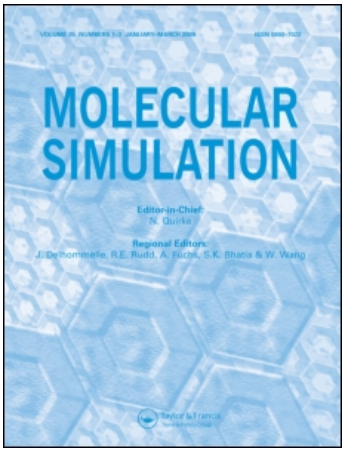

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AN MD STUDY OF SF_6 AND FINITE SIZE ANNEALING*

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The stress-free molecular dynamics method has been used to study the low temperature structure and the plastic-to-crystalline transition of SF_6. When the simulation is performed at low-temperature the structure of the system is monoclinic with space group $C2/m$ which is consistent with neutron diffraction data. A crystal with grain boundaries is obtained when the system is cooled from the plastic phase at a higher temperature. No intermediate phase between the plastic and the monoclinic crystalline phase has been found. This result is in agreement with neutron diffraction experiments but differs from electron diffraction experiments. A tentative explanation of the difference is given.

KEY WORDS: Stress-free molecular dynamics, plastic–crystalline transition, SF_6, finite size annealing.

1. INTRODUCTION

It has been known for some time that SF_6 has a plastic crystalline phase at temperatures between 96 K and 223 K [1]. But below 96 K, there has been a controversy about the structure. On the one hand, results from neutron powder diffraction experiments show that the substance has only one truly crystalline phase which has a monoclinic structure [2]. In this low-temperature crystalline phase, the molecules have two orientations. The proportion of the numbers of the molecules of these two orientations is 1:2. Later in this paper we will refer to these two kinds of molecules as the minority and majority respectively. On the other hand, an electron diffraction experiment [3] showed some evidence of the existence of another phase at the temperatures between 96 K and about 50 K. This phase, the intermediate phase as we will call it, has a structure of trigonal symmetry. In this phase, the minority molecules become orientationally disordered and the majority remain ordered. Below 50 K, both the two experiments agree with very similar results.

So far, MD simulation has been used to study this material and it has helped a great deal in understanding the low-temperature structure [7] and the dynamics in the plastic phase. MD simulation [4] has also achieved an intermediate phase which is in agreement with the electron diffraction experiment. In those MD simulations, a modified constant-volume method was used, whereby the system could be kept at a certain pressure but shear stress could still develop. In the present work, we use a stress-free molecular dynamics to study SF_6. The main purpose of the work is to look for the intermediate phase and to try to explain the difference between the two experimental results.

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The stress-free molecular dynamics of condensed phases has been developed by Parrinello and Rahman [5], following the ideas of Andersen [6]. When using this technique, transitions between two single crystals can happen within a reasonable simulation time. One of the early examples of such a transition is that of rubidium changing from FCC to BCC under the effect of pressure [5]. But, as will be explained later, this could have resulted because of finite-size effects in a small carefully chosen system. In the present work, however, a result which cannot be a finite-size artefact will be presented. We will illustrate that the transition does not need to be a transition between two perfect single crystals. Our conclusion is that the Parrinello-Rahman (PR) [5] technique has aided the discovery of the developing phase to a considerable extent, and that its use for such model prediction is totally justified.

2. STRESS-FREE MD SIMULATION

In a traditional constant-volume MD simulation of a solid substance, the shape and volume of the MD cell are fixed. In order to keep the pressure in the sample balanced with the external pressure, the lattice parameter and cell size have to be readjusted when the pressure deviates from the required value, thus changing the overall volume. This procedure is useful, but it cannot remove the shear stress in the system. The PR method, however, allows the shape as well as the volume to change in response to the imbalance between the internal stress of the system and the external pressure. In this way, the pressure is held constant and there is literally no shear stress. This property of the method can be very important when structural change is involved in the simulation because this is precisely the situation where significant shear stress develops. In this situation, if the PR method is used the shear stress of the system is constantly relieved and the structural deformation of the system as a whole may happen smoothly.

