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Computer modeling of disordered molecular solids: Six-state model of glassy crystal cyanoadamantane

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A six-state pseudo-spin model has been proposed to understand the phase transition mechanism and kinetics of the cyanoadamantane glassy crystal. Implementation of this model has significantly improved ergodicity in computer simulations (Monte Carlo technique) of the system. In particular, an order–disorder phase transition from an orthorhombic to a cubic phase has been reproduced for the first time. It has been also shown that this transformation goes through metastable states. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1478769]

I. INTRODUCTION

Glassy crystals have been objects of extensive studies for many years. Among them, ethanol,[1] cyanoadamantane (CNadm) and is mixed crystals (so called cyanoadamantane family)[2] have been model systems for glassy behavior of molecular crystals. 1-cyanoadamantane (1-cyanotricyclo[3,3,1,1]decane, ($C_{10}H_{15}CN$)), is a molecule of C_{3v} point group symmetry composed of a globular adamantane and a cyano group. It possesses a strong dipole moment ($\mu = 3.83$ D) along the threefold axis of the molecule. The phase diagram of CNadm at ambient pressure (Fig. 1) has been studied by a large number of experimental techniques. It has been shown that at high temperature, from 280 K up to the melting point at about 460 K, the crystal exists in the solid rotator (plastic) phase with molecules occupying lattice sites of the fcc structure ($Fm3m$ space group symmetry[3]). In this phase an orientational disorder of molecules results from a dynamical, random distribution of molecular long axes among six orientations corresponding to six crystallographic directions [±100], [±010], and [±001]. Experimentally, the rotator phase can be easily supercooled to give a metastable cubic phase. Further evolution of the supercooled structure depends on a way it was cooled down. After slow cooling to temperatures around 220–230 K the metastable phase easily transforms into a stable ordered monoclinic phase (space group $C2/m$).[4] On the contrary, when quenched to $T=170$ K the crystal transforms to an orientationally disordered phase (glassy crystal).[5–7] A decrease of configurational entropy on approaching the glass transition seen in experiment has been described by the phenomenological theory of Luty *et al.*[8] and

attributed to a development of an antiferroelectric short range order[7] and frustrated tetragonal local ordering (domains) in the quenched system.

The equilibrium phase diagram of the CNadm crystal (and other glassy systems) does not provide the whole information related to the stability and kinetics of phase transformations because of a very characteristic dependence of structural properties on a thermal history of a sample. Depending on a temperature of quenching and a time of annealing, a sample on heating may exist either in only stable phases or may evolve through a sequence of phases, often metastable and of relatively long lifetimes. (Such a behavior has been observed for CNadm. Crystals cooled down close to a glassy transition temperature and annealed during 2 h, relaxed into metastable pseudotetragonal structure before transforming into the stable one.[9]) This means that there are several relaxation mechanisms that lead to the thermodynamically stable configuration; some of them being much slower than others. As a result, such systems are difficult to study numerically because accessible simulated real times are much shorter than a time scale of relaxation of a system.

In general, different time scales of molecular dynamics are a consequence of high activation barriers of molecular flips in the plastic phase. When the probability of flips is very low, computer simulations of a system become quasi- or nonergodic within the accessible simulation time. Quasiergodicity (also called broken ergodicity[10]) may yield results that are completely wrong due to insufficient sampling of a configurational space during simulations.

There are two ways to decrease nonergodicity in computer simulations: First, a preferential sampling (procedures based on the variable step algorithm and/or force-bias methods[11]) can be used instead of conventional Metropolis
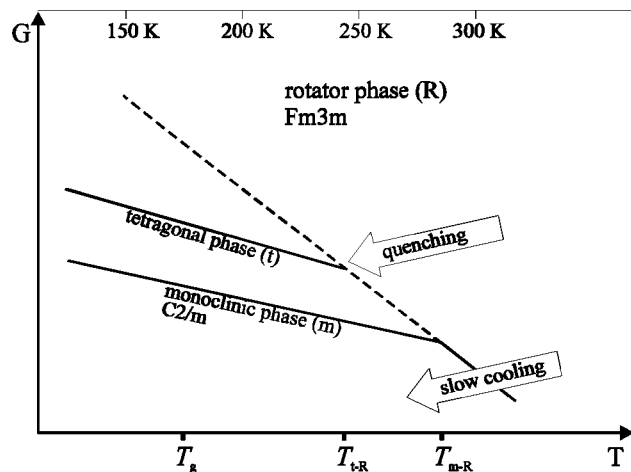
FIG. 1. Schematic diagram (free enthalpy as a function of temperature) of thermodynamic stabilities of different phases of cyanoadamantane crystal. T_g, T_{t-R}, and T_{m-R} indicate the transition temperatures from the rotator phase into glassy state, tetragonal metastable arrangement, and monoclinic stable phase, respectively.

