ISOTHERMAL-ISOBARIC MOLECULAR DYNAMICS SIMULATION OF POLYMORPHIC PHASE TRANSITIONS IN ALKALI HALIDES

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1. INTRODUCTION

Since the invention of ensemble dependent molecular dynamics (MD) simulation methods several systems have been modelled during phase transitions. The most frequently studied transitional phenomena are glass formation and solid-solid structural transformations.¹

The initial aim of the present work was to study the conditions of crystallization *versus* glass formation of alkali halide melts. The melting and the freezing of RbBr as an example, however, has such a large hysteresis at system sizes and cooling rates feasible in computer simulations of reasonable length that no crystallization could be achieved. The pressure-induced polymorphic phase transition of alkali halide crystals is a by-product of the work that turned out to be at least as interesting as the original idea.

A brief account of this work is presented in the following. For a more detailed version see Ref.2.

2. THE SIMULATION METHOD

The known Andersen-Nosé molecular dynamics algorithm has been applied as reported, for example, in Ref.3. The pair interactions in alkali halides were modelled by a Born-Huggins-Mayer potential with Fumi-Tosi parameters.⁴ Since the Coulombic interactions decay slowly, this part of the pair potential must be corrected for pairs outside of the simulation box. The cubic harmonic expansion of the Ewald sum according to Adams and Dubey⁶ proved to be a convenient method. The cubic harmonic expansion is simple, easily vectorizable and avoids Fourier transformation. A further advantage of the cubic harmonic expansion is that it can be easily

generalized to a brick-shape simulation box. The latter modification of the algorithm proved to be fruitful because the independent boxlength fluctuations decreased the strains in the system. Clearly, studying phase transitions in solid state by the method of Parrinello and Rahman (PR)⁶, while allowing changes in the MD cell shape, would be more powerful. Because of the original aim, however, the program has not been equipped by this possibility. The more general PR method will be used in subsequent studies.

Our simulations were started from regular lattices with each particle in the local potential energy minimum. Initial velocities were distributed randomly, according to a Maxwell distribution so that the box, as a whole, neither translated nor rotated. Then the first four steps of the simulation were started by solving the equations of motion by the Runge-Kutta method, which produced the necessary "history" of the variables needed for the four-point predictor-corrector routine⁷.

The boxlengths in constant pressure MD algorithms are controlled by the difference between the kinetic energy on one hand and the sum of the virial and the pV term on the other. The virial, however, is calculated with quite a large error due to the artificial cancellation of long-range forces at the surface of the minimum image box around each particle. Therefore, instead of the "real" pressure we applied some "effective pressure", whose ratio to the corresponding experimental pressure depends on the number of particles and the topology of the periodic boundary conditions. This has been determined *prior* to the actual simulations, requiring the system to

keep the experimental lattice distances. (In fact, these test runs produced the accidental observation of the fcc-bcc transition applying larger "effective pressure" than necessary.)

For monitoring the changes in local symmetry, we used the rotational invariants of the spherical harmonics^{8,9} and the pair-correlation functions.

3. RESULTS AND DISCUSSION

Experimentalists report that potassium and rubidium chlorides, bromides, and iodides transform from a NaCl-type face-centered cubic to a CsCl-type body centered cubic crystal by an audible "click" when put under a few kbars of hydrostatic pressure^{10,11}. The same transformation has not been observed for Li halides. NaCl can be forced to change crystal form only at much higher pressure (~300 kbars).¹²

The first system simulated was a RbBr fcc crystal of 216 particles. In order to determine the orientation of the crystal with respect to the simulation box, we projected all particles onto the box planes xy , xz , and yz , and calculated the density maps. The simulation was started from a lattice with the (100), (010), and (001) directions parallel to the axes of the simulation box. Monitoring the pair-correlation functions after the pressure has been increased instantaneously the peaks characteristic of the fcc structure disappeared, while peaks of the bcc lattice appeared simultaneously (Fig. 1).

The same information has been provided by the orientational parameters. Fig. 2. shows the projections of cation configurations to the box planes between 13 and 15 ps of the history. Cations and anions are mapped separately not to make the graphs too dense. It is obvious from Fig. 2c that the yz plane is perpendicular to the (111) direction of a bcc lattice, since one can see the spots arranged in a hexagonal symmetry which is the result of the projection of the vertices of a cube along the three-fold axis. By the distance relationship in x and y direction, and by the requirement that this direction must be perpendicular to (111), one can conclude that Fig. 2a is the projection in direction $(1/2 \ 1/2 \ \bar{1})$. Consequently, Fig. 2b must be the projection in direction $(\bar{1}01)$. The projections in this latter direction show the highest disorder due to the existence of quite a number of empty channels which, as a matter of fact, are accompanied by several interstitials indicated by the large differences in

FIGURE 1

the line densities of the spots corresponding to occupation densities.

The orientational relationships revealed by these figures confirm the mechanism suggested by Watanabe, Tokonami, and Morimoto¹¹ and disprove that of Buerger¹⁰.

The reverse transformation was simulated by starting from the end configuration of the fcc-bcc transition and from a regular bcc lattice. In the former case, the decrease of pressure is accompanied by the transition to an fcc lattice with the same orientation as at the very beginning of the simulation. However, when starting from a regular bcc lattice the reverse transition was successful only if there were many defects in the bcc crystal. Perfect bcc crystals, in contrast, underwent a transition to glassy state at pressures much lower than that required for the forward transition. Since this observation may be an artifact due to the inherently fast rate of pressure changes in simulations, the reversibility of these polymorphic transitions needs further methodological studies.

The fcc-bcc transition of RbBr was also studied by letting the boxlengths fluctuate independently in the three spatial directions. This time the change of pressure was not instantaneous but gradual, in order to get as close as possible to the minimum pressure at which the transformation takes place. These modifications produced the transition with less defects than previously. This simulation was repeated with 64, 432, and 512 ions in several runs in order to study the effect of the sample size and shape. Fig.3 shows the dependence of transformation pressure as a function of $N^{-1/3}$. The extrapolation of these data is not in contradiction with the experimental value $p_{tr} \sim 5$ kbar. Yet the systematic error in the pressure calculation is so large that the simulation has no predictive power in this aspect.

We also simulated the transition for other alkali halides. The calculated thermodynamical quantities of these substances, as in the case of RbBr, are in good agreement with the experimental values. The pressures of transformation in the NaCl-KCl-RbBr series correspond to what would be expected by simple packing rules based on the ratio of cationic and anionic radii.

FIGURE 2abc

FIGURE 3

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