When we use the PR method to study the structural deformation of solids, the constraints from boundary conditions are very important. At present, even with very powerful computers it is still unrealistic to simulate a system which has many more than several thousand molecules. Since the samples are small, cyclic boundary conditions are often imposed so making the simulated system conceptually infinite. Space could then be seen as being filled up with copies of the same MD cell, resulting in a system which is strongly constrained. Only when a structure is compatible completely with the boundary conditions can the system make a single crystal. Otherwise, the structure can only form as a polycrystalline system, or it may not be able to form at all. If the structure of the substance being simulated is known, one can choose suitable cyclic boundaries so that a single crystal can be formed. In the simulation of a structural transformation, only when the structures of both phases are compatible with the boundary conditions can the transition between two perfect single crystals occur. Thus the correlation between the boundary conditions and the structure of the system is very strong, and this may well give rise to spurious phenomena.

In the MD simulation of Rb by Parrinello and Rahman [5], the structural change between FCC and BCC was studied. The two structures of Rb were both compatible with the boundary conditions. It was observed that the system could change from FCC single crystal to BCC single crystal. In the light of the above discussion, one might ask if the transition observed was simply an artefact of the constrained system.

In a constant-volume MD simulation, however, shear stress will develop in a

structural change and this stress can only be relieved through the nucleation of a number of crystallites that have different orientations, and this can only happen provided that the sample is large enough. In Pawley and Thomas's [7] MD study of SF_6 the sample used had as many as 4096 molecules forming roughly 13 × 13 × 13 body centred unit cells. In the simulation, the pressure is kept constant by adjusting the lattice parameter. The results from the low-temperature simulation have shown that the sample is large enough for multiple nucleation to occur. In some relatively big crystallites the crystal structure is very close to the structure obtained from neutron powder diffraction [8]. However, though the sample is big enough to allow some crystallites to develop, a large proportion of molecules are involved in the grain boundaries so that the effect from these grain boundaries has to be taken into account.

In the present work, the PR method is used to study SF_6. The calculation has been performed on an AMT DAP510 with 1024 processing elements (PEs). A comprehensive description of the implementation of MD on the DAP was given by Pawley and Thomas [9]. The central problem is caused by the fact that the DAP has a fixed number of PEs and these PEs are connected in such a way that only lattices of one or two dimensions can easily be mapped onto the machine. The solution to the problem is to set up MD cells with skew cyclic boundary conditions. An MD cell with such boundary conditions is a parallelepiped and can thus fill space. Further details about the boundary conditions and the PR method on the DAP can be found in Refson and Pawley's work on *n*-butane [10].

In the present simulation, the sample has 3072 molecules interacting through the potential suggested previously [11], three times as many as the PEs on the DAP510. This is because we need the number of molecules to be a multiple of three so that the system can make a single crystal at low temperature. As discussed earlier, the cyclic boundary conditions were chosen carefully to be consistent with the structures involved. The program for the sample of 3072 molecules can also easily be adapted to simulate samples of fewer molecules.

3. RESULTS

The first part of the work is to simulate the low-temperature phase. The initial molecular orientations are chosen to be near those in the real system and the molecules are put initially on a BCC lattice. Then the system is kept at a certain low temperature for more than 100 ps. Once we are sure that equilibrium is reached, or, to be more realistic, nearly reached, the crystal structure is measured. We have found that the structure is monoclinic, the space group is $C2/m$. The cell parameters of the monoclinic structure also agree well with those from the neutron powder diffraction experiment [2].

Figure 1 shows one layer of the configuration of the molecules, which are represented by octahedra. The detailed crystallographic results of this part of the work are to appear in a separate publication. Repeating the above process, we also found that on some occasions the system fell into a metastable rhombohedral structure, which transformed into monoclinic when annealed.