algorithm. We applied this technique in our previous studies of the cyanoadamantane crystal.[5,12] It improved the quality of the sampling but did not eliminate nonergodic behavior. To further decrease the nonergodicity in simulations an appropriate model of a system should be created, in which all relevant features of a system are preserved and energy barriers of molecular flips are neglected. If such a model can be constructed, the use of the standard Metropolis method of acceptation of Monte Carlo moves may suffice to observe an ergodic behavior of a system during computer simulations.

In this paper we present results of implementation of a six-state pseudo-spin model of the cyanoadamantane crystal in Monte Carlo calculations. This model has significantly improved the ergodicity in simulations. For the first time, we have been able to observe an order–disorder phase transition during MC runs, to follow the kinetics of this transition and identify transient metastable states. Consequently, this work offers a new approach to deal with problems of broken ergodicity in simulations not only of the CNadm but also of other glassy materials.

II. SIX-STATE MODEL OF THE CYANOADAMANTANE CRYSTAL

Computer simulations of cyanoadamantane are a difficult challenge for two main reasons. The first obstacle is the size of CNadm itself. It is a relatively big molecule consisting of 27 atoms, which makes models of the intermolecular interaction be complicated. The other difficulty comes from two different time scales of dynamics in the rotator phase of CNadm. The first one corresponds to the molecular flips among six most probable orientations with long residence time of 10^{-6} s and activation energy of around 5900 K [determined by RT dielectric relaxation[13] and NMR (Ref. 14) experiments]. The second component is a rapid rotation of a molecule around the dipolar axis with a relaxation time of the order of 10^{-11} s and an activation energy of about 1200 K.[13,14] The difference in energies of activation barriers of

molecular motions in the crystal leads to the ergodicity problem because the slower motion cannot be sufficiently probed during simulation time. As a consequence, molecular orientations are not uniformly distributed over all equivalent configurations.

To overcome the problem of the relatively big size of the molecule and to afford runs as long as possible, a simple rigid three-site model of the CNadm molecule has been proposed.[5] The molecule has been represented by three centers of interactions: two atomic sites corresponding to C and N atoms of the cyano group, and one site replacing the entire adamantane ($C_{10}H_{15}$) group. Coulomb interactions have also been included in this model to preserve a dipole moment of the CNadm. More details about parameters and a potential form can be found in Ref. 5.

With this model a Monte Carlo study of metastable structures of cyanoadamantane has been done.[5] At high temperature, fluctuations deforming the cubic symmetry into tetragonal arrangements have been observed. This has given indirect evidence that the rotator phase could transform into a state where dipoles are antiferroelectrically ordered along one of the fourfold axes of the parent cubic lattice. Further distortion could lead to an orthorhombic structure or even to monoclinic. However, no phase transformation has been observed during these calculations. All phase remained metastable regardless of a length (time) of MC runs. Clearly, simulations suffered from typical nonergodicity traps as it has been shown in the previous paper.[12] As a consequence, in the next step we made attempts to reduce the quasiergodicity in MC simulations of the plastic phase of cyanoadamantane crystal. First, we have introduced a quantitative measure of nonergodicity and we have shown that the use of preferential sampling decreases nonergodicity in simulations but at a noteworthy expense of computational time.[12]

Therefore, as the final approach, a six-state model of the cyanoadamantane crystal has been defined. The idea behind such a model has been to choose only these configurations of the possible arrangements of the CNadm molecules in the $Fm3m$ crystal structure that are the most probable. Therefore, in our model each molecule has been allowed to adopt only one of six possible orientations (along $[\pm 100]$, $[\pm 010]$, $[\pm 001]$). In other words, the rotational degrees of freedom are discrete and only these six orientations are generated during computer simulations. It also means that a flip from one configuration to another does not require calculating energy values at points in-between these two configurations. From a point of view of computation efficiency, no computational time is wasted on probing a statistically irrelevant part of the configurational space. It is important to emphasize, that the interaction model is the same as that described in Ref. 5. The only difference is that the orientations are limited to six discrete states instead of the continuous representation.

