ATOMISTIC SIMULATIONS OF SHOCK-INDUCED PHASE TRANSITIONS

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Abstract. We report on large scale non-equilibrium atomistic simulations of shock-induced solid-solid phase transformations. As an example the $\alpha \rightarrow \epsilon$ transformation in iron and the A11 (GaI)→c112 (GaII) transformation in gallium are discussed. The use of semi-empirical descriptions of the inter-atomic forces and today's parallel computing resources allow for a quantitative comparison of the theoretically calculated data with the experimental results. The discussion will include the crystallographic orientation dependence on the transformation process in single crystals. Simulations containing several millions of iron atoms reveal that above a critical shock strength, many small close-packed grains nucleate in the shock-compressed bcc crystal. For shock waves in the [001] direction the initially small grains are growing on a picosecond time scale to form larger, energetically favored, grains. For the two other major crystallographic directions, here the annealing processes are slower and have not finished within the time scales accessible with atomistic simulations (up to 50 ps). Furthermore, crystals shocked in [111] direction produce solitary waves ahead of the actual shock front.

INTRODUCTION

Atomistic computer simulations on shock-induced plasticity and phase transformations have been done by several authors within the past years. In 1991 the first split two-wave structure has been seen by non-equilibrium molecular-dynamics (NEMD) simulations in a polymorphic phase transition for a two dimensional material undergoing a dissociative transition [1]. Later, large-scale NEMD simulations have been used to study the plasticity of face-centered cubic materials [2, 3], the orientation dependence of shock-induced chemistry [4], and shock-induced structural transformations in iron [5, 6]. As a computationally cheaper alternative to the direct method of NEMD, ensembles of atoms can be driven by homogeneous uniaxial compression toward the final defective Hugoniot state [7, 8].

The use of the SPaSM (“Scalable Parallel Short-range Molecular dynamics”) code allows one to simulate and analyze routinely millions of atoms on parallel machines [9, 10], and has been tested for up to some 20 billion atoms on a fraction of Los Alamos' Q-machine [11], paving the way for atomistic simulations on the $\mu$m scale [12, 13]. In this work we use the embedded atom method (EAM) [14, 15] for the description of the interaction of the iron atoms. EAM has been successfully applied for metals and has been extended to the modified EAM (MEAM) [16] in order to describe materials in which covalent character is important, like the element gallium [17].

SHOCK-INDUCED TRANSFORMATIONS IN IRON

Shock experiments found that iron undergoes a structural transition from the body-centered cubic (bcc) $\alpha$ ground state to the hexagonal close-packed (hcp) $\epsilon$ structure at a pressure of 13 GPa [18] $^2$. Hydrostatic compression experiments at room temperature reveal about the same transition pressure for the $\alpha \rightarrow \epsilon$ transformation, but the reverse transformation takes place at 8 GPa [19]. This hysteresis decreases with

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$^2$ Here the transition pressure is the pressure component $P_{zz}$ in the direction of the shock propagation.
increasing temperature, and vanishes at the triple point of the phase diagram (≈ 800 K, 10.5 GPa).

The atomistic modeling of iron has been done with different EAM potentials: a Voter-Chen potential [21] and the Meyer-Entel potential [22]. The latter has the advantages that it is also fit to zone-boundary phonon frequencies, and therefore can describe the vibrational spectrum well, which is, for example, important for the description of the temperature-induced martensitic phase transitions [23]. However, this potential is too stiff upon compression (Fig.1), resulting in an extremely high transition pressure (55 GPa) for the shock-induced α → ε transition. The Voter-Chen potential has the advantage of using the empirical Rose equation of state and compares well to 

\[ E(\text{atom}) \] with GGA (generalized gradient approximation) electronic structure calculations of the ferromagnetic bcc ground state of iron [20]. Arrows indicate where the shock-induced transformation occurs for each potential.

\[ E(\text{atom})(\text{Ryd}) \]

**FIGURE 1.** Cold curve for the Meyer-Entel potential (dashed line) and the Voter-Chen potential (full line). The circles correspond to FLAPW (Full Potential Augmented Plane Wave) with GGA (generalized gradient approximation) electronic structure calculations of the ferromagnetic bcc ground state of iron [20]. Arrows indicate where the shock-induced transformation occurs for each potential.

and reduce the energy barrier for the transformation [23]. This leads to a slightly reduced transition pressure for samples simulated at room temperature.