Having achieved the low-temperature structure, we increased the temperature of the system gradually and monitored the change of both the structure of the system and the thermal motion of the molecules. The system remained in its monoclinic structure until the temperature reached about 140 K, and above this temperature the

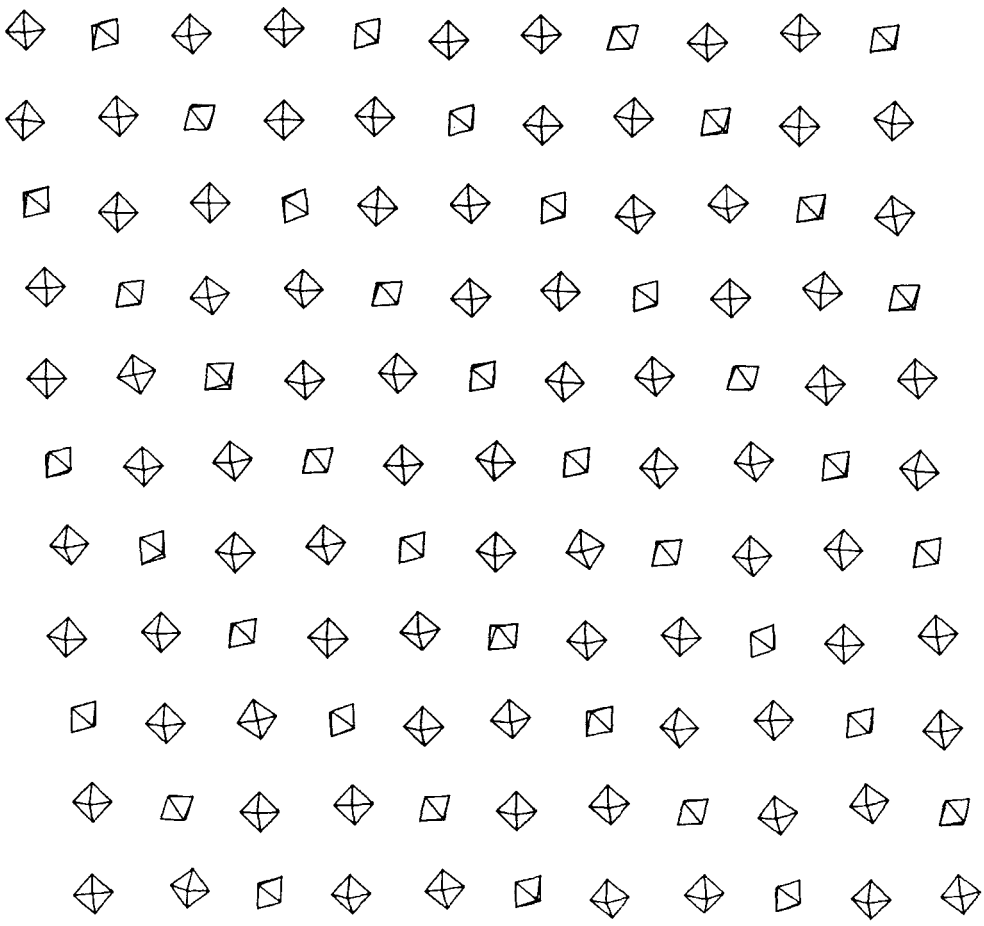

Figure 1 One layer of molecules from a single crystal at 85 K. These molecules lie in the (0,0,0) plane of the BCC lattice, and the close neighbours are next-nearest.

system became a plastic crystal of BCC structure. There is no sign of an intermediate phase.

We then cooled the system from the plastic phase to about 90 K and kept the system at this temperature by extracting energy from it until it was equilibrated. We carried out the process for both the system of 3072 and 1536 molecules. In both cases, we found that the shapes of the systems change when temperature decreases and the resulting systems become big crystals with grain boundary defects. The structure of the crystallite is the same as that for the single crystal. In Figure 2 we can see the BCC structure of the plastic phase change gradually.

