Nucleation, kinetics and morphology of displacive phase transformations in iron

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An extensive, systematic molecular dynamics (MD) study is performed for analysing the nucleation, kinetics and morphology characteristics of thermally-induced, displacive phase transformations from face-centred cubic (fcc) to body-centred cubic (bcc) iron. At the atomic level these transformation characteristics are influenced by a number of factors, including (i) the appearance of free surfaces, (ii) the initial presence of fcc-bcc grain boundaries, (iii) the existence of point defects (i.e., atomic vacancies) near a grain boundary, (iv) the initial thermal velocities of the atoms, and (v) the specific interatomic potential used. Other MD studies that capture the overall transformation behaviour of iron well have often underestimated or ignored the influence by these factors on the transformation response, with the risk of putting the accuracy, generality and physical explanation of the MD results on loose grounds. The present research illustrates the relative contribution of each of the above factors by means of a detailed comparison study for three different interatomic potentials. The accuracy of the interatomic potentials is established by validating for the fcc and bcc phases the calculated elastic moduli, cohesive energy, vacancy formation energy and interfacial energy against experimental and \textit{ab initio} data reported in the literature. The importance of calibrating material data of both the stable bcc phase and the metastable fcc phase – instead of the stable bcc phase only – is demonstrated. The numerical results call for general caution when interpreting phenomena that start close to instability points and therefore are sensitive to small disturbances; a large spread in the overall transformation time is found under different initial thermal velocities, interfacial lattice incoherence, boundary conditions (free vs. periodic), and interatomic potentials, where for completely transformed atomic systems the discrepancy between the maximum and minimum transformation time appears to be more than a factor of 150. The transformation time is phenomenologically related to the overall activation energy and the cohesive energy difference of the fcc and bcc phases, which, beyond a certain combination of values, may even prevent the transformation process from occurring. Also, the morphology of the bcc product phase is remarkably sensitive to the type of boundary conditions and the choice of interatomic potential, while the influence by both the set of initial thermal velocities and the interfacial lattice incoherence only becomes apparent for specific atomic samples that transform relatively slowly. The presence of fcc-bcc grain boundaries increases the spatial heterogeneity of transformation events, with the appearance of an increasing number of vacancies at the grain boundary giving rise to a larger overall transformation time. The 10 main results following from the present MD study are conveniently summarised at the end of this communication.

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1. Introduction

Displacive solid-state phase transformations are characterised by an abrupt, ordered movement of a large number of atoms over a distance typically smaller than the interatomic distance. The phase transitions are driven by specific changes in the thermal and/or mechanical loading conditions applied, and play an important role in the thermal processing of iron and its alloys, as well as in their forming and operation (e.g., the application of multiphase steels assisted by transformation induced plasticity in the automotive industry). The rapid change in crystal structure inherently alters the physical properties of iron and iron alloys, a process that needs to be understood in detail in order to efficiently improve the manufacturing and industrial application of these materials. For this purpose, over the past 30 years various modelling studies on displacive phase transformations were carried out, with special attention focused upon the development and application of continuum theories at scales ranging from microscopic to macroscopic, see Leblond et al. (1986a), Leblond et al. (1986b), Stringfellow et al. (1992), Diani and Parks (1998), Levitas et al. (1999), Govindjee and Miehe (2001), Anand and Gurtin (2003), Turteltaub and Suiker (2005), Suiker and Turteltaub (2005), Tjahjanto et al. (2008) and references therein.

Within a multiscale modelling framework, the accuracy and applicability of macro- and microscopic phase transformation models is typically related to the kinetic and kinematic hypotheses adopted for upscaling the transformation characteristics from the atomic level to the continuum level. An illustrative example refers to the use of the “crystallographic theory of martensitic transformations”, which was originally proposed by Wechsler et al. (1953), and was later extended with an energy minimisation framework by Ball and James (1987) and other investigators (Bhattacharya, 1993; Hane and Shield, 1998, 1999; James and Hane, 2000). This theory has been incorporated in various continuum models in order to transfer crystallographic details from the atomistic scale to higher scales of observation, such as the orientation of the transformation interfaces (often named ‘habit planes’), the transformation volume fractions, and the anisotropic stiffness characteristics of the austenitic parent and martensitic product phases (Thamburaja and Anand, 2001; Anand and Gurtin, 2003; Turteltaub and Suiker, 2005, 2006; Suiker and Turteltaub, 2007). The theory relies on the “Cauchy-Born hypothesis”, stating that the deformed atomic structure within a volume element is adequately approximated by a crystal lattice homogeneously deforming under a uniform deformation gradient. With the use of this hypothesis the so-called “Hadamard jump condition” across a straight and coherent transformation interface can be formulated, which assumes that the jump in the uniform deformation gradients of the hypothetically stress-free parent and product phases adjacent to the interface is described by a rank-one tensor, see e.g., Bhattacharya (2003). The habit plane equation following from these kinematic assumptions is typically satisfied for a martensitic product phase composed of twin-like variants, which is a microstructure observed in metals with a relatively high resistance against dislocation slip, e.g., steels with a high carbon concentration (Sugimoto et al., 1997), or NiTi-based shape-memory alloys (Bhattacharya, 2003; Noebe et al., 2007). Although under the above conditions the morphology of the transformation product phase is well described and understood, under more general circumstances the characterisation of the crystalline structures resulting from displacive phase transformations in metals is rather unexplored. Also, there is still limited atomistic information available about the nucleation and kinetic processes governing the phase transformation behaviour, causing the incorporation of these aspects in continuum models to be commonly based on heuristic reasoning (Liu et al., 2007).

A simulation tool suitable for thoroughly examining atomic structures subjected to displacive phase transformations is Molecular Dynamics (MD), see Meyer and Entel (1998), Pinsook and Ackland (1998), Pinsook and Ackland (2000), Lill and Broughton (2001), Morris and Ho (2001), Bos et al. (2006), Hildebrand and Abeyaratne (2007), Engin and Urbaske (2008), Tateyama et al. (2010), Kastner et al. (2011) and Urbaske and Sandoval (2012). The present research concerns an extensive, systematic MD study on the nucleation, kinetics and morphology characteristics of thermally-induced, displacive phase transformations from face-centred cubic (fcc) to body-centred cubic (bcc) iron. At the atomic level these transformation characteristics are influenced by a number of factors, including (i) the appearance of free surfaces, (ii) the initial presence of fcc-bcc grain boundaries, (iii) the existence of point defects (i.e., atomic vacancies) near a grain boundary, (iv) the initial thermal velocities of the atoms, and (v) the specific interatomic potential used. Other MD studies that capture the overall transformation behaviour of iron well, often underestimate or ignore the influence by these factors on the transformation response, with the risk of putting the accuracy, generality and physical explanation of the MD results on loose grounds. In the current study the contribution of each of the above factors is systematically identified, analysed and categorised in terms of the overall transformation time, with the aim of understanding the complex transformation characteristics in detail, and providing a useful source of atomistic information for the further development and refinement of continuum theories applied at higher scales of observation. For this purpose, two types of tetragonal-shaped atomic configurations are subjected to a temperature of 810 K, which are (i) a lattice system initially composed of only fcc atoms, named the “fcc-only system”, and (ii) a lattice system initially composed of an fcc lattice and a bcc lattice separated by a straight interface, named the “fcc-bcc system”. Under the application of periodic boundary conditions in all three spatial directions, the first configuration is considered to be representative of an fcc structure embedded within a (much) larger fcc grain, while the latter configuration reflects an fcc structure that has (periodic) grain boundaries with a bcc structure, thus assuming that transformation nucleation already has occurred.

In Section 2 the effect of the boundary conditions on the thermally-induced transformation behaviour is examined for the fcc-only and fcc-bcc systems, by comparing configurations with periodic boundary conditions in all three directions to configurations with periodic boundary conditions in the axial direction of the sample and free boundary conditions in the two lateral directions. In addition, the influence of the interatomic potential on the computational results is analysed, an
aspect that to date has not received much attention in MD studies published in the literature. Simulations were performed for three potentials with different levels of refinement, namely the Johnson–Oh potential (Johnson and Oh, 1989), the Zhou–Johnson–Wadley potential (Zhou et al., 2004), and the Lee–Baskes–Kim–Cho potential (Lee et al., 2001). The results of this comparison study suggest a dependency of the transformation behaviour on the initial conditions. Accordingly, in Section 3 the effect on the transformation behaviour is examined for (i) different sets of initial atom velocities, (ii) various uniform, positional shifts of the initial atom locations across an fcc-bcc interface (i.e., interfacial lattice incoherence), and (iii) the presence of vacancies in the atomic layers near the initial fcc-bcc interface. The effective velocity of the fcc-bcc interface is determined in order to verify that the phase transformation process for each of the three interatomic potentials is of a displacive nature, and for estimating the activation energy during transformation growth. The accuracy of the three interatomic potentials in predicting the phase transformation behaviour of iron is assessed quantitatively in Section 4, by comparing MD material data of the fcc and bcc phases to experimental and ab initio material data reported in the literature. Finally, in Section 5 the 10 main results of the current MD study on phase transformations in iron are conveniently summarised, which, although obtained for the specific MD models examined in the present work, may apply to other lattice configurations and metals as well.

2. Influence of global system characteristics on transformation behaviour

The size of the atomic sample is generally known to play an essential role in the accuracy at which the effective (bulk) properties of the material are computed. A preliminary comparison study on the sample size (not presented here) has shown that under periodic boundary conditions the bulk transformation behaviour of three-dimensional MD systems typically converges between 8000 and 10,000 atoms. For generally meeting this requirement and for performing a substantial number of variation studies within a reasonable amount of time, the fcc-only system and the fcc-bcc system analysed in this study contain 16,016 and 17,160 atoms, respectively. The interactions between the atoms were simulated alternatively with Embedded Atom Model (EAM) potentials and a Modified Embedded Atom Model (MEAM) potential. The MEAM potential extends the EAM potential with the effect of covalent (directional) bonding by taking into account the angular distribution of the background electron density of adjacent atoms (Baskes, 1997). The EAM potentials considered in the present study are the Johnson–Oh potential (Johnson and Oh, 1989) and the Zhou–Johnson–Wadley potential (Zhou et al., 2004), and the MEAM potential considered is the Lee–Baskes–Kim–Cho potential (Lee et al., 2001). These three interatomic potentials are characterised by different levels of refinement, and from hereon will be abbreviated as the JO-potential, the ZJW-potential and the LBKC-potential, respectively (thus using the first character of the surnames of the developers). For clarity reasons, the main characteristics of each potential are summarised in Appendix A. The effective material properties for fcc and bcc iron calculated with these potentials (which also includes the cut-off distance) are presented further in this communication, see Table 6 in Section 4, where the parameters values of each of the interatomic potentials were taken equal to those reported in the original papers mentioned above.

At the atomic scale the examination of displacive phase transformations in iron appears to be a rather difficult and extensive problem, where numerous aspects can have a specific influence on the transformation characteristics. The three aspects analysed first in this study are: (i) the lattice configuration, (ii) the interatomic potential, and (iii) the boundary conditions. The two lattice configurations considered are an “fcc-only system” and an “fcc-bcc system”, which are characterised by tetragonal domains of comparable initial dimensions of 40.39 × 51.41 × 95.47 Å³ and 40.55 × 51.82 × 99.86 Å³, respectively. Note that the names “fcc-only system” and “fcc-bcc system” explicitly refer to the initial configuration of the corresponding lattice, thus losing their distinctive definition once transformation from fcc to bcc iron has occurred. The tetragonal geometry of the original fcc-bcc lattice is displayed in Fig. 1. The global coordinate system shown in the figure is defined by an orthonormal vector basis \( \{f_1, f_2, f_3\} \), where the basis vectors are directed normal to each of the three mutually perpendicular boundaries of the tetragonal domain.

