Structural Transition on Cooling of Plastic Adamantane: A Molecular-Dynamics Study

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(Received 28 April 1987)

The new molecular-dynamics methods of Andersen and others have been used to study the structural phase transition that occurs in solid adamantane. While the transition between ordered and plastic-crystal phases is spontaneous on heating, cooling leads to metastable structures. The transition to the ordered phase can, however, be induced by extension to the complete molecular-dynamics sample of the short-range orientational correlations characteristic of the high-temperature phase.

PACS numbers: 61.50.Ks, 61.41.+e, 64.70.Kb

The new molecular-dynamics (NMD) methods of Andersen,[1] Parrinello and Rahman,[2] and Nosé[3] have proved useful in the study of structural phase transitions in atomic crystals. Successful applications of this type have been reported for simple systems,[4,5] metals,[6] and ionic salts.[7] The generalizations needed to treat molecular solids have also been given.[8-10] The implementation has been up to now restricted to systems which have a high-temperature rotator phase and a low-temperature ordered phase.[11-14] In these cases there has been no difficulty in finding the disordering transition that occurs when the crystals are heated. The rearrangement of the molecules needed to give an ordered structure on cooling is less easy to obtain since one is dealing with a slow process. The problem is compounded in the simulation because in the NMD constant-pressure technique it is only the translational degrees of freedom of the molecules that are directly coupled to the external pressure. There are then two different possibilities.

(i) There is a strong rototranslational coupling in the molecular crystal which implies a high rotational frequency typically of the order of $10^{12}\ \mathrm{s}^{-1}$. Then with a sufficiently slow cooling, the molecules are able to reorient in a manner consistent with the order characteristic of the low-temperature phase. The NMD methods are therefore almost as efficient as in atomic problems.

(ii) The reorientational motion is a strongly activated process. Its rates, which are rather slow compared with the time scale of the simulation in the plastic phase, are exponentially slower in the cooling of the system. Straightforward application of NMD techniques to such systems gives rise to very long-lived metastable structures. The failure of the NMD technique in predicting the low-temperature phases on cooling in case (ii) is a major problem, since it is frequently the structures of the low-temperature phases that are experimentally not well defined.

Recently, Klein and co-workers[11,12] have shown how to treat case (i) by use of NMD techniques to locate certain of the structural changes that occur on cooling of the disordered phases of alkali cyanides. In this paper we introduce a method to overcome the problem of orientational metastabilities presented by case (ii). We describe it by taking as an example the cooling of an adamantane crystal. We show that the correct low-temperature, ordered structure is obtained when the NMD technique is adapted in such a way as to extend to the complete MD sample the short-range orientational order observed in the high-temperature phase.[15] We assume that the setting up of a local order is a precursory effect which has to be extended to the whole system to produce the phase transition. The success achieved implies that the metastabilities that appear in the standard approach are linked to the slowness of the reorientational motion needed to extend the local order to the whole system. We should emphasize that the method makes no assumption about the structure of the ordered phase.

At room temperature, adamantane ($C_{10}H_{16}$) is a face-centered-cubic plastic with a lattice parameter

$a_c = 9.45$ Å. The adamantane molecule has tetrahedral symmetry and the nature of the orientational disorder in the plastic phase has been interpreted in terms of two (plus and minus) preferred T_d (tetrahedral) orientations of the molecule, with the four molecules in the unit cell randomly reorienting between the plus and minus configurations.[15-17] At $T = 208.6$ K, there is a transition[18] to a body-centered-tetragonal structure with lattice parameters $a_T = b_T = 6.60$ Å, $c_T = 8.81$ Å. In the tetragonal phase, the two molecules in the unit cell are ordered in plus and minus orientations, respectively, but are also rotated through angles of ±90° around the c axis. In previous work,[15] a potential model proposed by Williams[19] has been used in a conventional (normal fixed-volume, fixed-energy) MD study of the high-temperature phase. The results confirmed that jumps occur between the two T_d orientations but also showed that a degree of short-range orientational order exists in the crystal. Of the twelve nearest neighbors of a given molecule, four tend to have the same T_d orientation as the central one, and eight tend to be oriented in the opposite sense. The four molecules that are oriented in like fashion to the first one lie in one of the three (100), (010), and (001) planes, while the others are in the parallel planes above and below. This effect becomes more marked as the temperature is reduced. Our main idea is that the direction in which the alternating T_d order develops will be the one in which the crystal contracts on transition to the ordered phase, i.e., the tetragonal c axis.