Figure 3 shows a section of (0,0,0) molecules and their relation to a monclinic cell. Obviously, these molecules have basically two orientations and the whole pattern is well ordered. Comparing the molecular configurations in Figure 3 and Figure 1, one

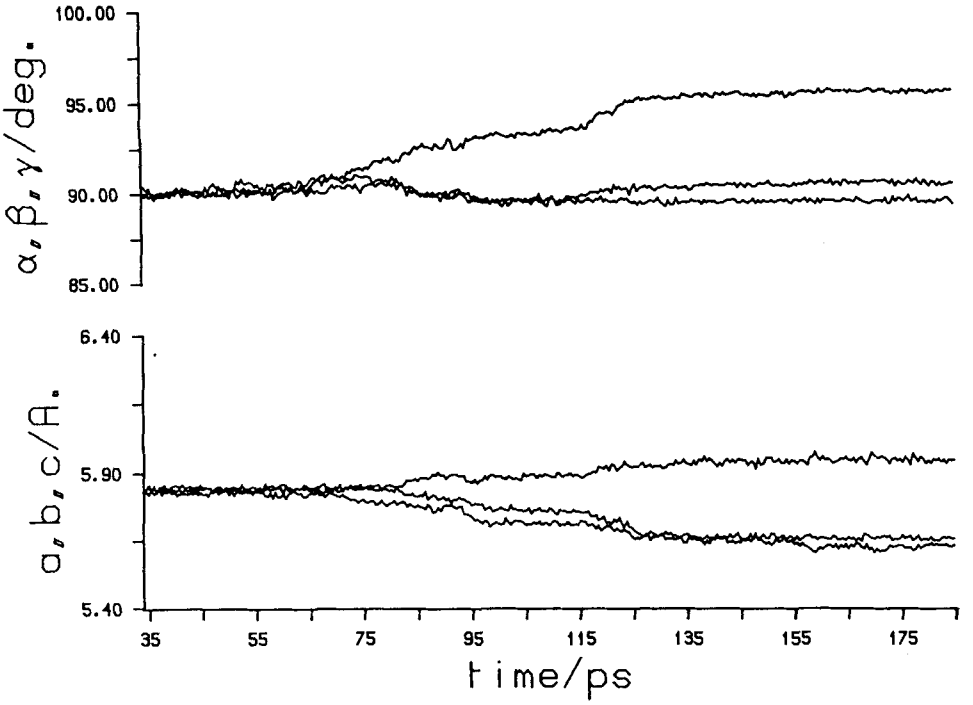

Figure 2 The deformation of the BCC structure to a low-temperature phase during a cooling process to 90 K. The velocities of molecules were rescaled a number of times to remove energy from the system. The cell lengths a, b, c and angles α, β, γ refer to the BCC structure and are not monoclinic parameters.

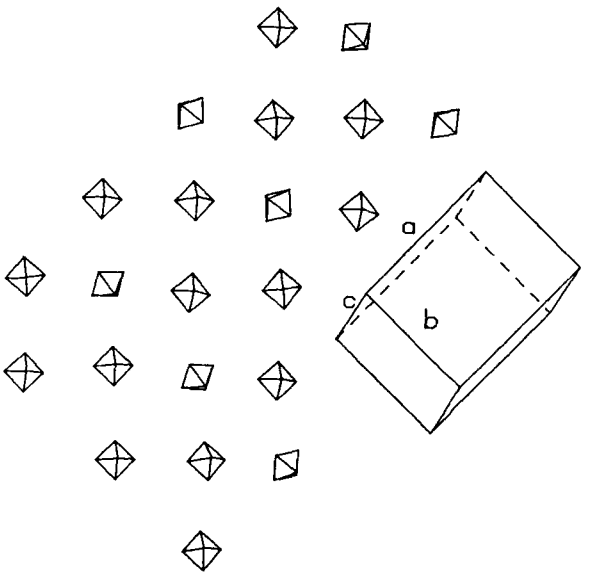

Figure 3 A section of ordered molecules and their relation to the monoclinic cell.