2.1. Description of lattice geometry, loading and boundary conditions

The crystallographic directions of the fcc and bcc crystals are expressed in terms of basis vectors \( \{e_1, e_2, e_3\} \) aligned with the cubic lattice axes. The orientation of the fcc lattice is described by connecting the \( \{100\}_{fcc} \) directions to the global coordinate system as

\[
f_k = e_k^{fcc} \quad \text{with } k = 1, 2, 3.
\]

(1)

For the fcc-bcc system, the orientation of the bcc lattice is taken in accordance with the Bain orientation relation: \( \{010\}_{fcc} \parallel \{010\}_{bcc}, \{100\}_{fcc} \parallel \{101\}_{bcc} \), which defines the orientation of the bcc crystal in the global coordinate system as

\[
f_1 = \frac{1}{\sqrt{2}}(e_1^{fcc} - e_2^{bcc}), \quad f_2 = e_2^{bcc}, \quad f_3 = \frac{1}{\sqrt{2}}(e_1^{bcc} + e_3^{bcc}).
\]

(2)

The above orientation relationship, proposed in the landmark contribution of Bain (1924), is most intuitive and chosen here for reasons of simplicity, although experiments have shown that the orientation relationship proposed by Nishiyama–Wassermann matches the transformation path of various iron alloys more closely (Nishiyama, 1978). The examination of alternative orientation relationships, however, falls beyond the scope of the present study. Note from Eqs. (1) and (2) that
the crystallographic directions \([100]\) \(_{\text{fcc}}\) and \(1/2\) 10 1 38\(_{\text{bcc}}\) (or, equivalently, the crystal planes \([100]\) \(_{\text{fcc}}\) and \(101\) 38\(_{\text{bcc}}\)) correspond to the direction of the global vector \(f_1\). The choice of using the global \(f_1\)-direction for expressing the crystalline orientation will be maintained for all crystallographic directions (and corresponding crystal planes) treated further in this communication. The tetragonal fcc-bcc domain was constructed by separately generating the fcc and bcc lattice parts of the domain at their equilibrium densities at room temperature (304 K), and assembling these domains at the common location of two opposite lattice boundaries in the \(f_1\)-direction to create a mutual interface. With the use of the JO-potential, a correction on the lattice parameters of the fcc and bcc crystals of, respectively, \(-0.004\%\) and \(+0.004\%\) was computed for warranting equal cross-sections of these crystals at 304 K. The initial velocities of the atoms were taken randomly from a Maxwell–Boltzmann distribution, where it was required that the linear momentum of the centre of mass of the sample equals zero. For consistency, for each of the two lattice systems all atomic configurations analysed in this section were subjected to one and the same set of initial thermal velocities.

The number of atoms and the number of fcc and bcc planes in the three global directions are presented in Table 1. Note that in the \(f_3\)- and \(f_3\)-directions the number of unit cells in the fcc-only system is equal to the number of fcc unit cells in the fcc-bcc system, and that in the \(f_1\)-direction the total number of unit cells for both systems is equal, i.e., 26. The axial boundary conditions of the domain are periodic in the \(f_1\)-direction, while the lateral boundary conditions in the \(f_2\)- and \(f_3\)-directions are either both periodic, or both free. The initial velocities of the atoms were taken randomly from a Maxwell–Boltzmann distribution, where it was required that the linear momentum of the centre of mass of the sample equals zero. For consistency, for each of the two lattice systems all atomic configurations analysed in this section were subjected to one and the same set of initial thermal velocities.

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The simulations were carried out under isothermal conditions at a temperature of 810 K, where the average normal stress in the system was maintained at zero in each direction normal to a periodic system boundary, by continuously adapting the position of the periodic boundary and the actual atom coordinate in that direction. These conditions were accomplished using a thermostat and a barostat of the Berendsen type, with damping times of 18 fs and 15 fs, respectively (Berendsen, 1984). The specific values of the damping times fall within a range in which their variation only leads to relatively small changes in the computational results. More specific information on the effect of the variation of these damping times can be found in Section 3.1.1. The equations of motion of the atoms were updated incrementally, using a variable timestep determined by the maximum atomic displacement. The maximum atomic displacement is set equal to 0.02 Å per timestep; this value was obtained from energy drift recordings on samples subjected to constant energy conditions, where it was required that the energy drift remained between acceptable bounds. At a simulation temperature...
of 810 K, a maximum displacement of 0.02 Å per timestep corresponds to a relatively small timestep of approximately 1.1 fs. All computational results shown in this communication relate to rapidly quenched, fully relaxed equilibrium states, which were obtained by abruptly switching the thermostat from 810 K to 0 K, and subsequently allowing the system to cool down to 0 K (which typically happens within a time span of 0.7 ps). It is emphasised that these quenching operations are not part of the actual thermodynamical loading process, but only serve as an auxiliary operation for the purpose of omitting the contribution by the instantaneous thermal vibrations from the displayed computational results. Although the computational results in this communication commonly are visualised at the surface of a lattice system, they are also representative for the interior of the lattice system, unless indicated otherwise.

In iron, the α-ferritic (bcc) phase is the experimentally stable phase at room temperature, which, under a temperature increase, remains stable up to 1184 K. Above this temperature, the bcc phase transforms into a γ-austenitic (fcc) phase, which remains the stable phase up to a temperature of 1667 K. Hence, at a simulation temperature of 810 K the bcc and fcc phases may be, respectively, considered as stable and unstable (or metastable, when the fcc lattice is sufficiently constrained). For determining whether an atom at an arbitrary time instant is characterised as fcc, bcc or some other ordered or disordered type of lattice structure, the crystallographic environment was computed for each atom. The computational algorithm used for determining the crystal type is described in Appendix B.

2.2. Variational study of interatomic potential, lattice configuration and boundary conditions

The evolution of the fraction of transformed fcc atoms is shown for the fcc-only system in Fig. 2a, and for the fcc-bcc system in Figs. 2b (time period: 0–14 ps) and 2c (time period: 0–225 ps). The response of the fcc-bcc system has been depicted for two different time periods, in order to highlight some significant differences in the transformation kinetics of the various cases analysed. The specific transformation times obtained from these figures are summarised in Table 2, and will be discussed in more detail further in this communication.

An overall comparison of the transformation curves of the fcc-only systems and fcc-bcc systems illustrates that the spontaneous nucleation of bcc atoms is promoted by the initial presence of an fcc-bcc grain boundary in the lattice system. This is concluded from the observation that, after a short period of 14 ps, in fcc-only systems – which initially do not contain a bcc phase – noticeable transformation (i.e., more than 0.05 volume fraction of transformed fcc atoms) has taken place only for 3 of the 6 cases considered, see Fig. 2a, while in fcc-bcc systems this holds true for all cases except one, see Fig. 2b. The fluctuations observed in the transformation curves represent the appearance of small nuclei of bcc iron that subsequently transform back into fcc iron as a result of their subcritical size. It may be further observed that for all three interatomic potentials the transformation from fcc to bcc iron in a lattice system with free lateral boundary conditions occurs faster than in a lattice system with periodic lateral boundary conditions. The largest difference is found for the LBKC-potential, where both for the fcc-only system and the fcc-bcc system a complete transformation under free lateral boundary conditions already becomes manifest after about 5 ps, while under periodic boundary conditions this happens much later in these systems, namely after more than 200 ps. Note from Fig. 2a that the completion of transformation of the fcc-only system at 267 ps falls outside the time domain considered here; however, the specific transformation kinetics for this case will be treated in detail in Section 3.1.2. The JO-potential does not predict transformation at all when periodic boundary conditions are applied, both for the fcc-only system and the fcc-bcc system. Although not illustrated here, a continuation of the simulation for the fcc-only system until reaching a time $t = 64 \times 10^3$ ps has confirmed that even over a very large time period the transformation from fcc to bcc iron remains absent.

For an fcc-bcc system modelled with the JO-potential and free lateral boundary conditions, the time needed for attaining a complete transformation is relatively large, namely 89 ps, see Fig. 2c. The final volume fraction thereby has a small deviation of 0.05 with respect to unity, which results from limitations of the numerical detection algorithm to adequately identify for all three interatomic potentials the crystal type of all atoms at the free boundaries of the lattice system. For the JO-potential, the identification of the crystal plane of boundary atoms is most inaccurate when the number of neighbouring atoms is substantially lower than in the interior of the sample, see also (the caption of) Fig. 3. Since the deviation of 0.05 is relatively small and does not seem to decrease to zero under further thermal loading, the transformation at this stage is considered as “completed”. This case was examined previously by Bos et al. (2006), who reported a similar transformation behaviour as depicted in Fig. 2c, i.e., a nucleation phase characterised by a relatively low transformation rate, which, at approximately 0.2–0.3 volume fraction of transformed fcc atoms, turns into a rapid completion of the transformation process. It was demonstrated that the shape of the transformation evolution curve does not significantly change under an increasing volume-to-surface ratio of the sample geometry – an effect not considered in the present work –, although the total time required for reaching complete transformation then typically increases. The authors argued that the relatively long nucleation phase may be ascribed to the development of a screw-type dislocation structure, which must be necessarily formed at an initial fcc-bcc interface before completion of transformation can take place. The nucleation of transforming fcc atoms from the initial fcc-bcc interfaces is visualised in Fig. 3 for $t = 68.8$ ps, at which the volume fraction of transformed fcc atoms equals 0.28. This stage characterises the end of the nucleation phase, where the coherent cluster of remaining fcc atoms (indicated in green) is about to shrink fast and vanish under a full transformation into bcc iron. As a result of the non-uniform nucleation of bcc atoms across the sample height and thickness, the initially straight fcc-bcc interfaces near the centre and periodic boundary of the sample have developed a certain roughness, a phenomenon that is commonly referred to as interface roughening.
In contrast to the JO-potential, the transformation of fcc-bcc systems modelled with the ZJW- and LBKC-potentials and free lateral boundary conditions spontaneously develops from the onset of thermal loading and completes very fast, see Figs. 2b and c. To obtain further insight into the differences in transformation characteristics, for all three interatomic potentials (JO, ZJW, LBKC) and lateral boundary conditions (free, periodic), the fraction of transformed fcc atoms is monitored over time. 

**Fig. 2.** Evolution of the fraction of transformed fcc atoms for fcc-only and fcc-bcc systems with different interatomic potentials (JO, ZJW, LBKC) and lateral boundary conditions (free, periodic). (a) fcc-only system, time period: 0–14 ps, (b) fcc-bcc system, time period: 0–14 ps and (c) fcc-bcc system, time period: 0–225 ps.

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potentials the specific bcc crystal planes appearing in the fcc-bcc system with free boundary conditions are analysed just after completion of transformation. The numerical algorithm developed for identifying the Miller indices of the crystal planes measured along the global $f_1$-direction depicted in Fig. 1 is summarised in Appendix B.

The application of this algorithm leads to the results depicted in Fig. 4, illustrating that for the JO-potential the bcc phase at completion of transformation becomes manifest by a monocrystalline {440} structure (Fig. 4a), while for the ZJW- (Fig. 4b) and LBKC- (Fig. 4c) potentials the bcc phase has a polycrystalline structure.

Both for the ZJW-potential and LBKC-potential the polycrystalline structure is dominated by {440} (brown) and {400} (blue) bcc crystal planes, where the former family of crystal planes essentially characterises the original [10T] bcc structure occupying the front part of the sample (considered w.r.t. $f_1$-direction), and the latter family of crystal planes is found at the back part of the sample where originally the fcc crystal was present. Due to the differences in the bcc crystal planes generated, the overall deformation behaviour related to the individual potentials is also significantly different: The transformed, back part of the sample for the JO-potential has extended in the $f_1$-direction and has shortened in the $f_3$-direction, see Fig. 4a. Conversely, for the ZJW- and LBKC-potentials it has shortened in the $f_1$-direction and has extended in the $f_3$-direction, see Figs. 4b and c.

The polycrystalline behaviour of the systems modelled with the ZJW- and LBKC-potentials can be quantified by plotting the time evolution of the volume fractions of the bcc crystal planes from the completion of transformation, see Fig. 5a and b, respectively. Both for the ZJW-potential and the LBKC-potential the 5 most dominant bcc crystal planes were selected, for which at any time instant the total sum of the corresponding volume fractions is, respectively, larger than 0.94 and 0.92 (thus representing almost the complete bcc volume fraction). As mentioned previously, at completion of transformation the

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Table 2

<table>
<thead>
<tr>
<th>Interatomic potential</th>
<th>JO</th>
<th>ZJW</th>
<th>LBKC</th>
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<tbody>
<tr>
<td></td>
<td>Free</td>
<td>Periodic</td>
<td>Free</td>
</tr>
<tr>
<td></td>
<td>$t_{0.95 \text{ tr. fcc}}$ (ps)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc-only system</td>
<td>$\infty$ (nt)</td>
<td>$\infty$ (nt)</td>
<td>1.6 (ft)</td>
</tr>
<tr>
<td></td>
<td>$t_{mc, bcc}$ (ps), crystal plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc-bcc system</td>
<td></td>
<td>$\infty$</td>
<td>8.5 (400)</td>
</tr>
<tr>
<td></td>
<td>89 (st)</td>
<td>$\infty$ (nt)</td>
<td>1.8 (ft)</td>
</tr>
<tr>
<td></td>
<td>89 (440)</td>
<td>$\infty$</td>
<td>151 (400)</td>
</tr>
</tbody>
</table>

‡ The results for st-systems are sensitive to small changes in the initial conditions, see Section 3.
bcc phase is mainly characterised by \{440\} and \{400\} crystal planes, for which the volume fraction is close to 0.4 for both potentials. The other bcc crystal planes initially appear at a much lower volume fraction, and have an orientation that is either close to \{440\} (i.e., \{441\}, \{442\}, \{430\}) or to \{400\} (i.e., \{410\}). It is further remarkable that for the two interatomic potentials the sets of the 5 most dominant crystal planes only differ by one specific crystal plane; i.e., for the ZJW-potential the set of dominant crystal planes contains \{442\}, while for the LBKC-potential \{430\} is included. With increasing time the polycrystalline system for both potentials gradually recrystallises into a monocrystalline system characterised by \{400\} bcc crystal planes. This also means that under free lateral BC the \{440\} crystal planes characterising the initial bcc lattice fully recrystallise into \{400\} planes. Despite the strong correspondence in the bcc crystal planes generated, for the ZJW-potential
the specific time $t_{mc,bcc}$ required for attaining a monocrystalline (abbreviated as 'mc') bcc phase is considerably less (i.e., 150 ps) than for the LBKC-potential (250 ps).

