Atomistic modelling of the Shape Memory Effect

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Abstract

This paper reviews the status of molecular dynamics as a method in describing solid-solid phase transitions, and its relationship to continuum approaches. Simulation work done in NiTi and Zr using first principles and semi-empirical potentials is presented. This shows failures of extending equilibrium thermodynamics to the nanoscale, and the crucial importance of system-specific details to the dynamics of martensite formation. The inconsistency between experimental and theoretical crystal structures in NiTi is described, together with its possible resolution in terms of nanoscale effects.

Introduction

This paper reviews work done on atomistic modelling of martensitic phase transitions, and discusses the unresolved issues in linking various methods of modelling solid-solid phase transitions. In addition to discussing phase transitions in NiTi and Zr, following the spirit of the meeting, I attempt to review and highlight what is not widely known or properly appreciated. My benchmark for "what is known" is primarily based on actual discussions with other scientists, regardless of whether it has appeared in the literature.

The molecular dynamics method is in principle the most versatile way of describing solid-solid phase transitions. The crystal and interfacial structures arise automatically from the interatomic potential, as are the long range strain effects and there is no need for the implicit assumptions about microscopic detail and symmetry entailed in continuum methods. In particular, thermodynamics emerges from molecular dynamics rather than being an input, so all the fluctuations are incorporated properly.

The downside of molecular dynamics is twofold - the models for interatomic forces are unreliable and the timestep is very short because it is set by the phonon vibrational frequencies which typically not relevant to nucleation and diffusive processes.

It may appear that methods which access longer timescales and larger systems, such as kinetic monte carlo or phase fields are more useful, however this appearance is misleading. These methods have conspicuous success in certain systems where their assumptions are valid, but cannot be applied in general.

Thus, molecular dynamics is an essential part of any attempt to model real materials. In this paper we discuss a number of issues and questions which have arisen from our work in molecular dynamics, but which tend to be ignored or glossed over in other techniques. Along the way, I discuss a few points which appear to have been ignored in much of the literature, highlight some of the current unresolved issues and include the consensus of many discussions at the meeting in Phoenix.
Throughout, we discuss only structural transitions, assuming the chemical composition to be constant. The transitions may then be driven either by stress or temperature.

Complete atomistic modelling of the shape memory effect has not yet been done. It has been delayed primarily by the lack of appropriate potentials for the interesting materials such as NiTi. It is likely that some information about the mechanisms could be obtained for Parrinello-Rahman dynamics with very simple potentials which describe the B2-B19 phase transition on cooling, however efforts to date has concentrated on the B2-B19′ transition exhibited by real shape memory alloys, such as NiTi, and hcp-bcc in elements such as Zr and Ti, which do not exhibit the shape memory alloy.

The theory of the shape memory effect is straightforward: the material undergoes a martensitic transition on cooling to a lower symmetry structure, in which there is a one to one correspondence between atoms in each phase. The set of lower symmetry structures which preserve this unique relationship to the austenite is referred to as the Eriksen-Pitteri neighbourhood (EPN) of the austenite. Deformation of the martensite occurs by twin boundary motion, again preserving the EPN. The standard theory for shape memory alloys required that at no point in the transformation or deformation of the structure do the atoms leave this EPN. A minimum constraint here is that the transition is displacive, not diffusive.[15]

There is also a two-way shape memory effect, in which the high-symmetry austenite phase stores a memory of the low-symmetry martensite phase. This effect is not usually so pronounced, and cannot be explained in terms of EPN - a high symmetry phase cannot lie in the EPN of the low symmetry one.

Applicability of Thermodynamics and Statistical Mechanics

Avogadro’s is one of the larger numbers, but it isn’t always infinite

Thermodynamics is a continuum limit approximation to statistical mechanics. Statistical mechanics is a probabilistic approximation to the chaotic dynamics of particles. At base, everything is made of atoms and electrons.