Since one molecule can occur in any of six allowed orientations it follows that there are 36 (6×6) possible relative arrangements of every two CNadm molecules. Adopting the linear three-site model for cyanoadamantane, a number of these relative arrangements reduces to 10 in case of the first nearest neighbors and only to 8 for the second nearest neighbors. The reduction is possible because some of the arrange-
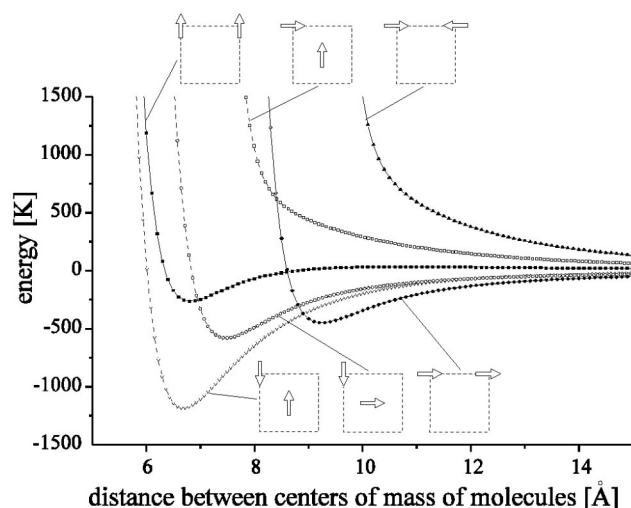
FIG. 2. Some (out of all 18, see the text) energy curves describing interaction between two CNadm molecules (first and second neighbors) in the $Fm3m$ crystal structure.
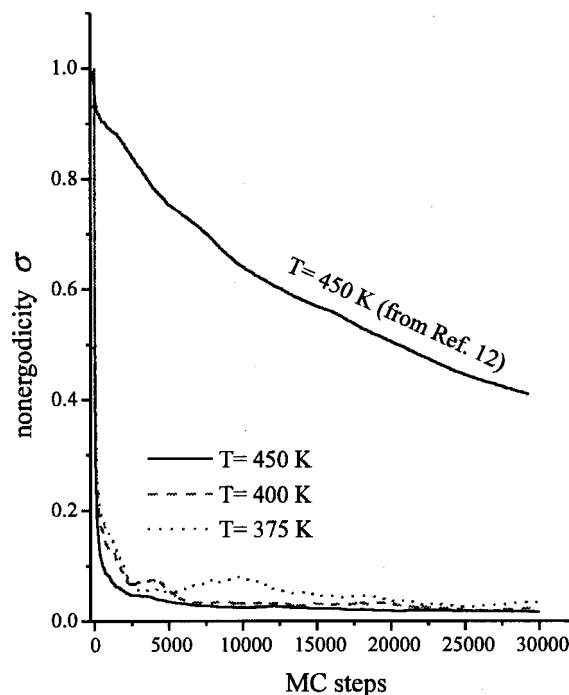

FIG. 3. Nonergodicity in MC simulations of the CNadm (cumulative nonergodicity parameter σ plotted as a function of the MC steps). For comparison, nonergodicity in simulations using a model with continuous rotational degrees of freedom and preferential sampling of configurations (from Ref. 12) is also presented.

ments are energetically equivalent.[15] The further neighbor interaction has not been included in the calculations (cutoff radius of 14 Å). Thus, interactions between molecules can be described by 18 (10+8) different energy curves (an interaction energy as a function of a distance between two interacting molecules). Some of these energy curves are plotted in Fig. 2. It can be noticed that some arrangements stabilize the crystal (these being negative in energy), but there also exist layouts of two CNadms possessing only positive energy values.

An approach where an order–disorder transition is approximated by a spin model is not entirely new, e.g., a phase transition associated with a molecular conformation change (a twist transition) in *p*-terphenyl was approximated by a two-dimensional Ising model.[16] However, in the present work we use interactions from an already proven model[5,12] and allow for a relaxation of intermolecular distances.