Table 2 summarises the main transformation and crystallisation characteristics of all cases discussed so far. The time $t_{0.95 \text{ tr. fcc}}$ necessary or reaching 0.95 volume fraction of transformed fcc iron – henceforth referred to as the transformation time – has been determined from the transformation evolution curves plotted in Fig. 2. For the fcc-bcc systems modelled with ZJW- and LBKC-potentials and free lateral boundary conditions, the values of the time $t_{mc,bcc}$ required for attaining a monocrystalline bcc phase are provided by Figs. 5a and b, together with the corresponding family of crystal planes. These values have been complemented with those of the other fcc-only and fcc-bcc systems analysed, in order to obtain an overview of the crystalline characteristics of all cases.

From the results in Table 2 and Fig. 2 three transformation categories may be defined, namely (i) fast-transforming (ft) systems, where the transformation starts immediately after the thermal loading has been applied, and completes rapidly in a single, uninterrupted step, (ii) slowly-transforming (st) systems, where the transformation occurs in multiple steps as a result of the occurrence of a slow, distinctive nucleation stage and a subsequent growth stage, possibly complemented with a temporary or permanent arrestment of the transformation, and (iii) non-transforming (nt) systems, for which the transformation remains absent. The transformation time of a fast-transforming system here seems to be bounded by the time domain $0 < t_{0.95 \text{ tr. fcc}} < 5.0$ ps, while for slowly-transforming systems it is characterised by $5.0 \text{ ps} \leq t_{0.95 \text{ tr. fcc}} < \infty$, and for non-transforming systems it is defined as $t_{0.95 \text{ tr. fcc}} \to \infty$, with the symbol '∞' denoting an undefined, long time. For clarification, the transformation category of each lattice system is indicated in Table 2 by the abbreviation 'ft', 'st', or 'nt'. In accordance with these definitions, all lattice systems modelled with the ZJW-potential are observed to be fast-transforming. In contrast, for the LBKC-potential the lattice systems with free boundary conditions are fast-transforming, while the lattice systems with periodic boundary conditions are slowly-transforming. The JO-potential gives rise to one slowly-transforming
system (i.e., the fcc-bcc system with free boundary conditions), and three non-transforming systems. The main observations drawn from the data reported in Table 2 are summarised below.

(i) The transformation time \( t_{0.95 \ tr\ fcc} \) of fast-transforming systems is shorter under free lateral boundary conditions than under periodic boundary conditions. The longer transformation time under periodic boundary conditions can be ascribed to the constraining effect caused by the periodicity. The phenomenon of free surfaces facilitating the transformation process has also been reported in other MD studies (Bos et al., 2006; Urbassek and Sandoval, 2012).

(ii) For fast-transforming systems, the fcc iron in an fcc-only system converts more rapidly into bcc iron than in an fcc-bcc system, despite the number of fcc atoms in the former system being larger, see Table 1. This is due to a different nature of the transformation process in these systems; e.g., in the fcc-only system modelled with the ZJW-potential and periodic boundary conditions the transformation nucleates spontaneously from a large number of sites that are approximately homogeneously distributed over the lattice system, see Fig. 6a, whereas in the fcc-bcc system the transformation nucleates for a substantial part from one of the two fcc-bcc interfaces, i.e., grain boundary nucleation, see Fig. 6b. The local, heterogeneous character of the latter type of nucleation mechanism causes, on average, a fewer atoms per time unit to transform. This can be confirmed from Fig. 6, showing that at \( t = 0.07 \) ps the volume fractions of transformed fcc atoms are 0.56 and 0.37 for the fcc-only system and the fcc-bcc system, respectively, and thus at an early stage already are substantially different, such that the fcc-bcc system eventually needs a larger time for completing the transformation process.

(iii) In fast-transforming systems, the orientation of the bcc crystal planes characterising the final monocrystalline phase is dependent of the type of boundary conditions applied. The monocrystalline bcc phases are identical for the ZJW- and LBKC-potentials, and are further consistent for the fcc-only and fcc-bcc systems, i.e., \( \{400\} \) under free lateral boundary conditions and \( \{440\} \) under periodic boundary conditions. Note, however, that in the fcc-bcc systems with periodic boundary conditions the orientation of the final monocrystalline phase is imposed, through the boundary conditions, by the \( \{440\} \) crystal orientation of the initial bcc lattice.

(iv) For fast-transforming systems, the time \( t_{mc,bcc} \) required for reaching a final, monocrystalline bcc phase is (much) shorter in an fcc-only system than in an fcc-bcc system. Under free lateral boundary conditions, the difference in \( t_{mc,bcc} \) is the largest, since then the \( \{440\} \) bcc structure present in the original fcc-bcc system also needs to be converted to a \( \{400\} \) bcc structure in order for the sample to eventually become monocrystalline. Under periodic boundary conditions, the difference
in $t_{\text{mc,bcc}}$ can be explained by visualising the specific polycrystalline structures generated at completion of transformation, see Fig. 7 for the ZJW-potential. This figure reveals that the volume fractions of the \{440\} family of bcc crystal planes, which for the fcc-only system and the fcc-bcc system characterise their final monocrystalline phase, at completion of transformation are of a similar proportion. Hence, the difference in $t_{\text{mc,bcc}}$ is mainly caused by configurational differences in the polycrystalline bcc structure. Indeed, the fcc-only system has a more regular polycrystalline structure than the fcc-bcc system, with the two dominant bcc crystal planes appearing as alternative bands of specific width, see Fig. 7a. Note that the spacing and inclination of these bands is influenced by the system size through the application of periodic boundary conditions. In relation to the rather arbitrary polycrystalline structure of the fcc-bcc system, see Fig. 7b, the development into a monocrystalline bcc phase from a regularly banded lattice structure apparently goes faster.

(v) The simulation results for slowly-transforming systems are inconsistent with the four features formulated above for fast-transforming systems. This is possibly due to a difference in the sensitivity of the system response to the initial conditions applied. In order to better understand this behaviour, the influence of the initial conditions on the transformation evolution and morphology will be assessed in more detail in Section 3.

(vi) For an fcc-bcc system with free lateral boundary conditions the JO-potential results in a relatively large transformation time $t_{0.95 \text{ tr. fcc}}$, whereby the bcc phase just after completion of transformation is monocrystalline, composed of \{440\} crystal planes. Conversely, the fcc-bcc systems modelled with ZJW- and LBKC-potentials are characterised by much shorter transformation times, with the bcc phase at completion of transformation initially being polycrystalline, and subsequently turning into a monocrystalline phase with \{400\} crystal planes. The overall time $t_{\text{mc,bcc}}$ required for attaining a monocrystalline bcc phase nevertheless is the shortest for the JO-potential (89 ps), followed by the ZJW-potential (150 ps) and the LBKC-potential (250 ps).

(vii) In an fcc-bcc system with free lateral boundary conditions, at completion of transformation the relative atom displacement, which is the displacement of an atom measured relative to the mean location of its neighbouring atoms at the previous timestep, for the three interatomic potentials on average equals 0.18 (JO), 0.11 (ZJW) and 0.10 (LBKC) times the interatomic distance in bcc iron, $r_{\text{bcc}}$. Furthermore, for all three potentials more than 95% of the atoms experience a relative

Fig. 7. The bcc crystal planes at completion of transformation for samples modelled with the ZJW-potential and periodic BC. The two dominant bcc crystal planes are \{440\} (indicated in brown) and \{400\} (indicated in blue). (a) An fcc-only system evaluated at $t=3.1$ ps and (b) An fcc-bcc system evaluated at $t=5.7$ ps. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)
atom displacement that is less than the interatomic distance in the bcc crystal. This suggests that the phase transformation is of a displacive nature, a result that will be investigated in more detail in Section 3 by computing the fcc-bcc interface velocity during transformation growth. For the LBKC- and ZJW-potentials, the average relative atom displacement further increases during the subsequent recrystallisation phase by 0.57 and 0.80 times \( t_{rbcc} \), respectively, where about 30% of the atoms experience an increase in relative displacement between 1 and 5 times \( t_{rbcc} \). This implies that the recrystallisation process is facilitated by the generation of a significant amount of dislocation slip.

(viii) For an fcc-bcc lattice system with free lateral boundary conditions, the transformation process modelled with the JO-potential gradually nucleates from one of the initial fcc-bcc interfaces (i.e., grain boundary nucleation), leading to an heterogeneous transformation pattern across the sample, see Fig. 3. Conversely, for the ZJW-potential the transformation pattern in that case is strongly homogeneous, and nucleates spontaneously from numerous interior locations in the fcc lattice (similar to the nucleation mechanism in an fcc-only system, depicted in Fig. 6a). This demonstrates that homogeneous (heterogeneous) nucleation typically is associated to relatively fast (slow) transformation processes.

3. Influence of initial conditions on transformation behaviour

The comparison study performed in Section 2.2 suggested an effect by the initial conditions on the transformation behaviour, in particular for slowly-transforming systems. In the present section this effect is studied for various lattice configurations, starting with the fcc-bcc system subjected to free lateral boundary conditions. The variation of initial conditions thereby focuses upon the central fcc-bcc interface, and concerns the effects of (i) the initial thermal velocities of the atoms in the atom layers adjacent to the interface, (ii) a small, uniform shift of the initial atom positions across the interface (i.e., an interfacial lattice incoherence), and (iii) the presence of initial atomic vacancies near the interface. It can be reasonably expected that these factors do have an influence on the transformation response, but that their magnitude remains small. It will be shown, however, that this is not always the case. The effective velocity of the fcc-bcc interface is calculated in order to verify that for each interatomic potential the phase transformation is of a displacive nature. Using a classic kinetic model, the interface velocity is employed for estimating the activation energy during transformation growth, where the values computed are related to the computational results presented in Section 2.2. In addition, slowly-transforming systems modelled with the LBKC-potential are analysed, where it is demonstrated that the distribution of the initial atom velocities may have an effect on both the transformation kinetics and the morphology of the bcc product phase.

3.1. Variational study of the initial atom velocities

3.1.1. Lattice systems with free lateral boundary conditions

The computational results presented previously in Fig. 2b and c and Table 2 have demonstrated that the fcc-bcc system with free lateral boundary conditions is the only system leading to a complete transformation for all three interatomic potentials investigated. Hence, this system was chosen for comparing the computational results of 10 simulations subjected to different initial conditions. For this purpose, only the initial thermal velocities of the 308 fcc atoms and 360 bcc atoms present in the two atomic layers adjacent to the central fcc-bcc interface were varied per simulation, by randomly taking different samples from the same Maxwell-Boltzmann distribution. The initial thermal velocities of the 16,492 atoms in the remaining layers of the lattice system remained unchanged in the 10 simulations. As for the simulations described in Section 2, for each of the three interatomic potentials the MD analyses were performed on tetragonal samples subjected to a temperature of 810 K.

The transformation kinetics is illustrated in Fig. 8a for the JO-potential, and in Figs. 8b and c for the ZJW- and LBKC-potentials, respectively. It is evident from Fig. 8a that the transformation evolutions for the slowly-transforming system modelled with the JO-potential display a relatively small spread during the initial stage of the transformation process, i.e., up to a volume fraction of 0.15. However, in the transition period towards a rapid completion of transformation the spread in the transformation responses noticeably grows, eventually resulting in remarkable differences in the transformation time \( t_{tr.fcc}^{0.95} \). As illustrated by Figs. 8b and c, for the fast-transforming systems modelled with the ZJW- and LBKC-potentials the differences in the transformation evolution curves are far less significant; the transformation times for these potentials apparently are too short to create substantial deviations in the dynamic path under a small change in the initial atom velocities.