Gibbs’ free energy is thus an emergent property of particle dynamics. In bulk materials, it is an exceptionally good one - when averaging over say 1022 atoms the statistical errors are around 10-11, so for any practical purpose we can treat thermodynamics as an exact theory for bulk phases at equilibrium. The notion of a driving force based on a differential of a free energy is less well motivated since the existence of a gradient means that the system is out of equilibrium. Strictly speaking, the Maxwell-Boltzmann distribution underlying statistical mechanics then does not apply, and so nor does equilibrium thermodynamics. Again, we are saved by a division of time and lengthscales. The entropic contribution in crystalline solids is contained in phonon vibrations, whose frequency is many orders of magnitude greater than the typical timescales of a phase transition. Similarly, the typical lengthscales involved in microstructures are several orders of magnitude larger than interatomic spacings. Thus we can usually regard local regions as being at equilibrium because a sufficiently large number of atoms are vibrating for a sufficiently long time for the approximations underlying thermodynamics to be valid.

The movement of interfaces driven by a free energy difference is similarly ill-defined. One can envisage two limits, in one the interface moves freely back and forth on a timescale much faster than its net drift. This is a promising case for using free energy differences, since the system is sampling both phases efficiently. In other cases the interface is sessile - unable to move thermally, and tends to advance by a stick-slip process. In neither case, however, is the rate of motion of the interface given by the free energy gradient - one has to introduce
some arbitrary timescale. In simple cases, where only a few types of interfaces are present, there may be only one timescale, so the dynamics of the transition can be captured correctly. In more complex cases where some boundaries are sessile and others mobile, the transition kinetics and resultant microstructure will be primarily determined by boundary mobility rather than bulk free energies.

In continuum modelling of martensites, the interface sets an energy, and hence length, scale. In real materials the interfacial energy varies strongly with angle, and has cusps at special values (so called low sigma boundaries). Normally they are atomically sharp, which presents a further challenge.

Thus methods based directly on thermodynamics will become a problem in very fast transitions (e.g. shock waves on martensites) or extremely fine microstructures (the canonical example being a glass transition\[1\]).

**Invariant Plane Interfaces**

The interfacial plane between two solid phases of the same composition, with one having transformed from the other, may be uniquely determined if the transition mechanism is known. Where the transition mechanism is assumed to be purely displacive, the interfacial plane is purely determined by crystalline geometry - the invariant plane. This is defined by taking a slice through the unit cell of each crystal such that the two faces are identical in area and shape.

The requirement for the transformation to occur on an invariant plane has some microstructural consequences: any volume change must be absorbed by contraction of the cell normal to the interface plane, this generates a strain energy around a nucleating region: hence growth in this direction is hindered and martensite typically grows as a plate. In general, the invariant plane is at an arbitrary angle to the crystallographic directions.

The invariant plane should not be confused with the transformation mechanism. This determines how the atoms get from their positions in one crystal structure to their positions in the other. After the material is fully transformed, it is the transformation mechanism which determines the orientation of one grain to another.

**Viewing the microstructure**

It is essential for analysis of the MD that some we have some way of assigning individual atoms to particular twins or crystal structures. This process is rather arbitrary, but a good method is to use the distribution of cosines of angles to nearest neighbours to distinguish structures. This allows one to determine fcc, hcp and bcc regions of a crystal, and at the same time determine the orientation of the structures.\[9\]

**Atomistic simulation of martensite - zirconium**

Atomistic simulation gives the possibility of studying martensitic phase transitions without any of the assumptions required in the continuum approaches. The interatomic potential used determines whether the simulation reflects any particular material, however the topological and geometric features arising will be generic. From a number of simulations carried out on zirconium, the detailed structure of the twin boundary emerges as the crucial feature for the dynamics. Details of boundary structure is generally ignored in the continuum or phase field approaches, at best boundaries are assumed to have some constant energy or behaviour irrespective of orientation. However, for shape memory effect the boundary must be capable
Table 1: Energy function and parameters for zirconium potential where \( H(x) \) is the Heaviside step function, \( r_{ij} \) is the separation between atoms \( i \) and \( j \)

of moving without leaving the EPN the austenite. This places constraints on the mechanism by which the boundary can move.