In the present work, a series of constant-temperature, constant-pressure ($P = 1$ bar) MD simulations have been carried out for a periodic system of 32 adamantane molecules. The edges of the MD cell **A**, **B**, and **C** are parallel to the axes of the cubic lattice with lengths $A = B = C = 2a_c$. For the tetragonal cell, **A** and **B** are parallel to the diagonals $\langle 110 \rangle$ and $\langle \bar{1}10 \rangle$, respectively, while **C** is parallel to the c axis. In this case, $A = B = 2\sqrt{2}a_T$ and $C = 2c_T$.

The potential of Williams[19] was used in all calculations, and the equations of motion were solved with a time step of 0.01 ps for stable-state runs and of 0.005 ps for transition-state runs. Run lengths were typically 5000–10000 steps. The first calculation was at 163 K and was initiated from the experimentally observed structure. The structure was maintained throughout the full (35 ps) run, with averaged tetragonal lattice parameters given by $a_T = b_T = 6.64$ Å and $c_T = 8.91$ Å. The molecular orientations were monitored continuously via the instantaneous value of the rotator function $M_1^{(a)}$, defined[15] as

$$M_1^{(a)} = \frac{3\sqrt{3}}{4} \sum_{i=1}^{4} x_i^{(a)} y_i^{(a)} z_i^{(a)}.$$

Here $x_i^{(a)}$, $y_i^{(a)}$, and $z_i^{(a)}$ are the components of a unit vector directed from the center of mass of molecule a towards the four tertiary carbon atoms, labeled i, of the same molecule. If we take into account the experimental value of 9° for the angle of rotation, the M_1 function would have in the chosen reference frame the values ±0.951 for the two molecules in the unit cell. The calculations showed that, in fact, $\langle M_1^{(a)} \rangle$ was ±0.95 for every molecule. This average value of the rotator function corresponds to an angle of rotation of 9° around the c axis, but this is not the average angle of rotation. Direct analysis of the single-molecule orientational distribution showed that in the simulations the tetrahedra are rotated on average through ±7° around the c axis, which is close to the experimental value (±9°).

At the end of the run, the external temperature was set equal to 400 K. As expected, a spontaneous transition occurred to an orientationally disordered, fcc structure. The expansion along the c axis is accompanied by a virtually complete loss of single-molecule orientational order.

In the second stage, a more systematic study was made of the effects of variation in temperature. Experiment shows that the tetragonal-to-cubic transition is associated primarily with an expansion of the c axis, with only minor changes taking place in the plane orthogonal to C_T. In Table I we list the average values obtained for A ($=B$) and C over the temperature range between 140 and 400 K. In order to locate the transition, we define an order parameter $\eta(T)$ by

$$\eta(T) = \frac{C(T) - A(T)}{C(140) - A(140)}.$$

The temperature dependence of $\eta(T)$ is plotted in Fig. 1; this quantity shows a rapid decrease at temperatures above 220 K and is essentially zero for $T \simeq 400$ K.

The next calculation was an attempt to recover the ordered structure by slow quenching of the configuration equilibrated at 300 K. Following the suggestions of Refs. 11 and 12, we cooled the system through the phase-transition region using temperature steps of 8° every 4000 steps. The attempt failed: The crystal contracted almost uniformly, and the orientational disorder became frozen in. The variation of the order parameter

TABLE I. MD box axes A, B, and C at different temperatures T. Also listed are the total lengths of runs (in picoseconds). The error on A, B, and C is ±0.05 Å.

T (K)	A (Å)	B (Å)	C (Å)	Time (ps)
140	18.76	18.75	17.77	20
163	18.78	18.78	17.81	35
180	18.78	18.78	17.88	20
220	18.86	18.85	17.95	60
260	18.85	18.87	18.45	60
300	18.83	18.91	18.90	60
400	19.17	19.15	19.15	60

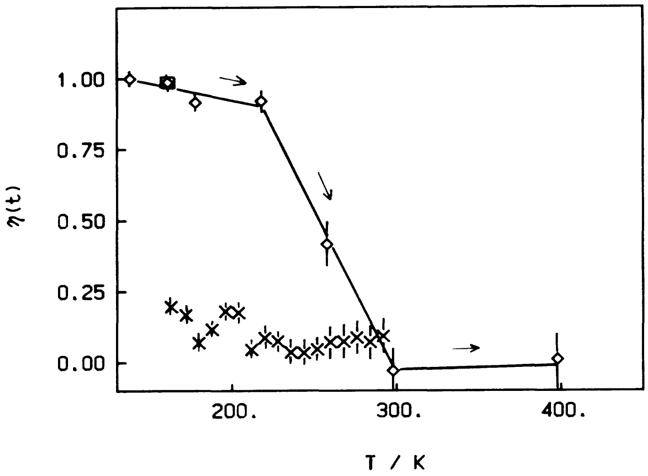

FIG. 1. Order parameter as a function of temperature. At $T=163$ K there are three different values: (i) initial state (lozenge); (ii) state reached by cooling with reordering (square) (the first two are coincident); (iii) state reached by slow quenching (cross).