The mean value \( t_{m}^{0.95 \ tr.fcc} \), sample standard deviation \( \sigma_{std}^{0.95 \ tr.fcc} \) and coefficient of variation \( \frac{\sigma_{std}^{0.95 \ tr.fcc}}{t_{m}^{0.95 \ tr.fcc}} \) of the transformation time can be computed as follows:

\[
\begin{align*}
t_{m}^{0.95 \ tr.fcc} & = \frac{1}{N} \sum_{i=1}^{N} t_{i}^{0.95 \ tr.fcc} , \\
\sigma_{std}^{0.95 \ tr.fcc} & = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left( t_{i}^{0.95 \ tr.fcc} - t_{m}^{0.95 \ tr.fcc} \right)^2} , \\
\frac{\sigma_{std}^{0.95 \ tr.fcc}}{t_{m}^{0.95 \ tr.fcc}} & = \frac{\sigma_{std}^{0.95 \ tr.fcc}}{t_{m}^{0.95 \ tr.fcc}} 
\end{align*}
\]

where \( N=10 \) equals the number of Maxwell-Boltzmann samples taken. Using the data plotted in Fig. 8, the values calculated with these expressions are summarised in Table 3 (columns 1–3). The transformation times of the lattice
Fig. 8. Evolution of the fraction of transformed fcc atoms for lattice systems (fcc-bcc, free lateral BC) modelled with different interatomic potentials (JO, ZJW, LBKC). The response is plotted for 10 systems with different Maxwell-Boltzmann samples for the atoms at the central fcc-bcc interface. (a) JO-potential, (b) ZJW-potential and (c) LBKC-potential.
systems modelled with the ZJW-potential appear to have the smallest mean value and standard deviation, followed by the LBKC-potential and the JO-potential. The coefficient of variation for the lattice system modelled with the JO-potential is, respectively, 4.4 and 5.5 times larger than for systems modelled with ZJW- and LBKC-potentials, which for the JO-potential quantifies the remarkably strong sensitivity of the transformation time to variations in the Maxwell–Boltzmann samples.

As mentioned in Section 2.1, the values of the damping times for the Berendsen-type thermostat and barostat, used for maintaining a constant sample temperature of 810 K and a zero average normal stress, equal 18 fs and 15 fs, respectively. In order to check the influence of the variation of these parameters on the computational results, two additional simulations were performed for each of the three systems characterised by the transformation curves shown in Fig. 8. In the first simulation, the two damping times were increased by a factor of 5, leading to values of 90 fs and 75 fs for the thermostat and the barostat, respectively. In the second simulation, the damping times were decreased by a factor of 5, leading to values of 3.6 fs and 3 fs, respectively. It was found that the transformation evolution curves for the higher and lower damping times are qualitatively similar to those depicted in Figs. 8a–c for the reference damping times of 18 fs and 15 fs. For estimating the quantitative differences, for each of the three interatomic potentials the time required for reaching a volume fraction of 0.7 transformed fcc was computed and compared to the corresponding values computed with the reference damping times. The differences in value appear to be rather small for the ZJW-potential and LBKC-potential, ranging from 0.4% to 3.5% of the total transformation time. Although these differences in some cases somewhat increased for volume fractions of transformed fcc larger than 0.7 (as caused by the flattening of the transformation curves near completion of transformation, see Fig. 8), this result is certainly acceptable, especially considering the fact that the damping times were varied over a relatively large range. For the lattice system modelled with the JO-potential a maximal difference of 17.1% of the total transformation time was found. This difference, however, can be associated to the slowly-transforming nature of this system, which makes it not only relatively sensitive to a change in physical initial conditions, see Fig. 8a, but also to a change in numerical conditions, such as the damping times.

In summary, it may thus be concluded that the dynamic trajectory characterising the sample response during the transformation process is influenced to some extent by the specific choice of the values of the thermostat and barostat damping times, where it is important to establish a-priori that this influence remains minor and a variation of these damping times within a certain range only has a relatively small effect on the computational result.

For checking whether the simulated phase transformation processes can be classified as ‘displacive’, the effective velocity of the fcc-bcc interface is determined from the transformation evolution curves plotted in Fig. 8. This is done by linearly approximating the rate of the transformed volume fraction between 0.6 and 0.8 volume fractions of transformed fcc iron, and multiplying this value by the length of the initial fcc lattice in the sample. Accordingly, it is assumed that the phase transformation process nucleates from one (of the two) original fcc-bcc interface(s), and develops uniformly across the fcc lattice, in the axial ($f_1$) sample direction. Note that this working assumption may not be strictly valid, since, as already indicated, the transformation process may originate from multiple nucleation sites within the original fcc lattice. However, considering the fact that the transformation velocity for displacive and diffusional transformations differs by several orders of magnitude, it may be reasonably expected that this effect will not strongly influence the determination of the nature of the phase transformation process.

Fig. 9 depicts the effective interface velocity in an fcc-bcc system with free boundary conditions for the 10 different Maxwell–Boltzmann samples. The effect of the sample variation on the interface velocity is clearly not similar for the three interatomic potentials, and thus non-systematic. Nonetheless, for each of the individual samples the JO-potential provides the lowest interface velocity (where the mean value equals $v_m=516\text{ ms}^{-1}$), followed by the LBKC-potential ($v_m=823\text{ ms}^{-1}$) and the ZJW-potential ($v_m=2415\text{ ms}^{-1}$). The relatively high and low interface velocities for, respectively, the ZJW- and JO-potentials, indeed can be ascribed to a different spatial character of the phase transformation events, which in the former case is more homogenous (due to the presence of numerous nucleation sites across the sample) than in the latter case (where heterogeneous, grain boundary nucleation is the governing mechanism). Using experimental values commonly reported for the shear modulus (at room temperature), $\mu = 82\text{ GPa}$, and density, $\rho = 7874\text{ kg m}^{-3}$ of iron, the shear wave
configurations are comparable to those used in the present study. The parameters stress-free, tetragonal-shaped samples of a large number of iron atoms that interact through the JO-potential (i.e., the MD were performed under zero stress conditions (Δe, p = 0), the Gibbs free energy difference, at zero temperature (T = 0 K), see Table 6 (more details on these simulations can be found in Section 4). Converting the units of these values from [eV/atom] to [J/mol] leads to \( \Delta E = \Delta E_c = -2740, -6600, \) and \(-9099\) J/mol for, respectively, the JO-, LBKC- and ZJW-potentials. Since the MD simulations were performed under zero stress conditions (p = 0), the Gibbs free energy difference at zero temperature (T = 0) is equal to the internal energy difference, \( \Delta G = \Delta E \), see Eq. (5). Inserting the values of \( \Delta G \) - as reported in Table 4—in Eq. (4), and combining the result with interface velocities at two different temperatures, allows for the determination of the parameters \( \Delta G^a \) and \( \nu_0 \). Hence, in addition to the interface velocity \( \nu(810\) K) obtained from the MD simulations discussed earlier in this section (using the mean value computed from the 10 Maxwell–Boltzmann samples, see Table 4), for this purpose a second interface velocity needs to be calculated at a different temperature. This is done by using a linear relationship between the interface velocity and the temperature, as proposed in Bos et al. (2006):

\[
\nu(T) = \nu_0 \exp\left(-\frac{\Delta G^a}{RT}\right) \left(1 - \exp\left(\frac{\Delta G}{RT}\right)\right),
\]

with \( T \) the temperature, \( \Delta G^a \) the activation energy (or energy barrier) for transformation growth, \( \Delta G \) the Gibbs free energy difference between the product (bcc) and parent (fcc) phases, \( R = 8.314472\) J K\(^{-1}\) mol\(^{-1}\) the gas constant, and \( \nu_0 \) a calibration parameter. For the sake of clarity, the activation energy \( \Delta G^a \) and the Gibbs free energy difference \( \Delta G \) are indicated in the schematisation of the effective Gibbs free energy \( G \) for a phase transition from fcc to bcc iron, see Fig. 10.

For each of the three potentials the effective activation energy \( \Delta G^a \) can be estimated from Eq. (4) as follows. First, the Gibbs free energy difference \( \Delta G \) needs to be determined, which, under the typical conditions of constant temperature and stress, satisfies the usual thermodynamical relation:

\[
\Delta G = \Delta E + p \Delta V - T \Delta S,
\]

with \( \Delta E \) the difference in internal energies of the product (bcc) and parent (fcc) phases, \( p \) the pressure\(^2\), \( \Delta V \) the volume difference, and \( T \Delta S \) the entropy difference. The value of \( \Delta E \) for each of the three interatomic potentials is set here equal to the cohesive energy difference \( \Delta E_c \) of the bcc and fcc phases, as obtained from MD simulations on cuboidal bcc and fcc samples subjected to periodic boundary conditions, evaluated at their relaxed, equilibrium state at \( T = 0 \) K, see Table 6 (more details on these simulations can be found in Section 4). Converting the units of these values from [eV/atom] to [J/mol] leads to \( \Delta E = \Delta E_c = -2740, -6600, \) and \(-9099\) J/mol for, respectively, the JO-, LBKC- and ZJW-potentials. Since the MD simulations were performed under zero stress conditions (p = 0), the Gibbs free energy difference at zero temperature (T = 0) is equal to the internal energy difference, \( \Delta G = \Delta E \), see Eq. (5). Inserting the values of \( \Delta G \) - as reported in Table 4—in Eq. (4), and combining the result with interface velocities at two different temperatures, allows for the determination of the parameters \( \Delta G^a \) and \( \nu_0 \). Hence, in addition to the interface velocity \( \nu(810\) K) obtained from the MD simulations discussed earlier in this section (using the mean value computed from the 10 Maxwell–Boltzmann samples, see Table 4), for this purpose a second interface velocity needs to be calculated at a different temperature. This is done by using a linear relationship between the interface velocity and the temperature, as proposed in Bos et al. (2006):

\[
\nu(T) = \epsilon T + \nu_{10}.
\]

The above relationship was derived by Bos et al. (2006) from MD simulations performed at multiple temperatures, using stress-free, tetragonal-shaped samples of a large number of iron atoms that interact through the JO-potential (i.e., the MD configurations are comparable to those used in the present study). The parameters \( \epsilon \) and \( \nu_{10} \) can be determined by subsequently substituting in Eq. (6) the interface velocity \( \nu(810\) K), and the zero interface velocity, \( \nu=0 \), that formally

\[\]

\( ^2 \) Although in solid materials the stress and strain are formally described by a second-order tensor, for reasons of simplicity the scalar representations \( p \) (pressure) and \( \Delta V \) (volume difference) are used here instead; this simplification, however, does not influence the subsequent result and discussion.
corresponds to the transition temperature at which the stable phase changes from (α-ferritic) bcc iron to (γ-austenitic) fcc iron. Although experimentally this phase transition takes place at $T = 1184$ K, the MD simulations discussed in Bos et al. (2006) clearly indicated that the JO-potential is not able to accurately mimic this result; instead, a linear extrapolation of the temperature-dependent Gibbs free energy difference presented in Fig. 1 of Bos et al. (2006) suggests that fcc iron becomes the stable phase at a much higher temperature of about 2500 K. For consistency reasons and from the fact that an artificially high transition temperature, or even the absence of a transition temperature, is a rather common feature of interatomic potentials used for iron (Müller et al., 2007; Urbassek and Sandoval, 2012), the transition temperature of 2500 K is also adopted here for the LBKC- and ZJW-potentials, leading to the values of $\epsilon$ and $v_{T0}$ presented in Table 4.

Substituting the interface velocities computed at the two different temperatures in Eq. (4) then allows for solving $\Delta G^a$ and $v_0$, see Table 4 for the result. The data in Table 4 clearly indicates that the JO-potential requires by far the largest activation energy $\Delta G^a$ for the transformation to grow – and thus is characterised by the highest resistance against transformation –, followed by the LBKC-potential, and subsequently, with a very low value, by the ZJW-potential. Conversely, the Gibbs free energy difference $\Delta G$ – which acts as the driving force for transformation – has the smallest value for the JO-potential, followed by the LBKC-potential, and finally the ZJW-potential. The sequence in magnitude of both $\Delta G^a$ and $\Delta G$ is consistent with the computational results previously summarised in Table 2, which showed that for the JO-potential the resistance against transformation generally is relatively high (as demonstrated by the appearance of slowly- and non-transforming systems), while for the LBKC-potential the transformation resistance is moderate (fast- and slowly-transforming systems), and for the ZJW-potential it is low (only fast-transforming systems). Despite this consistency in results, it is important to mention that the activation energy $\Delta G^a$ is derived from the interface velocity at transformation growth, and thus does not reflect the influence by the nucleation barrier on the total transformation time (assuming that transformation nucleation and growth are fully independent processes). Furthermore, $\Delta G^a$ is derived by means of several assumptions introduced through Eqs. (4)–(6), so that the parameter values reported in Table 4 should be interpreted as global estimates. Nonetheless, the values for $\Delta G$ and $\Delta G^a$ are in good correspondence with those reported in Müller et al. (2007), where, under the application of a Bain path, for 5 interatomic potentials – which all are different from those examined in the present study – the energy

<table>
<thead>
<tr>
<th>Parameter</th>
<th>JO</th>
<th>LBKC</th>
<th>ZJW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface velocity $v(810$ K $)$ [$\text{ms}^{-1}$]</td>
<td>516</td>
<td>823</td>
<td>2415</td>
</tr>
<tr>
<td>$v(304$ K $)$ [$\text{ms}^{-1}$]</td>
<td>670</td>
<td>1069</td>
<td>3138</td>
</tr>
<tr>
<td>Gibbs free energy diff. $\Delta G$ [$\text{J mol}^{-1}$]</td>
<td>$-2740$</td>
<td>$-6600$</td>
<td>$-9099$</td>
</tr>
<tr>
<td>$\Delta G$ [meV/atom]</td>
<td>$-28$</td>
<td>$-68$</td>
<td>$-94$</td>
</tr>
<tr>
<td>Activation energy $\Delta G^a$ [J mol$^{-1}$]</td>
<td>1707</td>
<td>537</td>
<td>41</td>
</tr>
<tr>
<td>$\Delta G^a$ [meV/atom]</td>
<td>17</td>
<td>6</td>
<td>0.4</td>
</tr>
<tr>
<td>Calibration parameters $v_0$ [$\text{ms}^{-1}$]</td>
<td>1989</td>
<td>1427</td>
<td>3279</td>
</tr>
<tr>
<td>$\epsilon$ [ms$^{-1}$ K$^{-1}$]</td>
<td>$-0.305$</td>
<td>$-0.487$</td>
<td>$-1.429$</td>
</tr>
<tr>
<td>$v_{T0}$ [ms$^{-1}$]</td>
<td>763</td>
<td>1217</td>
<td>3572</td>
</tr>
</tbody>
</table>

Fig. 10. Schematisation of the Gibbs free energy $G$ for a phase transformation from fcc to bcc iron, with $\Delta G$ the Gibbs free energy difference and $\Delta G^a$ the activation energy.