**Pretransition phenomena and intermediate phases**

In transitions from bcc via the Nishiyama-Wassermann mechanism the \((110)_{bcc}\) planes convert to basal \((0001)_{hcp}\) planes in hcp. Different hcp variants arise from different original sets of \((110)_{bcc}\). This means that the variants must be rotated with respect to each other by 30 or 60 degrees. If one investigates the high temperature crystal structure of Zr on cooling from the bcc phase prior to the transition, the structure is found to fluctuate\[10\], a snapshot being shown in fig1.

In this figure we see the effects of stress-induced preferential nucleation. In the bcc-hcp transformation, the strain along the \((111)_{bcc}\) direction (a line of near neighbours) is small (perpendicular to the plane) thus once the materials begins to transform to an hcp variant, and large stress filed is developed in the plane, which induces a transformation into the other two variants which share the particular \((111)_{bcc}\) plane. Thus the stress nucleates cp basal planes from the \((01\overline{1})_{bcc}, (1\overline{1}0)_{bcc}\) and \((10\overline{1})_{bcc}\) planes. This rapid nucleation gives rise to a columnar microstructure fig1.

However, these variants cannot tile a plane with all interfaces being 60 degrees. In this nanostructured material, the large boundary energy of the 30 degree twin is sufficient to prevent a microstructure comprising only these three variants. What appears is a region of fcc, stabilised by the low energy of the interface between it and the adjacent hcp (the interface is simply a basal stacking).

The existence of metastable crystal phases close to the martensitic transition is reported in many systems, notably the R phase in NiTi. They are usually referred to as “intermediate” phases, often with the implication that they are thermodynamically stable over a small region. This simulations suggests another picture, the “intermediate” phases (R in NiTi, fcc here) actually are stabilised at the nanoscale both by the strain field of the precritical hcp phase nuclei and their very low interfacial energy. As the structure coarsens, they become metastable but their elimination may be kinetically hindered. The existence of such metastable phases could play a important role in compensating the strain field, and delaying the full transformation to martensite.
Twins and intervariant boundaries

The angle between martensitic twins formed by cooling from an austenite is fully determined by crystal structure and transition mechanism. There is no reason for it to be a low energy boundary. In the case of zirconium it turns out that the 30 degree boundary is very high energy and is not seen in the simulations. This restricts the variants which can be observed.

It is well established that the strain minimising microstructure is a laminate of twins, and the boundary energy difference means they are always 60 degree tilt this is clearly seen in the simulations. A 60° tilt is close to the a 61.5° symmetric tilt boundary of the (10\overline{1}1) twin, a cusp in the energy vs angle graph and with low boundary energy (0.58mJm^{-2} according to this potential). For an isolated twin boundary, the discrepancy in angle is made up by twinning dislocations, however, when the twins are small these dissociate into partial twinning dislocations with a basal stacking fault extending through the twins[2].

The structure is shown in Figure 2. The density of twin boundary partial dislocations is determined by crystal geometry (in particular, the c/a ratio of hcp zirconium). Thus to simulate a real material, using a potential which reproduces the lattice parameters accurately is crucial.

Twin boundary motion

As explained elsewhere in these proceedings[14] a twin boundary dislocation is free to glide in the twin only if its Burgers vector lies in the twin plane. This is not the case for the twin boundary partial dislocations in Figure 2. Thus the twin boundary cannot move in a diffusionless manner by motion of these twin boundary partial dislocations.

The boundary does move, however, in response to external stress[11]. The role of twin boundary partial dislocations is to act as stress concentrators which cause nucleation of other twin boundary dislocation which are mobile in the boundary. The mechanism is similar to that observed for the interaction of a crystal dislocation with a twin boundary [13]. In the absence of the twin boundary partial dislocations, there is no source for mobile dislocations and so a perfect (10\overline{1}1) twin cannot move[11].