**Crystallographic orientation dependence**

We have carried out a series of molecular-dynamics (MD) simulations for different shock strengths with shock waves propagating in the three major crystallographic directions [001], [011], and [111] of a bcc iron single crystal [6, 5, 24]. To initiate shock waves the momentum mirror method [2] has been employed. Simulation cells containing up to some eight million atoms (Fig.2) show a structural transition from the initial bcc structure into a close-packed structure (Fig.3) for pressures above 15 GPa in the [001] direction. For the two other directions the transition pressure is approximately 20 GPa.

For shock strengths just above the transition pressure a split two-wave structure is observed, with a leading elastic wave followed by a slower transformation wave 3. For high shock strengths, the shock is overdriven and has only one transformation front. This behavior is typical for a material that exhibits a phase transformation [25]. The Hugoniot for the different crystallographic shock directions compares favorably with experimental polycrystalline data [18] for the overdriven region (Fig.4). The fact that the shock speed for the [001] direction in that region is larger than for the other two directions reflects denser packing due to fewer grain boundaries. Different elastic properties for the various directions result in differences of the elastic part of the Hugoniot and therefore in in the split two-wave region. Yet it is not clear if the higher transition pressure in the [011] and [111] direction is an effect of the short time scales accessible in NEMD [8], or if it is an effect that can be measured experimentally. Preliminary simulations of polycrystalline samples show a reduction of the transition pressure by heterogeneous nucleation at grain boundaries, thus coming closer to the experimental 13 GPa threshold.

The different crystallographic shock directions favor different structural transformation pathways, so

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3 Due to the increased Hugoniot elastic limit in perfect single crystals, we see no evidence for bcc plasticity before the onset of the phase transformation.
FIGURE 2. Samples containing \(\approx\) eight million atoms (\(\approx 40 \text{ nm} \times 40 \text{ nm} \times 57 \text{ nm}\)) after 6.57 ps shocked in the bcc [001], [011], and [111] direction (top to bottom). Piston velocity \(u_p = 1087 \text{ m/s}\). Atoms are color-coded by the number of neighbors \(n\) within 2.75 Å: the unshocked bcc \((n = 8)\) is gray, uniaxially compressed bcc \((n = 10)\) is blue, and the transformed close-packed grains \((n = 12)\) are red, separated by yellow \((n = 11)\) grain boundaries.

FIGURE 3. Radial distribution functions of the transformed material for crystals shocked in different directions with a piston velocity \(u_p = 1087 \text{ m/s}\). As a reference the ideal positions of the fcc and the hcp structure as well as the distribution function for the unshocked bcc are shown.

FIGURE 4. Hugoniot for the different crystallographic shock directions for iron single crystals as obtained by MD, with experimental polycrystalline data [18]. The arrows indicate the sound speeds of the potential for the bulk and the [001], [011], and [111] directions (bottom to top).

different dynamics are observed for each direction (Figs.5 and 6). For shocks in [001] only two equivalent twin variants of the product phase, separated by twin boundaries, are observed. Here, the initially small grains anneal on a picosecond time scale and form larger grains with most of the relaxation process completed within the accessible simulation time (up to 50 ps). However, in the two other directions, more variants with more complicated grain
FIGURE 5. Profiles of the longitudinal \((P_{zz} V)\) and twice the shear \(\left[2P_{ij} - (P_{xx} + P_{yy})/2\right] V\) components of the pressure-volume tensor \((P_{ij} V, i,j = x, y, z)\). The shock waves propagate from left to right. Profiles are shown for the three major cubic crystallographic orientations for a piston velocity \(u_p = 1087 \text{ m/s}\).

FIGURE 6. Temperature profiles for the major cubic crystallographic orientations for \(u_p = 1087 \text{ m/s}\). The shock waves propagate from left to right. For the [011] and [111] directions the annealing process of the transformed material takes much longer than for the [001] direction.

boundaries are formed. In these cases the relaxation processes are far from complete by the end of the simulation. The temperature (Fig.6) is rising, which indicates a structural relaxation to lower potential energies for the constant energy simulations presented here. The grain size remains small (Fig.2) and the number of grain boundary atoms is significantly larger than in the [001] case [this can also be seen in the broader peaks of the radial distribution functions (Fig.3)]. Hayes [26] has experimentally observed different kinetics for the KCl shock-induced phase transformation for different orientations.

