

THE ONE-DIMENSIONAL PLASTIC PHASE OF SF₆: A SIMULATION

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Molecular dynamics now reproduces all the solid-state phase transitions in SF₆. The potential function is unchanged, and the results agree with experiment. In the intermediate phase, two-thirds of the molecules form an ordered honeycomb structure, the remaining third residing in the one-dimensional channels and are orientationally disordered.

The aim of a molecular dynamics simulation is to present a very simple model for the appropriate many-body problem and to use that model to gain insight into the possible behaviour of the real system which prompted the study of the model. Such a model is best based on a minimum number of adjustable parameters, and these should not be continually altered to improve the fit with experiment. It is the fundamental properties of the model system which are important, and these are not usually altered significantly by juggling the parameter values.

Earlier work on the simulation model for the condensed phases of SF₆ was aimed at achieving a plastic phase, and for this an intermolecular potential was needed which was sensitive to relative molecular orientations as well as positions [1,2]. An atom-atom interaction between F atoms was taken as sufficient [1], giving forces between the F atoms of one molecule and those of its nearest neighbours and its next-nearest neighbours. The S-F and S-S interactions were assumed to be included in the F-F interaction chosen, so that a two-parameter Lennard-Jones interaction was all that was needed for the whole simulation. The two parameters were chosen to give the measured cubic unit cell and a reasonable sublimation energy. These parameters have not subsequently been altered, although the plastic phase unit cell edge equilibrates in the simulation to a value a little smaller than that observed in the real system.

The first simulation of this system [1] was per-

formed on a very small sample of 54 molecules and demonstrated plastic behaviour. A larger sample of 4096 molecules was set up on the DAP at QMC, London, which seemed to be showing plastic behaviour at 80 K. This system was suddenly cooled to 25 K and the constant pressure sample was observed to contract over many simulation time steps, giving off excess energy. The configuration at 25 K was analysed by drawing out the molecular pattern [2] and many crystallites of an ordered triclinic structure were observed. The diagrams showing this ordering were of (100) sections (with respect to the cubic structure axes) where neighbouring molecules are in fact the next-nearest neighbours. The ordering is best appreciated by a three-dimensional diagram (fig. 1). Ordering takes place along one (111) direction, giving two chains of molecules of one orientation (let us say A) and one chain of a different orientation (say B). Fig. 1 shows a view looking down the (100) direction as in ref. [2], but only those molecules lying on a (110) plane are seen. The (111) direction goes diagonally across this surface, and in the stereo diagram the (111) direction of interest comes towards the observer rising to the right. This diagram has been drawn by the computer from a selected sample crystallite, and small orientational variations will be apparent as the temperature was 25 K.

This structure is entirely compatible with the result of a recent electron diffraction crystallographic study [3]. However this experimental work suggests that at 80 K the structure is partially but not fully disordered,

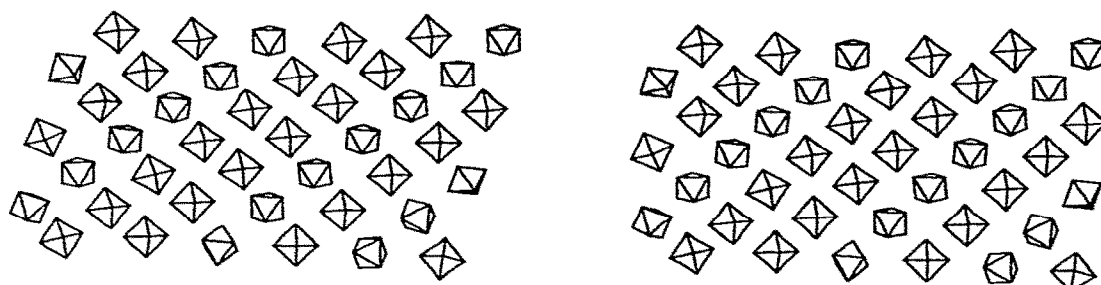


Fig. 1. Stereoscopic view of a (110) plane of the ordered triclinic structure reported in ref. [1].