η in this simulation is given in Fig. 1. The reason for this failure is not difficult to understand. Orientational disorder in adamantane arises from rapid but infrequent jumps between different T_d orientations ($\nu_4=1.7\times10^{10}$ s^{-1} at $T=309$ K[15]). Any rearrangement of the molecules is therefore a very slow process. Even though the thermodynamic conditions may favor an ordering of the molecular orientations, there is no efficient mechanism to induce it. What can be done, as we now describe, is to prepare the system in a suitable initial state that triggers the transition.

As already discussed, the high-temperature phase acquires a certain short-range orientational order as the temperature is lowered. In particular, the majority of first neighbors tend to adopt opposing T_d orientations. If the "ideal" local order were to extend throughout the system, molecules in alternate parallel planes of (100) type would be characterized respectively by orientations of plus or minus type. To initiate the final simulation, we chose an equilibrated configuration from the 400-K run in the fcc phase. One molecule was selected at random and rotated into a perfect T_d orientation. All molecules lying in the same (001) plane as the first one were then given identical orientations, while those in the upper and lower planes were given the opposite T_d order, and so on. The centers of mass, however, remained unaltered. The reordered system was then quenched to 163 K and allowed to evolve under the usual constant-temperature, constant-pressure conditions. A transition to a tetragonal phase occurred almost immediately, the lattice parameter c contracting to the same value as obtained in the original run at 163 K; at the same time, the molecules rotated through angles of ±7° around the c axis. The structural changes occurred on about the same time scale as the spontaneous cubic-to-tetragonal transition that occurred when the system was abruptly heated from 163 to 400 K; the behavior of C in this time interval is illustrated in Fig. 2.

We have shown that the transition to the ordered solid phase of adamantane is easily achieved by quenching of the high-temperature phase provided that the short-range orientational order characteristic of the latter is artificially enhanced. What in effect we have done is, first to identify the precursory effects that manifest when one approaches the phase transition. Then we prepared the system in a state that maximizes the order associated with the precursory effect. Viewed in this way, the method should have a general applicability, though its implementation may be less straightforward when the crystal structures are more complicated or the molecular symmetry is lower than in the example presented here. It should also be remembered that ultimately the relative thermodynamic stability can only be checked by calculation of the free energy.[20]

It is a pleasure to thank M. J. Gillan, I. R. McDonald, and M. L. Klein for useful discussions and the first two for a critical reading of the manuscript. Ian McDonald has helped (reluctantly) with the English, but does not want to be held responsible for the remaining infelicities of expression. We acknowledge the help of the Italian Consiglio Nazionale delle Ricerche through allocation of computer time via the Cray "Project on Statistical Mechanics." We are also grateful for the support provided by the French Embassy in Rome, the "Direction de la Coopèration Scientifique et Technique du Ministère des Affaires Etrangères" (France), and Euro-

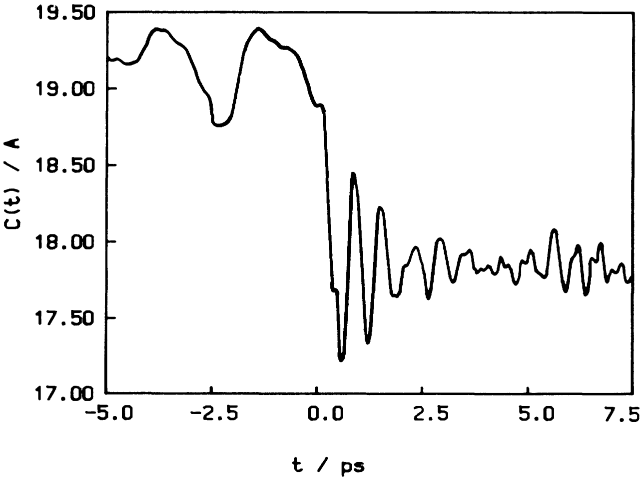

FIG. 2. Time evolution of C axis during the cooling with previous reordering. From $t=-5$ to $t=0$, $T=400$ K (cubic phase); from $t=0$ to $t=7.5$, and $T=163$ K. The behavior shown is the average over two independent runs.

pean Economic Commission Contract No. ST2J-0094.

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