One can also regard and try to compare our six-state model to a Potts model. There is, however, a main difference between our model and that of Potts. In the six-state model of the cyanoadamantane crystal the interactions between molecules are represented as energy curves, and that means they vary when a distance between interacting molecules changes. That renders the interaction model much more realistic than the conventional Potts model is. In particular, it allows the system to deform into stable and/or metastable structures and, it also allows each spin to "feel" orientation of neighboring spins (molecules).

III. RESULTS OF MONTE CARLO SIMULATIONS

Simulations were performed on a deformable 4×4×4 unit cell (256 molecules) MC box with periodic boundary conditions within constant-pressure constant-temperature (*NPT*) ensemble. The standard Metropolis Monte Carlo method was used to generate microscopic states of the crystal. Positions of molecules were kept fixed according to the $Fm3m$ space group. At the same time, distances between

molecules could change (deformable MC box). Orientational degrees of freedom were restricted to molecular flips in accordance with the model described above. Simulations were carried out in a temperature range from 50 K to 450 K, both on cooling and heating the system. At each temperature, the system had been first equilibrated (usually 60 000 MC steps) before production runs were started. At each MC step, degrees of freedom of the box were randomly changed first, and then followed by orientational moves of each molecule. To check finite size effects simulations were performed also on a 6×6×6 unit cells (864 molecules) MC box.

As discussed in Ref. 5, a lack of ergodic sampling may lead to stabilization of a metastable structure. Therefore, the first test of the six-state model was to check the nonergodicity in our simulations. The results are presented in Fig. 3, where a variation of the ergodicity parameter σ (defined in Ref. 12) during a MC run has been plotted. (For the purpose of this work, suffice it to now that $\sigma=0$ when the sampling is perfectly ergodic and $\sigma=1$ in a case when each molecule is stuck in one orientation and no jumps between different orientations are observed.) The use of the six-state model has significantly improved the ergodicity of the system compared to previous MC results (see Fig. 3). Eliminating barrier crossings (as in our model) instead of using special sampling techniques such as antitorque bias MC or non-Boltzmann MC let us have runs much longer and of better quality, as far as the ergodicity of simulations (a proper sampling of a configurational space) is concerned.

Variations of enthalpy and volume per molecule on slow cooling and heating are plotted in Fig. 4. As it has been
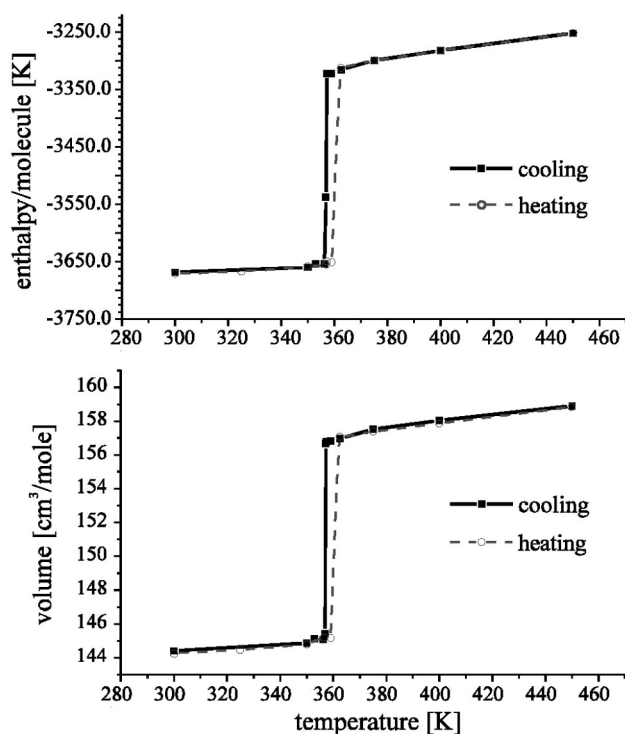
FIG. 4. Variations of enthalpy and volume per molecule on a slow cooling and heating of the CNadm crystal (results for 4×4×4 unit cells MC box).