and therefore we allowed our simulation at this temperature to proceed for a very long equilibration. Re-orientational jumps persisted, but a drawing of a (100)

section through the sample showed that there was some degree of ordering. This drawing is shown in fig. 2, where all those molecules with an S-F bond close

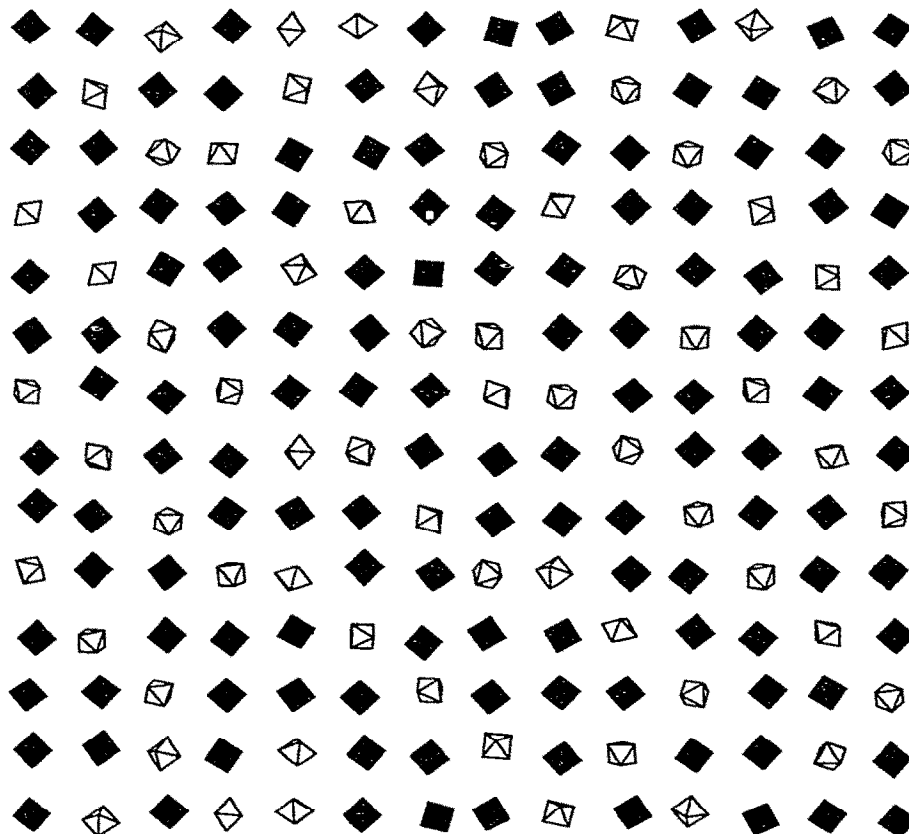


Fig. 2. A (100) section through the sample at 80 K, showing the partial disorder of the intermediate phase. Molecules ordered with one S-F bond near to the cubic phase (100) direction have been filled in. The closely positioned molecules are next-nearest neighbours.

to the (100) direction have been filled in. The ordering is clearly apparent in fig. 2, there being two diagonal rows of ordered molecules (filled) alternating with one row in which there is no orientational order. The A molecules are ordered as in the lowest phase, making a honeycomb structure with channels along one (111) direction of the plastic cubic structure, and in these channels the disordered B molecules reside.

The symmetry of the partially plastic phase can be deduced from the simulation after replacing the B molecules by a time-average distribution of spherical symmetry. The space group is found to be trigonal, $P\bar{3}m1$, in excellent agreement with the electron diffraction result [3]. Moreover because one molecule in three still enjoys orientational freedom, this result is in harmony with the NMR study [4]. The trigonal structure is contrasted with the triclinic structure in fig. 3, where the disordered B molecules are represented by circles.