Table 4
Parameter values used in Eqs. (4) and (6) for the three interatomic potentials.

The data in Table 4 clearly indicates that the JO-potential requires by far the largest activation energy $\Delta G^a$ for the transformation to grow – and thus is characterised by the highest resistance against transformation –, followed by the LBKC-potential, and subsequently, with a very low value, by the ZJW-potential. Conversely, the Gibbs free energy difference $\Delta G$ – which acts as the driving force for transformation – has the smallest value for the JO-potential, followed by the LBKC-potential, and finally the ZJW-potential. The sequence in magnitude of both $\Delta G^a$ and $\Delta G$ is consistent with the computational results previously summarised in Table 2, which showed that for the JO-potential the resistance against transformation generally is relatively high (as demonstrated by the appearance of slowly- and non-transforming systems), while for the LBKC-potential the transformation resistance is moderate (fast- and slowly-transforming systems), and for the ZJW-potential it is low (only fast-transforming systems). Despite this consistency in results, it is important to mention that the activation energy $\Delta G^a$ is derived from the interface velocity at transformation growth, and thus does not reflect the influence by the nucleation barrier on the total transformation time (assuming that transformation nucleation and growth are fully independent processes). Furthermore, $\Delta G^a$ is derived by means of several assumptions introduced through Eqs. (4)–(6), so that the parameter values reported in Table 4 should be interpreted as global estimates. Nonetheless, the values for $\Delta G$ and $\Delta G^a$ are in good correspondence with those reported in Müller et al. (2007), where, under the application of a Bain path, for 5 interatomic potentials – which all are different from those examined in the present study – the energy...
difference at 0 K was calculated, leading to values ranging between $-30$ and $-121$ meV/atom, while the activation energy appeared to vary between 0.7 and 36 meV/atom. From these results and the values of $\Delta G$ and $\Delta G^a$ presented in Table 4, it can be concluded that the (absolute value of the) energy difference for displacive phase transformations in iron typically is significantly larger than the activation energy.

3.1.2. Lattice systems with periodic lateral boundary conditions

The transformation evolutions depicted in Fig. 8 of Section 3.1.1 relate to systems with free lateral boundary conditions, where only slowly-transforming systems (i.e., the systems modelled with the JO-potential) appear to be strongly sensitive to a change in initial conditions. For studying the effect of initial conditions on samples subjected to periodic lateral boundary conditions, it was therefore decided to consider only slowly-transforming systems, which, in accordance with Table 2, comes down to an analysis of the fcc-only and fcc-bcc systems modelled with the LBKC-potential. In the fcc-bcc system the variation of the initial thermal velocities was carried out in the same fashion as described in Section 3.1.1, i.e., only the Maxwell–Boltzmann samples of the atoms in the two atomic layers adjacent to the central fcc-bcc interface were varied. For consistency, the 10 specific samples were taken identical to those of the lattice systems analysed in Section 3.1.1. Conversely, for the fcc-only system - which initially does not have an fcc-bcc interface - the Maxwell–Boltzmann samples of the total number of atoms were varied.

Figs. 11a and b display the transformation kinetics of the fcc-only system and fcc-bcc system, respectively. It can be confirmed that for these slowly-transforming systems the responses indeed show a strong sensitivity to small changes in the initial atom velocities. The transformation kinetics of the fcc-only system is characterised by a remarkable trend, where, after a relatively long period of no transformation activity at all, the fcc phase spontaneously converts into the bcc phase. In contrast to the fcc-only system with free boundary conditions, where the transformation from fcc to bcc iron starts

Fig. 11. Evolution of the fraction of transformed fcc atoms for lattice systems modelled with the LBKC-potential and periodic boundary conditions. (a) The fcc-only system: The transformation response is plotted for 10 systems with different Maxwell–Boltzmann samples for the total number of atoms. The solid and dashed lines indicate the lattice systems for which the final, monocrystalline bcc phase is characterised by $\{400\}$ and $\{440\}$ crystal planes, respectively. To illustrate the continuous character of the transformation evolution, the response indicated by the asterisk (*) is shown in more detail in the inset. (b) The fcc-bcc system: The transformation response is plotted for 10 systems with different Maxwell–Boltzmann samples for the atoms at the central fcc-bcc interface.
immediately from the onset of thermal loading, see Fig. 2a, under periodic boundary conditions the fcc lattice is more constrained, and therefore initially behaves metastable. However, the large thermal fluctuations of the fcc atoms after a certain time prelude the creation of several small nuclei of bcc iron, from which a cascade of additional transformation events develops that quickly completes the transformation process. The typical S-shaped kinetic curve reflecting this process is shown in detail in the inset of Fig. 11a.

The strongly random character of the thermal fluctuations gives rise to a large spread in the transformation times: Fig. 11a illustrates that the shortest and longest transformation times differ by approximately a factor of 10. The randomness of the thermal fluctuations further causes remarkable variations in the final bcc product phase generated: For 3 of the 10 simulations the monocristalline bcc product phase is characterised by {440} crystal planes (indicated in Fig. 11a by the dashed lines), whereas for the other 7 simulations {400} bcc iron is produced (indicated in Fig. 11a by the solid lines). The overall transformation deformation of the bcc samples composed of {440} crystal planes is characterised by 21% contraction in the global $f_2$-direction and 12% extension in the $f_1$- and $f_3$-directions. The volume change caused by the transformation is very close to zero and the strain values calculated in the specific directions essentially represent a Bain transformation (Bain, 1924; Urbassek and Sandoval, 2012). In contrast, the {400} bcc samples are characterised by 21% contraction in the $f_3$-direction and 12% extension in the $f_1$ and $f_2$-directions. The remarkable appearance of bcc product phases with different crystalline orientations did not occur for the fcc-bcc systems displayed in Figs. 8 and 11b: All 10 simulations for these cases lead to the generation of one and the same bcc crystal, see Table 2 for the specific orientations, although it should be mentioned that for the transformation responses in Fig. 11b the unique {440} crystal orientation of the bcc product phase is imposed, through the periodic boundary conditions, by the initial bcc lattice with the same orientation. It can further be observed that the transformation evolutions in Fig. 11b clearly show local fluctuations, which reflect the emergence and subsequent disappearance of bcc nuclei of subcritical size.

Despite the transformation kinetics and morphology being different for the two lattice systems evaluated in Figs. 11a and b, the spread in their transformation times is comparable, see Table 3 (columns 4 and 5). In addition, the mean transformation time and standard deviation of these two lattice systems are substantially larger than the values reported in Table 3 for lattice systems with free boundary conditions (columns 1–3).

Fig. 12a and b illustrate the spatial distribution of the fcc and bcc phases in, respectively, an fcc-only system and an fcc-bcc system modelled with the LBKC-potential and periodic boundary conditions. For both lattice systems the results

![Fig. 12. Intermediate stage of the transformation process for lattice systems modelled with the LBKC-potential and periodic boundary conditions. The fcc and bcc atoms are indicated in green and blue, respectively. The crystal type of the red atoms could not be classified. (a) A typical fcc-only system, evaluated at $t=266$ ps. The fraction of transformed fcc atoms is 0.42. (b) A typical fcc-bcc system, evaluated at $t=15$ ps. The fraction of transformed fcc atoms is 0.55. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)](image)
correspond to an intermediate stage of the transformation process, and, though referring to the two specific simulations depicted in Fig. 2, are representative of all 10 simulations shown in Fig. 11a and b. In the fcc-only system the growth of bcc iron happens from numerous nucleation sites, though this leads to a somewhat lesser homogeneous transformation pattern than for the ZJW-potential, see Fig. 6a. The transformation pattern in the fcc-bcc system is strongly heterogeneous, as characterised by the development of bcc iron from the fcc-bcc interfaces, with some additional nucleation from sites at interior locations of the original fcc lattice. This combination of nucleation behaviour from pre-existing fcc-bcc grain boundaries and interior sites of the lattice is known as mixed nucleation (Liu et al., 2007).

3.2. Variational study of the fcc-bcc interface configuration

The effect of the specific fcc-bcc interface configuration on the transformation kinetics is assessed by taking the original sample as depicted in Fig. 1, and shifting the initial atom positions of the fcc part of the sample uniformly over a specific distance while keeping the positions of the bcc atoms fixed. In terms of the interatomic distance of the fcc phase at 0 K, which for the JO-potential equals \( r_{\text{fcc}} \approx 2.608 \text{Å} \), three arbitrary positional shifts (i.e., interfacial lattice incoherence) are considered, namely case 1: \( r_{\text{fcc}} ( \frac{1}{2} f_2, \frac{1}{2} f_3 ) \), case 2: \( r_{\text{fcc}} ( \frac{1}{2} f_2, -\frac{1}{2} f_3 ) \), and case 3: \( r_{\text{fcc}} ( \frac{1}{2} f_2, -\frac{1}{2} f_3 ) \). Here, \( f_2 \) and \( f_3 \) represent the global, lateral directions of the lattice system, as shown in Fig. 1. Using a lattice with free lateral boundary conditions, for each shifted configuration again 10 simulations were carried out with different Maxwell–Boltzmann samples for the atoms at the central fcc-bcc interface. This variational study was performed only for slowly-transforming systems modelled with the JO-potential; additional simulations not presented here have indeed confirmed that for the ZJW- and LBKC-potentials only a small effect on the transformation response is generated by an initial shift of the fcc atoms. The transformation evolutions of these fast-transforming systems virtually fell within the narrow ranges of curves depicted in Figs. 8b and c for the unshifted sample, and therefore will not be presented here. The transformation evolutions related to the three interface shifts modelled with the JO-potential are plotted in Fig. 13.

Comparing the results displayed in Figs. 13 with those presented in Fig. 8 (unshifted case), it can be estimated that the mean value of the transformation time is smallest for case 1 and largest for case 3. For case 2 the spread in the transformation time is by far the greatest, although this is mainly due to one specific sample experiencing an exceptionally large transformation time of 246 ps.

Table 5 (columns 2–4) shows that the mean value of the transformation time for the three interface shifts maximally differs by a factor of almost 2, while the sample standard deviation and the coefficient of variation differ by a factor of 2 to 3. A comparison with the statistical values depicted for the unshifted sample (column 1) illustrates that an interface shift in accordance with case 1 decreases the mean transformation time by 30%; conversely, an interface shift in accordance with case 3 leads to an increase of the transformation time by 23%. The performance of additional statistical tests (i.e., student’s t-test, F-test) has indicated that the influence of a different interfacial lattice incoherence on the transformation kinetics is significant at the 5% uncertainty level. With the exception of the pair ‘case 2–case 3’, it appears that all pairs have significantly different transformation time means, variances, or both. In these statistical tests the unshifted sample was also included. It can thus be concluded that a small change in the fcc-bcc interface configuration may have a considerable impact on the transformation time of a lattice system.

It is intuitive to attribute the statistical differences in transformation time to possible differences in the interfacial energy of the fcc-bcc interface. Accordingly, the relaxed, initial interfacial energy, \( \Delta E_i \), was determined for the fcc-bcc systems by computing the total potential energy of the system at its relaxed equilibrium state at 0 K (using a relaxation time of 0.7 ps), subtracting the potential energies of the individual fcc and bcc parts of the system at their relaxed equilibrium states, and dividing the result by the total area of the two fcc-bcc interfaces. Table 5 (columns 1–4) summarises the values of \( \Delta E_i \) for the unshifted sample and the three shifted samples. The 4 values of the interfacial energy are clearly very close to each other, and appear to be in good correspondence with an interface energy value of 0.80 J m\(^{-2}\) deduced from experiments (Murr, 1975; Yang and Johnson, 1993). The close agreement of these 4 interfacial energies may indeed be the reason that the corresponding transformation evolution curves depicted in Figs. 8 (unshifted case) and 13 all have a similar shape. Obviously, it is not possible to systematically relate 4 similar interfacial energies to significantly different mean values and standard deviations of the transformation time. This suggests that the differences in the statistical values of the transformation time essentially result from the initial differences in lattice incoherence at the fcc-bcc grain boundary; the characterisation and quantification of such geometrical effects, however, falls beyond the scope of the present study and is a topic for future research.