NiTi

NiTi is the canonical example of a shape memory alloy. Ideally one would like to do calculations with a potential for NiTi, which described the high-T B2 phase, the low-T B19' phase and the metastable R phase. In this section we discuss the problems encountered in generating such a potential.

The B2-B19' phase transition observed in NiTi can be simply understood in terms of the Nishiyama-Wassermann-type mechanism observed in zirconium (see fig.3. If one ignores the difference between Ni and Ti atoms, B2 is simply bcc, the different species do not disrupt the cubic symmetry. B19 has the same symmetry as hcp, except that the two species break hexagonal symmetry making the structure to tetragonal. B19' is a small distortion from B19. We might thus hope that similar potentials to those used in zirconium would work for NiTi.

Interatomic potentials for NiTi

Experimental data for stress-free single crystal NiTi martensite is very hard to obtain. Crystallography has been done on samples prepared by strain-induced transformation above the
martensite start temperature, followed by quenching to ambient condition[12]. It is unclear whether such crystals are strain-free. In the absence of detailed calorimetry for the phase transition energies, the standard way to proceed in making potentials is to generate a database of ab initio energies. There are many free parameters in the B19’ structure, and great care has to be taken to ensure the true minimum is found[8]. When this is done, it turns out that the DFT minimum energy structure is different from that found in the experiment - the $\gamma$ angle in B19' is 107$^\circ$[8] rather than 98 degrees[12]. Moreover, 107 degrees is exactly the right angle to create a doubled unit cell with tetragonal symmetry - the B33 structure.

This conflict between DFT and experimental energetics makes it difficult to attempt to fit a potential to NiTi combining data from each. This explains why little progress has been made on the problem to date.

Ab initio calculations in NiTi

One way to avoid the problem with lack of accurate potentials is to use ab initio molecular dynamics DFT calculations for direct calculations of the microstructure. We have carried out density functional calculations based on pseudopotentials and plane waves using the VASP code, of up to 100 atoms in the B2 phase, cooling using a Nose thermostat from 400-200K, then quenching to 0K for analysis. Two supercell geometries were tried, in one the cell was orientated along (100), (011), (011) requiring 64 atoms, while in the other (011), (111) (211) with 96 atoms was used. The classical work with zirconium indicated that this may prove too small, and certainly finite size effect will be significant, and the 96 atom cell attempted to ease that problem being only 5Å thick in the z-direction.

On cooling the structures dropped out of the bcc phases. We used the angle based analysis[6] to assign hcp, fcc or bcc crystal structures. For a displacive transition, these would pick up local B19, L1$_0$ or B2 alloy structures respectively.

The 64 atom simulation (figure 4) remained almost entirely to a single phase strained bcc structure. The 96 atom cell, despite its high aspect ratio, was also too small to show any significant change from distorted bcc. The fully quenched structure has not gone back to B2: there is some evidence of a transformation towards an L1$_0$ or B19 structure in a few atoms, but the best description of the configuration is as distorted B2.

As with the metastable fcc phase in zirconium, the simulations of NiTi show that nano-sized structures can impose stabilizing strains on the existing structure. Moreover, the formation energy of its boundary may be high enough to alter the stable crystal structure in microstructures at a given lengthscale.

Conclusions

In conclusion, we have shown that in going from the atomistic scale to the continuum in describing martensitic microstructures the following features are important:

- The relative orientation of twins is defined by crystal symmetry, and will not normally coincide with a low energy twin boundary. The twin boundary might be a low-energy boundary with an array of geometrically necessary dislocations, but in general these dislocations will be sessile.

- Some geometrically-allowed boundaries between twins may not appear because of their high energy.
• Sessile twin-boundary dislocations may act as stress concentrators, and hence as sources for mobile dislocations which allow the boundary to advance.

• Nanoscale microstructures may stabilise different crystal structures from the thermodynamic limit, either inhibiting their appearance through the energy cost of twin boundaries, or allowing an altogether different phase with lower interface costs to nucleate.

