived. In addition the limited memory severely restricts the length of sequence which can be displayed, to about 5 ps in our case. At present the main use of the interactive technique might be to obtain an overall first impression and to select sequences and orientations for more detailed study by film making. As graphics devices improve, particularly as raster graphics become faster and incorporate significantly larger display lists, it is anticipated that interactive techniques will become very important in the study of dynamics.

ACKNOWLEDGEMENTS

REFERENCES

1 **Sherwood, J N (ed)** *The plastically crystalline state* John Wiley and Sons, New York, USA (1979)

2 **Dove, M T and Pawley, G S** *J. Phys. C: Solid State Phys* Vol 16 (1983) pp 5969–5983

3 **Dove, M T and Pawley, G S** *J. Phys. C: Solid State Phys.* Vol 17 (1984) pp 6581–6599

4 **Pawley, G S and Dove, M T** *Helv. Phys. Act.* Vol 56 (1983) pp 583–592

5 **Dove, M T, et al.** *Mole. Phys.* Vol 57 (1986) pp 865–880

6 **Hubbard, R E** in *Computer aided molecular design* Oyez Scientific, UK (1985) pp 99–106

7 **Dove, M T** *J. Phys. C: Solid State Phys.* (in press)

8 **Dove, M T** *J. Phys. C: Solid State Phys.* (in press)

9 **Coulon, G and Descamp, M.** *J. Phys. C: Solid State Phys.* Vol 13 (1980) pp 2847–2856