3.3. Variational study of atomic vacancies at fcc-bcc interface

The influence of atomic vacancies on the transformation evolution is studied for the JO-potential considering two cases, namely case A: 4 atomic vacancies located at the centre of each of the fcc and bcc layers adjacent to the central fcc-bcc interface, and case B: 4 atomic vacancies located at the centre of each of the 4 fcc and 4 bcc layers closest to the central fcc-bcc interface. The locations of the vacancies in the atom layers of the sample are presented in Fig. 14, with the measures being rounded off in Ångströms. The positions of 4 vacancies are alternatively shifted per atom layer, as sketched for 2 adjacent atom layers (vacancies indicated by solid circles) and \( n+1 \) (vacancies indicated by dashed circles), with \( n \) representing the atom layer number in the \( f_1 \)-direction. The transformation evolutions for cases A and B are depicted in...
Figs. 15a and b, respectively. It is clear that the mean transformation time and the spread in the transformation evolutions for case B are greater than for case A. This effect is quantified in Table 5 by the statistical values related to the transformation time (columns 5 and 6). The table further contains the interfacial energy $\Delta E_i$ (which is equal to the interfacial energy of the

Fig. 13. Evolution of the fraction of transformed fcc atoms for systems (fcc-bcc, free lateral BC, JO-potential) with different initial fcc-bcc interfaces. The response is plotted for 10 systems with different Maxwell–Boltzmann samples for the atoms at the central fcc-bcc interface. (a) Case 1: shift $r_{fc}(\frac{1}{2}, \frac{1}{3})$, (b) Case 2: shift $r_{fc}(\frac{1}{2}, \frac{1}{5})$ and (c) Case 3: shift $r_{fc}(\frac{1}{4}, \frac{1}{4})$.

Figs. 15a and b, respectively. It is clear that the mean transformation time and the spread in the transformation evolutions for case B are greater than for case A. This effect is quantified in Table 5 by the statistical values related to the transformation time (columns 5 and 6). The table further contains the interfacial energy $\Delta E_i$ (which is equal to the interfacial energy of the
The total vacancy formation energy \( \Delta E_{\text{tot}}^{\text{vf}} \) was determined by computing the total potential energy of the fcc-bcc system with vacancies at its relaxed equilibrium state at 0 K (using a relaxation time of 0.7 ps), and subtracting the potential energy of the relaxed fcc-bcc system without vacancies. Dividing the total vacancy formation energies listed in Table 5 by the corresponding number of vacancies in the system (8 for case A and 32 for case B) leads to the values 1.02 eV (case A) and 1.59 eV (case B). These values should not

### Table 5

Lattice systems (fcc-bcc, free lateral BC, JO-potential) with atomic shifts (columns 2–4) and atomic vacancies (columns 5–6) at the fcc-bcc interface: Mean value \( t_{0.95}^{\text{fcc}} \), sample standard deviation \( t_{0.95}^{\text{fcc}} \), and coefficient of variation \( t_{0.95}^{\text{fcc}} \) of the time needed for attaining 0.95 volume fraction of transformed fcc atoms, together with the initial interfacial energy \( \Delta E_i \) and the total vacancy formation energy \( \Delta E_{\text{tot}}^{\text{vf}} \). The statistical values were computed from 10 systems with different Maxwell–Boltzmann samples for the atoms at the central fcc-bcc interface. The statistical values for the unshifted lattice system without atomic vacancies (column 1) were taken from Table 3.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>No interf. shift &amp; no vacancies</th>
<th>Interf. shift Case 1</th>
<th>Interf. shift Case 2</th>
<th>Interf. shift Case 3</th>
<th>Interf. vacancies Case A</th>
<th>Interf. vacancies Case B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{0.95}^{\text{fcc}} ) [ps]</td>
<td>81.9</td>
<td>57.3</td>
<td>75.8</td>
<td>100.5</td>
<td>85.5</td>
<td>104.0</td>
</tr>
<tr>
<td>( t_{0.95}^{\text{fcc}} ) [ps]</td>
<td>18.1</td>
<td>17.4</td>
<td>58.6</td>
<td>39.3</td>
<td>14.9</td>
<td>31.4</td>
</tr>
<tr>
<td>( t_{0.95}^{\text{fcc}} ) [-]</td>
<td>0.22</td>
<td>0.30</td>
<td>0.77</td>
<td>0.39</td>
<td>0.17</td>
<td>0.30</td>
</tr>
<tr>
<td>( \Delta E_i ) [J m(^{-2})]</td>
<td>0.741</td>
<td>0.751</td>
<td>0.743</td>
<td>0.749</td>
<td>0.741</td>
<td>0.741</td>
</tr>
<tr>
<td>( \Delta E_{\text{tot}}^{\text{vf}} ) [eV]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.2</td>
<td>50.9</td>
</tr>
</tbody>
</table>

Fig. 14. Locations (rounded off in Ångströms) of vacancies in two adjacent atom layers \( n \) (vacancies sketched by solid circles) and \( n+1 \) (vacancies sketched by dashed circles), with \( n \) the atom layer number in the \( f_1 \)-direction.

The fcc-bcc system without atomic vacancies), and the total vacancy formation energy \( \Delta E_{\text{tot}}^{\text{vf}} \). The total vacancy formation energy was determined by computing the total potential energy of the fcc-bcc system with vacancies at its relaxed equilibrium state at 0 K (using a relaxation time of 0.7 ps), and subtracting the potential energy of the relaxed fcc-bcc system without vacancies. Dividing the total vacancy formation energies listed in Table 5 by the corresponding number of vacancies in the system - 8 for case A and 32 for case B - leads to the values 1.02 eV (case A) and 1.59 eV (case B). These values should not

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3 For the correct computation of the total vacancy formation energy, the potential energy of the system without vacancies needs to be multiplied by the scaling factor \( (N_{\text{atom}}-N_{\text{vac}})/N_{\text{atom}} \), although the number of atoms, \( N_{\text{atom}} \), typically is much larger than the number of vacancies, \( N_{\text{vac}} \), as a result of which this factor becomes very close to 1.
be confused with the vacancy formation energy related to a single vacancy in a fully periodic fcc or bcc lattice, which for the JO-potential were calculated as 1.80 eV and 1.57 eV, respectively, see also Table 6. Obviously, the difference between the average of these two values – reflecting that the number of vacancies in fcc and bcc parts of the lattice are equal – and the values in Table 5 divided by the number of vacancies can be ascribed to interactions of vacancies with the fcc-bcc interfaces, with the free boundaries, and with the other vacancies in the lattice system.

The close agreement between the statistical values of the transformation time for case A and for the sample without vacancies (column 1 of Table 5) would imply a relatively small effect on the transformation behaviour by the presence of atomic vacancies. Nonetheless, for case B the mean transformation time and the corresponding sample standard deviation increase by, respectively, 27% and 74% with respect to the values of the sample without atomic vacancies. The presence of more initial vacancies near the fcc-bcc interface thus enlarges with marginal significance the mean value and sample standard deviation of the transformation time. This trend, which is also characterised by a noticeable increase in the vacancy formation energy $\Delta E^{\text{tot}}_v$, becomes manifest despite the rapid rearrangements of atoms under thermal fluctuations, causing several initial vacancies to migrate to the surface of the sample, or to jump to neighbouring atomic layers well before the transformation process was completed. More specifically, at completion of transformation the number of vacancies that has migrated to the surface of the system equals 4 (out of 8) for case A and 18 (out of 32) for case B. The mechanical work related to the migration of vacancies relaxes the atomic configuration, thereby reducing the driving force for phase transformation. Consequently, the phase transformation process needs a longer time to complete when the number of vacancies increases.

4. Comparison between computational, experimental and ab initio material properties

Table 6 summarises material data of the fcc and bcc phases, as obtained from basic MD computations with the three interatomic potentials and experiments and ab initio simulations reported in the literature. The parameter values in the table relate to a temperature of 0 K, unless indicated otherwise. The results from the basic MD simulations refer to cubic fcc
and bcc samples of $10 \times 10 \times 10$ (4000 atoms) unit cells and $12 \times 12 \times 12$ (3456 atoms) unit cells, respectively, where the boundary conditions were taken periodic in all three directions. The equilibrium states of the fcc and bcc phases at 0 K were found by determining the interatomic distances at which the potential energy of the phases is minimal. The elastic moduli $C_{11}$, $C_{12}$ and $C_{44}$ followed from the application of three independent, incremental deformation paths. The linear coefficient of thermal expansion $\alpha_L$ was determined at room temperature in order to be consistent with the experimental values, using the incremental volumetric expansion calculated under an incremental increase in temperature.

The experimental and ab initio data were adopted from the overview presented in Müller et al. (2007). In this paper, the experimental elastic moduli for fcc and bcc iron were taken from Zarestky and Stassis (1987) and Acet et al. (1994). The experimental values of $\alpha_L$ for the fcc phase were taken from Acet et al. (1994). The experimental value of $\alpha_L$ for the fcc phase was adopted from Lide (2004). The experimental cohesive energy $E_{\text{c}}^{\text{f}}$ of the bcc phase, which corresponds to the potential energy at equilibrium at 0 K, was obtained from Kittel (1986). The ab initio value for the cohesive energy difference, $\Delta E_{\text{c}}$, which represents the difference in $E_{\text{c}}$ between the bcc and fcc phases, was taken from Chen and Sundman (2001), and was estimated from a theoretical evaluation of the phase diagram of iron. Combining this energy difference with the experimental value of $E_{\text{c}}^{\text{f}}$ as $E_{\text{c}}^{\text{f}} = E_{\text{c}}^{\text{b}} - \Delta E_{\text{c}}$, the volumetric ratio $V_{\text{bcc}}/V_{\text{fcc}}$ and the linear coefficient of thermal expansion $\alpha_L$ of the fcc phase were taken from Acet et al. (1994). The experimental value of $\alpha_L$ for the bcc phase was adopted from Lide (2004). The experimental cohesive energy $E_{\text{c}}^{\text{f}}$ of the fcc phase, which corresponds to the potential energy at equilibrium at 0 K, was obtained from Kittel (1986). The ab initio value for the cohesive energy difference, $\Delta E_{\text{c}}$, which represents the difference in $E_{\text{c}}$ between the bcc and fcc phases, was taken from Chen and Sundman (2001), and was estimated from a theoretical evaluation of the phase diagram of iron. Combining this energy difference with the experimental value of $E_{\text{c}}^{\text{f}}$ as $E_{\text{c}}^{\text{f}} = E_{\text{c}}^{\text{b}} - \Delta E_{\text{c}}$, the volumetric ratio $V_{\text{bcc}}/V_{\text{fcc}}$ and the linear coefficient of thermal expansion $\alpha_L$ of the fcc phase were taken from Acet et al. (1994) and Ehrhart (1991), respectively. The experimental elastic moduli of the fcc phase reported in Zarestky and Stassis (1987) relate to phonon dispersion measurements at 1428 K, while the experimental elastic moduli of the bcc phase reported in Lide (2004) correspond to room temperature. It may be reasonably expected that the elastic moduli at room temperature will not deviate much from those at a temperature of 0 K. The experimental values of $r_{\text{f}}$, $V_{\text{f}}$ and $\alpha_L$ of the fcc phase were derived from Acet et al. (1994) from the stable, high-temperature values measured at 1185 K, using an extrapolation to 0 K based on the lattice constant. The ab initio values of the elastic moduli of the fcc and bcc phases were computed by Müller et al. (2007), and the atomic distances of these phases, as well as the volume change $V_{\text{bcc}}/V_{\text{fcc}}$, were derived from the ab initio values reported in this work for the equilibrium volumes.

Since the interatomic potentials were calibrated to the properties of the bcc phase, a good correspondence is found between the calculated and measured values of the atomic distance, the elastic moduli, the cohesive energy and the vacancy formation energy. Table 6 further indicates that the elastic constants following from the ab initio computations overestimate the experimental values. In addition, the experimental value of the linear coefficient of thermal expansion of bcc iron is comparable to the values for the ZJW- and LBKC-potentials, while the value for the JO-potential is somewhat smaller than the experimental value.