• Twin boundary energy and mobility varies sharply depending on the boundary orientation. Continuum models need to take this into account.

The effects of nanostructure in stabilizing certain crystal structures outwith their thermodynamic stability ranges offers an resolution to a number of phenomena observed experimentally but ignored in phase-field and similar models. The nanostructure creates a variety of local environments subject to differing inhomogeneous stress whose minimisation calls for a variety of required interfaces. In particular metastable “intermediate” phases may be stabilised by particularly favourable local regions of stress and interface energies low energies. Moreover, the relative stability of austenite and martensite varies in different regions of the crystal depending of the local stress environment. Hence both can coexist at the same macroscopic (i.e. average) conditions of temperature and pressure. This explains at the microscopic level the existence of distinct “martensite start” and “martensite finish” temperatures.

There remains a need to simulate a binary alloy undergoing a B2-B19' transition in order to understand the atomic level behaviour of the shape memory effect. There remains a discrepancy between the theoretical perfect crystal structures for NiTi martensite, and experimental measurement. This discrepancy is serious, in that the theoretical structure does not even lie in the EPN of B2. A resolution is offered that the theoretical structure is very soft in shear[8] and so small internal stresses will recover the experimental value. This offers the possibility that the shape memory effect is in part due to microstructural stress, which offers a mechanism for the two-way effect.

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References

[1] The entropy of a glass remains problematic. In particular, should one include the configurational entropy of all possible glass structures as in the liquid. The argument for doing so is that on glassification the system could choose any such structure - a large phase space volume, however once the glassification process is complete the system is frozen into one small region of phase space, and cannot sample ”equivalent” structures in the way statistical mechanics assumes.

[2] The zirconium potential used in this work gives far too low a stacking fault energy, so this dissociation may not occur in real zirconium.

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[15] There is some confusion as to the precise meaning of displacive and diffusive at the atomic level. Here, I take displacive to mean that each atom in one structure can be mapped to a particular site in the other. This does not preclude transformations involving shuffles, or those proceeding by nucleation and growth.
Figure 1: (left) Snapshot of a slice through supercooled, dynamically stabilised bcc zirconium, showing instantaneous atom positions and allocating local crystal structure (red=hcp, green=fcc, blue=bcc, grey=boundary) according to method of Jones and Ackland[6]. Single lines of green represent stacking faults[4] in the hcp, e.g. ABABCBCB stacking. (right) Schematic representation of this type of structure. Lines show close packed planes viewed end on, which exist in more than one plane in fcc, allowing the stacking to continue unbroken across the interface. None of the arrangements hcp1-3 can replace fcc without introducing a high energy boundary or a variant which spans the simulation (and is therefore subject to large stress.
Figure 2: Structure of the 60 degree twin boundary in zirconium. The position of the twin boundary partial dislocations are made clear by the stacking fault emanating from it (circles: hcp, squares: boundary: crosses stacking fault) Figure created by U.Pinsook
Figure 3: Crystal structures in NiTi, and their relation via the soft-phonon mode transformation mechanism (a) doubled B2 structure oriented along (110) - here and elsewhere the conventional unit cell is shown by shading. (b) B19 structure obtained by tetragonal deformation of B2, plus shuffle of internal coordinates (c) monoclinic distortion of B19 to experimentally reported NiTi B19' martensite structure. (d) increased monoclinic angle to DFT minimum energy structure, B33, with additional tetragonal symmetry as shown.

Figure 4: Local crystal structures in NiTi, derived from cooling ab initio molecular dynamics from 400K to 200K and quenching to 0K. left: 64 atom simulation viewed along (001) right: 96 atom simulation viewed along (111). Blue atoms denote bcc, green fcc, red hcp, grey boundary. In each case the simulation cell is doubled - periodic boundary conditions are not applied in the sample boundary, so the outer two layers of particles are not reliably identified, but every atom in the simulation is correctly identified with all its neighbours in the central region of the figure.