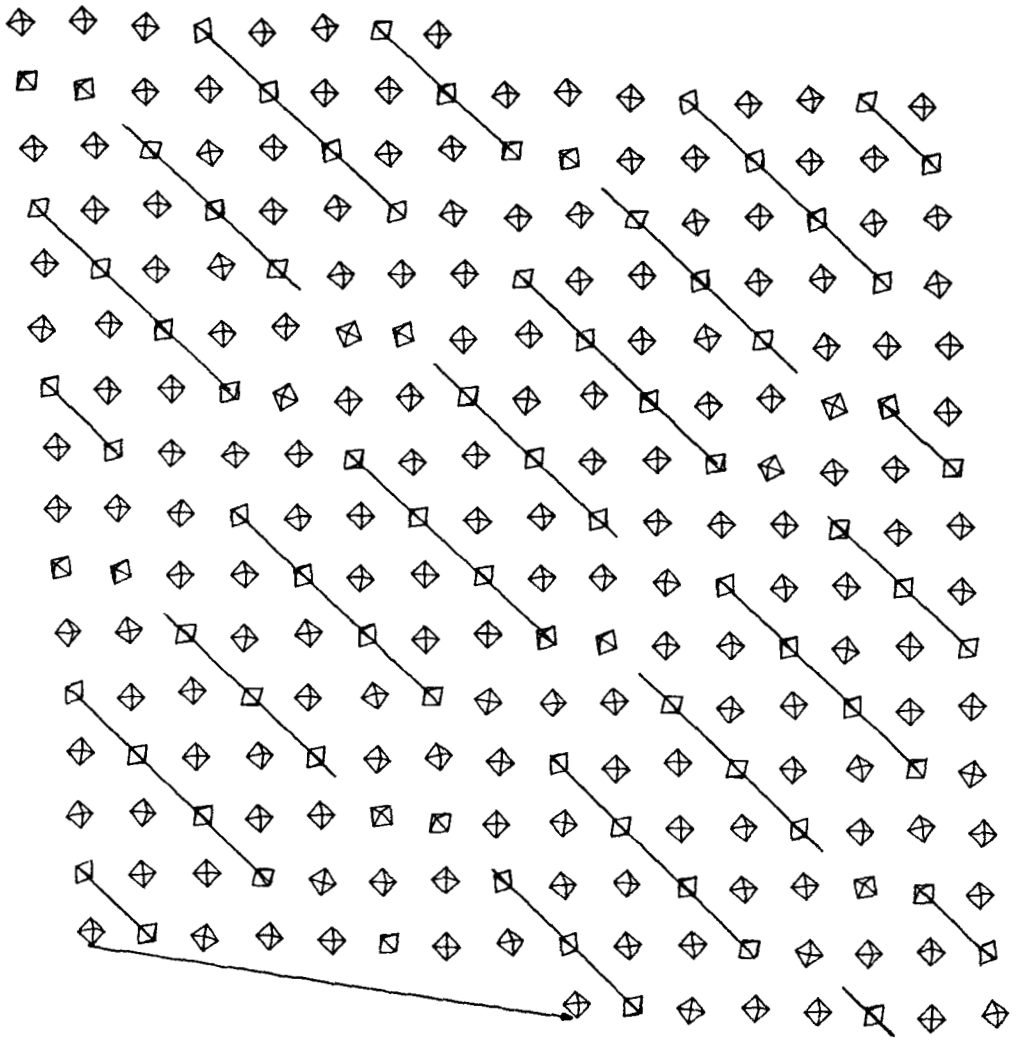

Figure 4 Crystallites and grain boundaries at low temperature. The repetition of the eight columns on the left is due to the skew cyclic boundary conditions, the arrow showing the repetition vector.

can see that the two have in fact the same structure. In Figure 3, the dimension b of the monoclinic cell is in the plane of the molecules depicted, and the sketched cell is deliberately tilted a little to give a three dimensional aspect.