For the fcc phase the differences between the calculated and measured parameters are clearly larger than for the bcc phase. All interatomic potentials seem to overestimate the experimental interatomic distance $r_{\text{f}}$, where the highest value of 2.608 Å is obtained for the JO-potential. Due to softening of a crystal at elevated temperature, it may be expected that the high-temperature elastic moduli experimentally measured for fcc iron lay (substantially) below the elastic moduli calculated

<table>
<thead>
<tr>
<th>Material data</th>
<th>JO</th>
<th>ZJW</th>
<th>LBKC</th>
<th>Experiment</th>
<th>Ab initio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>bcc lattice</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic distance $r_{\text{bcc}}$ [Å]</td>
<td>2.482</td>
<td>2.482</td>
<td>2.480</td>
<td>2.477</td>
<td>2.453</td>
</tr>
<tr>
<td>Elastic moduli $C_{11}$ [GPa]</td>
<td>230</td>
<td>230</td>
<td>244</td>
<td>226$^a$</td>
<td>277</td>
</tr>
<tr>
<td>$C_{12}$ [GPa]</td>
<td>136</td>
<td>136</td>
<td>138</td>
<td>140$^b$</td>
<td>147</td>
</tr>
<tr>
<td>$C_{44}$ [GPa]</td>
<td>117</td>
<td>117</td>
<td>122</td>
<td>116$^a$</td>
<td>96</td>
</tr>
<tr>
<td>Cohesive energy $E_{\text{c}}^{\text{bcc}}$ [eV/atom]</td>
<td>−4.29</td>
<td>−4.29</td>
<td>−4.29</td>
<td>−4.28</td>
<td>−</td>
</tr>
<tr>
<td>Vacancy formation energy $E_{\text{v}}^{\text{bcc}}$ [eV]</td>
<td>1.57</td>
<td>1.68</td>
<td>1.75</td>
<td>1.59−1.89</td>
<td>−</td>
</tr>
<tr>
<td>Coeff. of thermal exp. $\alpha_L$ [10$^{-5}$ K$^{-1}$]</td>
<td>7.2$^a$</td>
<td>11.3$^a$</td>
<td>12.5$^b$</td>
<td>11.8$^a$</td>
<td>−</td>
</tr>
<tr>
<td><strong>fcc lattice</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic distance $r_{\text{fcc}}$ [Å]</td>
<td>2.608</td>
<td>2.566</td>
<td>2.554</td>
<td>2.519</td>
<td>2.462</td>
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<tr>
<td>Elastic moduli $C_{11}$ [GPa]</td>
<td>231</td>
<td>110</td>
<td>233</td>
<td>154$^b$</td>
<td>309</td>
</tr>
<tr>
<td>$C_{12}$ [GPa]</td>
<td>125</td>
<td>100</td>
<td>142</td>
<td>122$^b$</td>
<td>152</td>
</tr>
<tr>
<td>$C_{44}$ [GPa]</td>
<td>106</td>
<td>81</td>
<td>81</td>
<td>77$^b$</td>
<td>201</td>
</tr>
<tr>
<td>Cohesive energy $E_{\text{c}}^{\text{fcc}}$ [eV/atom]</td>
<td>−4.26</td>
<td>−4.20</td>
<td>−4.22</td>
<td>−</td>
<td>−4.22$^c$</td>
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<tr>
<td>Vacancy formation energy $E_{\text{v}}^{\text{fcc}}$ [eV]</td>
<td>1.80</td>
<td>1.69</td>
<td>1.89</td>
<td>1.71</td>
<td>−</td>
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<td>Coeff. of thermal exp. $\alpha_L$ [10$^{-5}$ K$^{-1}$]</td>
<td>5.0$^a$</td>
<td>−</td>
<td>−</td>
<td>24.5$^a$</td>
<td>−</td>
</tr>
<tr>
<td><strong>bcc vs. fcc lattice</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diff. cohesive energy</td>
<td>$\Delta E_{\text{c}} = E_{\text{c}}^{\text{f}} - E_{\text{c}}^{\text{bcc}}$ [eV/atom]</td>
<td>−0.03</td>
<td>−0.09</td>
<td>−0.07</td>
<td>−</td>
</tr>
<tr>
<td>Volume change $V_{\text{bcc}}/V_{\text{fcc}}$ [-]</td>
<td>0.939</td>
<td>0.985</td>
<td>0.997</td>
<td>1.035</td>
<td>1.077</td>
</tr>
<tr>
<td>Cut-off distance $r_{\text{cut-off}}$ [Å]</td>
<td>3.460</td>
<td>3.500</td>
<td>3.600</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^a$ Corresponding to room temperature.

$^b$ Corresponding to 1428 K.

$^c$ Obtained from combining the experimental $E_{\text{c}}^{\text{f}}$-value with the ab initio $\Delta E_{\text{c}}$-value.
with the interatomic potentials at 0 K. This is indeed the case for the elastic moduli computed with the JO- and LBKC-potentials; nevertheless, the elastic moduli of the fcc and bcc phases are comparable for these potentials, whereas the elastic moduli obtained from ab initio simulations indicate that fcc iron typically should have somewhat higher elastic constants than bcc iron. The elastic moduli calculated with the ZJW-potential are definitely too low; the values for \( C_{11} \) (110 GPa) and \( C_{12} \) (100 GPa) even lay below the high-temperature elastic moduli determined experimentally (154 GPa and 122 GPa). Moreover, the stiffness difference \( C_{11} – C_{12} \), which equals the second eigenvalue of the stiffness tensor of a cubic lattice (Turteltaub and Suiker, 2005), is only 10 GPa for this potential, indicating that the fcc lattice is close to mechanical instability. The experimental coefficient of thermal expansion, obtained from extrapolating material data from the stable, high-temperature (as it indeed should do). Note that the computational value of the coefficient of thermal expansion of fcc is only with the JO-potential, since for the other two interatomic potentials the fcc lattice system behaved unstable at room temperature (as it indeed should do). Note that the computational value of the coefficient of thermal expansion of fcc is only about 20% of the experimental value.

The ab initio value for the energy difference, \( \Delta E_c = -0.06 \text{ eV/atom} \), approaches that of the LBKC-potential \((-0.07 \text{ eV/atom})\), while the JO-potential \((-0.03 \text{ eV/atom})\) and the ZJW-potential \((-0.09 \text{ eV/atom})\), respectively, significantly underestimate and overestimate this value. The relatively low and high contributions of \( \Delta E_c \) to the transformation driving force for, respectively, the JO- and ZJW-potentials, partly explains why the JO-potential leads to a complete transformation only in the case of an fcc-bcc system with free lateral boundary conditions, whereas the ZJW-potential leads to a spontaneous transformation for all lattice systems considered, see Fig. 2. Remarkably, for all interatomic potentials the volumetric ratio \( V_{bcc}/V_{fcc} \) is smaller than one – although for the LBKC-potential it is very close to one –, indicating a volume decrease under transformation, which is in contrast to the volume increases of 1.035 and 1.077 observed experimentally and computed with ab initio simulations, respectively.

In summary, from the above comparison it may be concluded that the material data calculated with the LBKC-potential has the closest agreement with the experimental data. The JO-potential seems to underestimate the transformation driving force, as indicated by the relatively low value of the cohesive energy difference \( \Delta E_c \). Conversely, the ZJW-potential appears to overestimate the transformation driving force; this is suggested by a low stiffness difference \( C_{11} – C_{12} \), as a result of which mechanical instability is close at hand, and by the relatively large value of \( \Delta E_c \). In addition, the values for the elastic moduli of the fcc phase are unrealistically low for this interatomic potential.

5. Concluding remarks

The elaborative MD study performed in this communication has provided a number of novel insights on the nucleation, morphology and kinetics of displacive phase transformation in iron, which are summarised below.

(i) The phase transformation processes studied in the present communication are of a displacive nature. This has been confirmed by computing the effective velocity of the fcc-bcc interface in typical lattice systems, which, for all interatomic potentials examined, at the simulated temperature of 810 K appears to be relatively close to, but smaller than the (bulk) shear wave velocity in iron. In addition, the relative displacements of almost all atoms in the lattice system were below the interatomic distance in the bcc crystal. Similar transformation velocities for other MD models of iron were reported in Bos et al. (2006).

(ii) The transformation times of the lattice structures analysed in the present study vary substantially, and can be classified by introducing 3 categories, i.e., “fast-transforming systems” (spontaneous transformation in a single step), “slowly-transforming systems” (partial or full transformation in multiple steps), and “non-transforming systems” (transformation remains absent), see Section 2.2 for a more detailed specification of these categories. These transformation categories are characterised by geometrical and physical features of the atomic sample, see points (v)-(x) below, as well as by the choice and calibration procedure of the interatomic potential, see point (iii) below.

(iii) The transformation behaviour of a lattice system strongly depends on the choice of the interatomic potential. The importance of this result, which typically is underestimated or ignored in MD studies performed with one interatomic potential, confirms comparable findings from the MD study of Müller et al., 2007 on 5 other interatomic potentials for iron. The present study shows that the sensitivity on the interatomic potential is reflected by the accuracy at which the potential is able to describe the material properties of the (unstable/metastable) fcc phase after being calibrated to properties of the (stable) bcc phase. A comparison with experimental data has demonstrated that for the JO-potential and ZJW-potential the material properties of the fcc phase are represented somewhat inaccurately, which leads to, respectively, an underestimation and an overestimation of the effective transformation driving force of iron (as reflected by the values of \( \Delta E_c \) in Table 6). This behaviour is indeed confirmed by the present MD simulations, which show that the JO- and ZJW-potentials may be associated to, respectively, slowly- (or non-) transforming systems (characteristic of a low transformation driving force) and fast-transforming systems (characteristic of a high transformation driving force), see Table 2. For the LBKC-potential the properties of the fcc phase are represented most accurately, resulting both in fast-transforming systems (under free BC) and slowly-transforming systems (under periodic BC). The above trend in transformation behaviour is also supported by the value of the activation energy \( \Delta G^\ddagger \) (or energy barrier) computed during transformation growth, which appears to be rather low for the ZJW-potential, moderate for the LBKC-potential, and relatively high for the JO-potential, see Table 4. Clearly, a strong dependency of the phase transformation behaviour on the choice of the interatomic potential generally requires a careful consideration and understanding of the characteristics of candidate potentials in order to
perform realistic MD simulations. In specific, special attention needs to be given to the calibration of material data of both the stable bcc phase and the metastable fcc phase, instead of - as usually occurs - the stable bcc phase only.

(iv) For all three interatomic potentials analysed the absolute value of the transformation barrier $\Delta G^\circ$ is significantly lower than that of the transformation driving force $\Delta G$, see Table 4. A similar result was found in the comparison study of Müller et al. (2007) on 5 other interatomic potentials, where the lattice configurations were different from those examined in the present study.

(v) The transformation time under free lateral boundary conditions is smaller than under periodic lateral boundary conditions as a result of the constraining effect caused by the periodicity. The phenomenon of free surfaces facilitating the transformation process has been reported previously in other MD studies for iron (Bos et al., 2006; Urbassek and Sandoval, 2012).

(vi) In fast-transforming systems the nucleation of bcc iron occurs (much) more homogeneously across the sample than in slowly-transforming systems.

(vii) In fast-transforming systems the bcc product phase at completion of transformation initially is polycrystalline, but, as a result of a subsequent recrystallisation process, turns into a monocrystalline phase. The displacements of the atoms relative to their neighbours increase substantially during recrystallisation; typical simulations have shown that about 30% of the atoms experience an increase in displacement between 1 and 5 times the interatomic distance of bcc iron, thus reflecting the development of a substantial amount of dislocation slip. The family of crystal planes of the final monocrystalline phase is identical for fcc-only and fcc-bcc samples, see Table 2. Conversely, in slowly-transforming systems the bcc product phase at completion of transformation is immediately monocrystalline (i.e., no recrystallisation occurs), where the crystal planes may be different for fcc-only and fcc-bcc samples, see Table 2.

(viii) The presence of an fcc-bcc grain boundary promotes the nucleation of bcc iron (compare Fig. 2a and b), resulting in a heterogeneous transformation pattern, see Fig. 6a for example. This phenomenon has also been reported in other MD studies (Urbassek and Sandoval, 2012). Conversely, in an fcc-only sample the nucleation process occurs homogeneously from numerous sites within the sample, see Fig. 6b for example.

(ix) The transformation time of slowly-transforming systems is relatively sensitive to a change in initial conditions. This has been demonstrated by varying, among other parameters, the initial atom velocities of a lattice structure for 10 simulations, using the same Maxwell–Boltzmann distribution. The crystal planes characterising the final bcc product phase may also vary under a change in initial conditions, see Fig. 11a. The effect by the initial conditions on the shape of the specific transformation evolution curve, however, is generally small.

(x) For slowly-transforming systems the mean value and standard deviation of the transformation time depend significantly on the initial lattice incoherence of the fcc-bcc grain boundary. There also appears to be a strong dependency on the presence of vacancies at the initial fcc-bcc interface, where an increasing number of vacancies (and thus an increase in the total vacancy formation energy) gives rise to a larger mean value and standard deviation of the transformation time.

As a final note, it is mentioned that a thorough generalisation of the present MD results would require the examination of several more aspects than those addressed in this communication, such as the effect of temperature, sample shape, applied stress, interface orientation, dislocations, etc. With this list of topics for future research the current investigation may not be considered as complete; it merely serves as a step forward.