The packing arrangement of the molecules can be appreciated from fig. 4. The arrangement of nearest and next-nearest neighbours about a given molecule is in the form of a rhombic dodecahedron (fig. 4a), the neighbour centres being positioned at the obtuse and acute vertices respectively. The edges of the dodecahedron are all (111) directions — this is the direction in

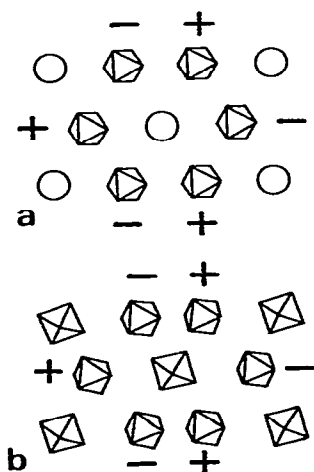


Fig. 3. The two structures (a) partially ordered trigonal at 80 K and (b) fully ordered triclinic at 25 K. The circles denote molecules orientationally disordered and the + and - signs denote a height perpendicular to the diagram of roughly $+1/3$ and $-1/3$ of a unit cell repeat.

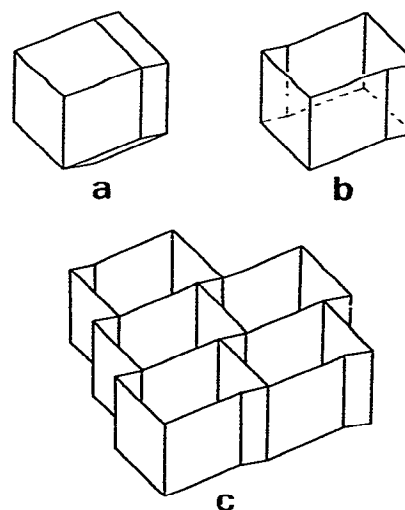


Fig. 4. The nearest-neighbour centre arrangement about a given molecule is represented (a) by a rhombic dodecahedron in the cubic phase. (b) In the trigonal phase ordering occurs along some of the edges of (a), leaving disordered molecules in the channel through the dodecahedron. (c) The partial dodecahedra displaying the ordering are arranged on a honeycomb, giving one-dimensional channels for the disordered molecules.

the cubic phase in which the nearest neighbour relative orientation is the most desirable and therefore contraction along these directions is energetically favourable. However it is not possible to reduce all these distances without reducing the (100) next-nearest neighbour separation — this is the direction which should not be reduced as it is energetically unfavourable, and the structure has to compromise between these competing requirements as it orders. The (100) directions are the short rhombus diagonals in fig. 4a. A contraction down one axis of the dodecahedron keeping some of the edges of the dodecahedron constant can satisfy both conditions (fig. 4b) but only for a limited number of interactions. The top, central and bottom molecules of fig. 4a cannot be satisfied by this deformation, and have been removed from fig. 4b. The distances of these molecules to those represented by fig. 4b are increased somewhat by the deformation, allowing the molecules mentioned greater freedom for reorientational motion.

The disordered molecules thus fill a one-dimensional channel through the dodecahedron, and fig. 4c shows the arrangement of a number of ordered partial dodecahedra, giving the honeycomb pattern of chan-

nels in which the disordered molecules reside. On cooling further this trigonal structure undergoes a further shear of $\approx 2^\circ$ and the B molecules then become ordered.

The partially plastic phase is thus characterised by one-dimensional disordered chains. This is an interesting variation on the phenomenon observed in methane [5] where the disordering is of zero dimensionality — three-quarters of the molecules are ordered (in one of the condensed phases), forming cages in which are trapped the remaining molecules, these molecules having the orientational disorder.

The simulated SF_6 system thus shows all the known behaviour of the real SF_6 condensed phases, with transitions at approximately the observed temperatures. It is based on a simple two-parameter model [1] proposed before the electron diffraction structural work [3] was done. We are therefore confident that it is worth the considerable amount of computer time needed to study the changes of phase of the model crystalline system first to the 1-D partially plastic phase, then to the fully plastic phase, and finally to the melting transition. This furnishes us with the first opportunity of studying these transitions at the molecular

level in full detail, considerably extending the value of molecular dynamics computer simulations.

One should always maintain a degree of caution and emphasise once again that this is and will always be a model calculation. Nevertheless we hope that our current neutron diffraction study of these phases will confirm the crystal structures beyond any doubt!

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