Figure 4 shows many more molecules on the same plane as in Figure 3. In the diagram, the 8 columns of molecules on the left are repeated on the right shifted down one row because of the skew cyclic boundary condition. The ordering is displayed by the lines joining the minority molecules. This result is from the system of 1536 molecules and the MD cell consisted of $8 \times 8 \times 12$ BCC cells. Another run for the system of 3072 molecules gave a similar result, the only difference being the orientation of the crystallites.

4. DISCUSSION

Although our simulation was carefully set up so that the phase transition could take place from one single crystal to another single crystal, this did not in fact occur. The transition is expected to be initiated by a fluctuation which acts as a nucleation centre. Such a fluctuation can occur with a possible 12 orientations, only three of which correspond to the lower phase single crystal. In the few independent cases we have studied, the fluctuation which determined the growth of the dominant grain has not been of the particular orientation just described. The system shape then shears as the dominant grain grows, giving a result with some molecules involved in a grain boundary. The PR method thus allows the whole system to grow with one crystal orientation, the boundary conditions being satisfied by the inclusion of a single grain boundary. From Figure 3 it is clear that this grain boundary develops at right angles to a crystal axis, thus minimising the number of molecules involved in the defect. It is of interest that in the few cases we have studied, the axis perpendicular to the grain boundary has always been the *b*-axis, which is the unique axis of the elusive intermediate phase.

The fact that no intermediate phase has been found in our present simulations is contrary to the earlier MD simulation of SF_6 [4], where a zero pressure method was used. This different behaviour might be related to the different grain boundary structure. In the system of 1536 molecules we used in this work, there are roughly 25 percent of the molecules involved in the single grain boundary, whereas in the earlier work about 40 percent of the molecules are involved in the various grain boundaries. This indicates that there is more energy associated with grain boundary defects in the original study, an energy which is frozen in because further annealing is not possible. The transition from the plastic phase to the crystal phase was found in the earlier work to be a two-stage process in which the first stage was a distortion to give the trigonal intermediate phase. Further cooling led to a second shearing of the structure to give the monoclinic phase, originally thought to be triclinic. Each of these first-order processes involve a latent heat which we can relate to the defect energy of the molecules in the grain boundaries.

Our suggestion is that the intermediate phase is maintained in the simulation where shearing of the MD cell is not allowed and the various grain boundaries do not have the chance to anneal out. In the real system as studied by electron diffraction the production of the sample is such that a very rapid cooling takes place to a temperature above 50 K, permitting the first stage of the transition but not the second. The intermediate phase is therefore a metastable phase which is frozen in.

Below 50 K in the original simulation the second stage of the transition takes place, the energy involved being due to the second shearing rather than any grain boundary annealing. This is in agreement with the electron diffraction experiments at these low temperatures. In the sample used for neutron scattering the low-temperature crystalline phase is reached in one step even at the higher temperatures, as the cooling is sufficiently slow that grain boundary annealing can take place along with the second shearing.

We have seen quite clearly in the present simulation study that grain boundary annealing can take place on cooling the plastic phase sample, giving behaviour more characteristic of the bulk neutron diffraction sample than the very thin electron diffraction sample. The fact that the whole MD sample can shear with the PR method results from the finite-size artefact introduced by using a small system with cyclic

boundaries. This greatly facilitates the annealing and thus the simulation search for new phase transitions. This "finite size annealing" does not, however, generate an artefact, but this must lead to a caveat if the low-temperature phase always grows as a perfect single crystal, as for very small samples [5].

We conclude that the PR method, allowing finite size annealing, greatly extends our ability to search for new phases through MD simulation. Perhaps we should add that care should be taken in the choice of periodic boundaries so that a transition between two perfect single crystals is not possible!

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