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Appendix A. Review of interatomic potentials

The interatomic potential energy $V$ of a system of atoms follows from the interaction between atom $i$ and the other atoms $j$, i.e.,

$$V = \frac{1}{2} \sum_{i,j \in \Psi} \phi(r_{ij}) + \sum_i F(\rho_i) \quad \text{with} \quad \rho_i = \sum_{j \in \Psi} f(r_{ij}).$$

(A.1)

The above expression shows that the interatomic potential is dependent of three functions, which are (i) the pair potential $\phi(r_{ij})$ reflecting the two-body interaction between atoms $i$ and $j$ at an interatomic distance $r_{ij}$, (ii) the electron charge density $\rho_i$ (which in Eq. (A.1) has the form specific for an EAM potential) and (iii) the embedding energy $F(\rho_i)$, which is the energy required for placing atom $i$ into a site with a specific electronic charge density $\rho_i$. The electron charge density is composed of contributions of the charge density $f(r_{ij})$ of atoms $j$ located at distance $r_{ij}$ from atom $i$. For practical purposes, the maximal distance $r_{ij}$ used in Eq. (A.1) is bounded by a cut-off value, see also Table 6. The EAM potentials considered in the present study are the Johnson–Oh (JO) potential (Johnson and Oh, 1989) and the Zhou–Johnson–Wadley (ZJW) potential (Zhou et al., 2004), and the MEAM potential considered is the Lee–Baskes–Kim–Cho (LBKC) potential (Lee et al., 2001). These three interatomic potentials are characterised by different levels of refinement; for clarity reasons, the main characteristics of each potential are summarised below.
A.1. Johnson–Oh (JO) potential

The pair potential used in the JO-potential is characterised by the cubic relation

$$\phi(r) = K_3 \left( \frac{r}{r_e} - 1 \right)^3 + K_2 \left( \frac{r}{r_e} - 1 \right)^2 + K_1 \left( \frac{r}{r_e} - 1 \right) + K_0.$$  \hspace{1cm} (A.2)

with $r$ the interatomic distance, $r_e$ the nearest-neighbour distance in the bcc crystal at equilibrium at 0 K, and $K_0$, $K_1$, $K_2$ and $K_3$ the potential parameters, see Johnson and Oh (1989) for more details.

The electron density contribution is expressed as

$$f(r) = f_e \left( \frac{r}{r_e} \right)^m,$$ \hspace{1cm} (A.3)

in which $f_e$ is a constant that for a mono-atomic potential is independent of the type of material considered, and the power $m$ is generally set equal to 6 (Johnson and Oh, 1989).

The embedding energy has the form

$$F(r) = F_e \left[ \ln \left( \frac{\rho}{\rho_e} \right) \right]^{n} + \left( E_c - E_{\text{rel}}^{\text{V}} \right),$$ \hspace{1cm} (A.4)

with $\rho_e$ the electron density of the bcc equilibrium crystal (i.e., at 0 K), $E_c$ the cohesive energy, $E_{\text{rel}}^{\text{V}}$ the unrelaxed vacancy formation energy and $n$ a parameter that is determined by other input data, see Johnson and Oh (1989) for more details.

A.2. Zhou–Johnson–Wadley (ZJW) potential

The ZJW-potential has been designed for describing 16 different metallic elements and their alloys, including fcc, bcc and hexagonal close-packed (hcp) elements (Zhou et al., 2004). Its pair potential is given by the difference between a repulsive term and an attractive term, i.e.,

$$\phi(r) = \frac{A \exp[-\alpha(r/r_e - 1)]}{1 + (r/r_e - \kappa)^{20}} - \frac{B \exp[-\beta(r/r_e - 1)]}{1 + (r/r_e - \lambda)^{20}},$$ \hspace{1cm} (A.5)

where $A$, $B$, $\alpha$ and $\beta$ are calibration parameters, and $\lambda$ and $\kappa$ are the two parameters that determine the cut-off of the potential.

The electron density function has a similar form as the attractive term in the above pair potential (with the same values for $\beta$ and $\lambda$), i.e.,

$$f(r) = f_e \exp[-\beta(r/r_e - 1)] \frac{1 + (r/r_e - \lambda)^{20}}{1 + (r/r_e - \lambda)^{20}},$$ \hspace{1cm} (A.6)

with $f_e$ a fitting parameter, as in Eq. (A.3).

In the formulation of the embedding energy, three different electron density ranges are distinguished, where the values and slopes at the transition points between the ranges need to match. The three functions describing the embedding energy are

$$F_r = \sum_{k=0}^{3} F_{nk} \left( \frac{\rho}{\rho_n} - 1 \right)^k \quad \text{for} \quad \rho_n < \rho \quad \text{with} \quad \rho_n = 0.85 \rho_e,$$

$$F_r = \sum_{k=0}^{3} F_k \left( \frac{\rho}{\rho_e} - 1 \right)^k \quad \text{for} \quad \rho_n < \rho < \rho_0 \quad \text{with} \quad \rho_0 = 1.15 \rho_e,$$

$$F_r = F_e \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right) \right]^{n} \quad \text{for} \quad \rho_0 < \rho,$$

where $F_{nk}$, $F_k$, $F_e$ and $n$ are calibration parameters. For iron, the electron density $\rho_e$ equals the electron density $\rho_e$ of the equilibrium crystal (Zhou et al., 2004), under which circumstances the high-$\rho$ part of the embedding energy, Eq. (A.7), obtains the same form as the embedding energy for the JO-potential, Eq. (A.4).

A.3. Lee–Baskes–Kim–Cho (LBKC) potential

The LBKC-potential is a Modified Embedded Atom Method (MEAM) potential, which, in principle, is suitable for simulating metallic, semiconductor, metalloid and gaseous elements (Baskes, 1992). The pair potential $\phi$ in the MEAM potential has a form that takes into account the first and second neighbour shells in the bcc crystal and enforces the bcc crystal to obey the zero-temperature universal equation of state $E^u$, see Rose et al. (1984) for more details. This implies that
the pair potential is constructed in the following way (Baskes, 1997):

\[
\phi(r) = \sum_{n=0}^{\infty} (-1)^{n} \left( \frac{Z_{i} S}{Z} \right)^{n} \psi(a^n r) \\
\text{with } \psi(a^n r) = \frac{2}{Z_i} [E_i(a^n r) - F_{ref}(r_{int}(a^n r))].
\]

Here, \( r \) is the interatomic distance, \( S \) is the angular screening factor on the second nearest-neighbour interactions, \( Z_1 \) and \( Z_2 \) are the number of atoms in the first and second neighbour shells (for bcc: 8 and 6, respectively), \( a \) is the ratio between the second and first neighbour shell distances (for bcc: \( a = \sqrt{3/4} \)), \( E^i \) is the universal equation of state, \( n \) is a summation index, and \( \rho_{ref} \) is the electron density at an atomic site of the reference crystal (here: bcc). In the function \( \psi \) the distance \( r \) expresses the nearest neighbour distance in the reference crystal (Baskes, 1997).

For an MEAM-potential the angles between the interatomic bonding vectors play an additional role to the lengths of the interatomic bonding vectors, so that the background electron density at atom \( i \) is determined in a more elaborative way than in Eq. (A.1), i.e.,

\[
\rho_i = \frac{2 \rho_{i}^{(0)}}{1 + \exp(-F_i)} \quad \text{with} \quad F_i = \sum_{l=1}^{3} t^{(l)} \left( \frac{\rho_{i}^{(l)}}{\rho_{ref}^{(l)}} \right)^{2}.
\]

The angular contributions that have modified the EAM formalism into an MEAM formalism are the quantities indicated by a subscript \( l \in \{1, 2, 3\} \). The spherical electron density \( \rho_{i}^{(0)} \) is determined in a similar fashion as \( \rho_i \) in Eq. (A.1), with the exception that the angular screening \( S \) needs to be included for atoms \( j \) that lie in the second neighbour shell of atom \( i \), see Baskes (1997) for more details. The angular electron densities \( \rho_{i}^{(l)} \) with \( l \in \{1, 2, 3\} \) are expressed in terms of triplet angles and interatomic distances, see Lee et al. (2001) for the specific forms of \( \rho_{i}^{(0)} \) and \( \rho_{i}^{(l)} \). Furthermore, the weight factors \( t^{(l)} \) are used for calibrating the model.

The embedding function has the form

\[
F(\rho) = C \cdot E_{c} \cdot \left( \frac{\rho}{\rho_e} \right)^{l} \ln \left( \frac{\rho}{\rho_e} \right)
\]

where \( C \) is a fitting parameter, \( E_{c} \) is the cohesive energy, \( \rho \) is the background electron density, and \( \rho_{e} \) is the electron density of the equilibrium crystal.

Appendix B. Algorithms for identifying the crystal type and the bcc crystal planes

In order to quantitatively determine the short-range crystalline environment at an atom position within an arbitrary MD configuration, for each atom \( i \) two sets of diagnostic numbers are computed. The first set is composed of six diagnostic numbers, \( Q_{l} \), with \( l \in \{2, 4, 6, 8, 10, 12\} \), which are used for determining the short-range crystal type of atom \( i \), and are defined by

\[
Q_{l} = \left\{ \sum_{j=1}^{Z_i} \sum_{k=1}^{Z_i} P^{(l)}(\cos \theta_{ijk}) \right\}^{1/2}.
\]

Here, \( Z_i \) is the number of neighbouring atoms of atom \( i \), \( P^{(l)} \) is the Legendre polynomial of order \( l \), and \( \theta_{ijk} \) is the angle between line segments \( ij \) and \( ik \) that connect atom \( i \) with neighbouring atoms \( j \) and \( k \), respectively. Note that the two summations in Eq. (B.1) run over all neighbouring atoms \( Z_i \) of atom \( i \). The numbers \( Q_{l} \) are rotationally invariant, i.e., they are independent of the spatial orientation of the crystallite. The second set contains 27 diagnostic numbers, \( q_{l}^{m} \), with \( l \in \{2, 4, 6\} \) and \( m = -l, -l+1, \ldots, -1, 1, l \), which determine the crystal plane of atom \( i \) (measured along the global \( f_{1} \)-direction depicted in Fig. 1), and are defined by

\[
q_{l}^{m} = \left( \frac{4 \pi}{2l+1} \right)^{1/2} \left\{ \sum_{j=1}^{Z_i} |Y_{l}^{m}(\theta_{ij}, \phi_{ij})| \right\}.
\]

In this expression \( Y_{l}^{m} \) is a spherical harmonic function of degree \( l \), with the integers \( l \) and \( m \) as defined above, and \( \theta_{ij} \) and \( \phi_{ij} \) are the polar and azimuthal angle, respectively, measured between the line segment \( ij \) (connecting atom \( i \) with a neighbouring atom \( j \)) and the global \( f_{1} \)-direction. For completeness, it is noted that the two diagnostic numbers are related as

\[
\sum_{m=-l}^{l} (q_{l}^{m})^2 = (Q_{l})^2.
\]

In order to determine the short-range crystal type of atom \( i \), the root mean square (rms) difference between the six numbers \( Q_{l} \) and the corresponding six numbers \( Q_{l,bcc} \) is calculated, where the latter six numbers are the numerical values for atom \( i \) in an ideal bcc nearest-neighbour environment. Denoting this rms difference as \( \Delta Q_{l,bcc} \), in the same fashion the rms differences \( \Delta Q_{l,fcc}, \Delta Q_{l,hcp}, \Delta Q_{l,dcc}, \) and \( \Delta Q_{l,ico} \) can be computed for ideal fcc, hexagonal close-packed (hcp), diamond cubic (dc) and icosahedral (ico) nearest-neighbour configurations. The smallest of these five rms differences is considered to be
the decisive indicator of the short-range crystal type of atom \( i \), but only if the smallest rms difference is less than 0.11. If it is greater than 0.11, the crystal type of atom \( i \) is considered as “unclassified”.

For determining the orientation of the crystallographic plane of atom \( i \) with respect to the \( f_1 \)-axis, the rms difference between the 27 numbers \( \Delta Q_{400} \) and the corresponding 27 numbers \( \Delta Q_{400} \) is calculated, with the latter 27 numbers being the numerical values for atom \( i \) in a \{400\} plane of a perfect bcc crystal. The direction of the plane normal is chosen here along the \( f_1 \)-axis, and the normalisation of the \{ HKL \} crystal planes is such that \( H = 4 \) and \( H \leq L < K \). This specific choice of normalisation also imposes the angular resolution at which the crystal orientations are computed. The rms difference obtained with this procedure is denoted as \( \Delta Q_{400} \), where a \{400\} crystal essentially is equivalent to a \{100\} crystal. In the same way, for atom \( i \) the rms differences for each of the bcc crystals \{410\}, \{420\}, \{430\}, \{440\}, \{411\}, \ldots, \{444\} are calculated. The smallest of these 15 rms differences is considered to be the decisive indicator of the bcc crystal plane in which atom \( i \) lies. Note that the bcc crystal plane is computed for each atom in the configuration, even if the short-range crystal type of an atom is not bcc.

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