On the unloading process, by the reflection of the shock wave at the end of the samples, the transformation reverts almost perfectly for all three directions investigated (in the [001] case it is perfect). Since the transformation is done by a collective movement of the atoms over short distances (martensitic-like), rather than by reconstruction, the transformation process is likely to be reversible and this has been observed in experiments on iron and other materials [25]. However, for extremely high shock strength the system melts during the rarefaction wave (e.g., \(u_p = 2899 \text{ m/s}\)).

**Solitary waves**

For shocks in the [111] direction solitary waves ahead of the actual shock front are observed (Figs.2, 5, and 6). We observe these waves also for [001] shocks at very high shock strength, though there is also some evidence at early time for lower shock strength (Fig.5). These solitary waves have also been observed for shocks along [011] in fcc crystals [3]. The waves can be seen in properties like pressure, particle velocity, or density. However, they only affect the longitudinal temperature and can not be seen in the transverse velocity profiles.

These waves are relatively stable and do not significantly interfere with each other, as can be checked by inducing two shock waves with opposed propagation directions at each end of the sample. Yet, they appear not to be ideal solitons [27] on the simulation time scale. The peak height decays in time (the peak width does not significantly change), as their initial velocity decreases (Fig.7). This process gets more pronounced with increasing temperature and eventually the solitonic peak vanishes. However, the shock front can emit new solitary waves. As for the dependence on the shock strength, here the simulations show that the velocity of the solitons do not necessarily increase with shock strength. Rather, it looks like there might be an optimal shock strength for a given system. For example, solitons emitted at shocks with \(u_p = 1087 \text{ m/s}\) are initially faster and their decay is slower than those created at fronts with \(u_p = 1812 \text{ m/s}\). For low shock strength
FIGURE 7. Time evolution (every 1.314 ps) of the shear stress profile ([111] bcc Fe, \( u_p = 1812 \text{ m/s}, T = 50\text{K} \)). The decay in peak height of the leading solitary wave can be seen as can the decrease of the velocity of the solitary wave (the straight line is a guide to the eye to the initial velocity). The curves have been shifted for clarity.

\( u_p = 471 \text{ m/s} \), as well as for moderate temperatures (320 K), solitary waves have not been observed (some evidence of soliton-like behavior remains in an oscillatory shock front).

Much more work on these interesting phenomena, in particular the connection to already existing theories and models of solitons, has to be done to understand this process in the framework of shock physics. However, a preliminary picture that emerges so far is that at the shock front, a soliton (as understood in the particle picture), emerges with an initial velocity and size. The initial velocity and size depends on the properties of the system (crystallographic direction, shock strength, temperature, ...). The soliton behaves nonideally (which gets more pronounced with increasing temperatures), as it interacts with its environment and loses energy, causing it to decay in size and velocity.

**TRANSFORMATIONS IN GALLIUM**

The ground state of gallium is an orthorhombic structure with a significant amount of dimerization (A11, GaI) (Fig.8). For \( T = 100 \text{ K} \), at \( P = 3 \text{ GPa} \) a transformation into the bcc c112 (GaII) structure occurs, the transition pressure dropping with increasing temperature [28]. Recently a MEAM model for gallium has been proposed by Baskes et al. [17] that describes the zero pressure properties for the various solid and liquid structures amazingly well. However, little is known about the quality of this potential under pressure. A first step is the calculation of the zero temperature transition pressures as obtained by the cold curves of the various structures (Fig.9). A tangent construction reveals A11→c112 to have the lowest
transition pressure, in agreement with the experimental phase diagram. The cold curve transition pressure is 4.9 GPa, which is a little bit larger than the experimental transition pressure at T = 100 K. However, the effect of temperature on the theoretical transition pressure is not clear at the moment. So far, dynamic simulations have just begun, yet no shock experiments on solid gallium have been performed.

OUTLOOK

Concerning the crystallographic orientation dependence of shock-induced transformations in iron, the authors look forward to future experiments, in order to see how they compare with our theoretical predictions. It would be interesting to see experimentally whether solitary waves can even be detected in single crystals at low temperatures. For gallium, we plan to do a series of NEMD shockwave simulations to study shock-induced structural transformations.

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