FIG. 6. Results of quenching of the CNadm crystal (4×4×4 unit cells MC box). See text for details.

reported, even a relatively slow cooling rate (5 K/min) allows the system to be directly supercooled into the glassy state.[9] That is why, at each temperature the system has been carefully equilibrated and a simulation in the successive temperature was started from one of the equilibrium states. This means that results in Fig. 4 correspond to very slow, quasi-static cooling and heating in the real system. There is a first order phase transition around 360 K with a characteristic discontinuity in both parameters and a small hysteresis related to the relaxation process and inertia of the system. Figure 5 presents a comparison of simulation results for two sizes of the MC box, containing 256 and 864 molecules. As it could be expected the hysteresis around the transition temperature broadens with increasing size of the simulation box because fluctuation amplitudes in the bigger system are
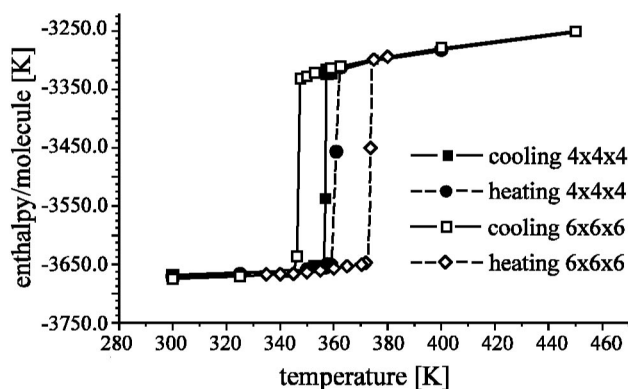

FIG. 5. Size effect in simulations of cyanoadamantane with six-state model (results for 4×4×4 and 6×6×6 unit cells MC boxes).

smaller and it is more difficult to get the system out from a metastable state. To better check details of finite size effects in simulations, a study on a bigger MC box (of 2048 molecules) is in progress.

Figure 6 presents behavior of the system as a result of fast quenching of the CNadm crystal. One of configurations corresponding to a stable state at 400 K (with disordered molecules and the cubic MC box) has been taken as a starting point for two MC runs: at 350 K and at 300 K. It follows that the initial disordered state is not stable (but could be metastable). In both cases a phase transformation into an ordered orthorhombic phase via a transient metastable tetragonal state (better seen for a run at 300) has been observed. It is also clear that the way of quenching or, in general, the thermal history of a sample effects kinetics of this transition. At 350 K, only a short living fluctuation towards a tetragonal state was observed. This may indicate that at this temperature the cubic and tetragonal states have comparable energy and a barrier between them is of an order of energy of thermal fluctuations. For the quenching at 300 K a tetragonal state existed much longer than for the run at 350 K. Although our results reproduce qualitatively experimental observations,[9] more studies are required to understand an energy landscape in this region and its influence on a dynamic behavior of stable and metastable structures. Moreover, as imposed by our model, orientations of CNadm molecules are discrete and hence a tilt of molecules in an orthorhombic phase seen in Ref. 5 cannot be observed here. That also means that we

cannot model a monoclinic phase in our simulations and indicates that there is still room for improvement in the model.

IV. DISCUSSION AND CONCLUSIONS

We have presented an implementation of a six-state model in simulations of structural order–disorder phase transitions in the glassy crystal of cyanoadamantane. The main goal of the model was to overcome the ergodicity problem encountered in previous studies of this system where a more realistic description of the crystal had been used. This task has been perfectly accomplished. By forcing the system to adopt states of only the highest probability the problem of insufficient sampling of the configurational space has been overcome and the ergodicity in simulations has been significantly improved. That, in turn, allowed MC runs to be longer with no need to use time consuming advanced sampling procedures.

The model let us also observe an order–disorder phase transition in the system and its kinetics going through metastable states. In addition, we can say that our runs are of the order of a second of real time. Indeed, as a residence time of a molecule in a given orientation (between flips) in the real crystal is of the order of 10^{-6} s, and as we perform 10^6 and more MC steps (each step includes flips of all molecules), by a simple multiplication it gives 1 s of real time of the system evolution. This value, compared to standard times of 10^{-9} s accessible today in molecular dynamics simulations, reflects power and efficiency of our model.

It is remarkable that experimental observations of the CNadm crystal[9] show a behavior which is qualitatively similar to that simulated by our model. It means that simplifications introduced by our model have retained the main qualitative characteristics of the real system. In spite of a spinlike nature of our model, a coupling with translational degrees of freedom allows the system to transform into phases with different symmetry of the lattice. For this reason the six-state approximation is the first model of CNadm crystals that exhibit a transition into an ordered phase.

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