Computing Bifurcation & Stability Properties of Crystals

Ryan S. Elliott†

John A. Shaw* & Nicolas Triantafyllidis*

†Department of Aerospace Engineering & Mechanics
The University of Minnesota

*Department of Aerospace Engineering
The University of Michigan

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Outline

• Introduction & motivation
  – Active materials & Martensitic transformations (MT’s)
  – Shape Memory Alloys (SMA’s)

• Atomistic modeling of MT’s
  – Temperature-dependent atomic potentials
  – Bifurcation & stability investigation of stress-free phases
  – Hysteretic proper MT between cubic $B2$ and orthorhombic $B19$ phases

• Computational challenges
  – Crystal stability
  – Equilibrium path following
  – Behavior near bifurcation points

• Summary & conclusions
Active Materials

- Multi-physics coupling — Crystal structure changes

Magnetostrictive Materials  Magnetic Field  ↔  Mechanical
Ferroelectric Materials  Electric Field  ↔  Mechanical
Shape Memory Alloys  Temperature  ↔  Mechanical

Martensitic Transformations
Materials on the cusp of an instability

Martensite  Austenite
Shape Memory Alloys (SMAs)

Tensile behavior of NiTi
(exhibiting the shape memory effect and pseudo-elasticity)
(J. Shaw 1997)

Materials Research Science and Engineering Center
at the University of Wisconsin - Madison
www.mrsec.wisc.edu/nano
The Crystal Structures of SMAs

- Prevalent austenite and martensite crystals in shape memory alloys

**Objective:** Develop an atomic model to capture *proper* martensitic transformations such as those found in shape memory alloys
Pair-Potential Model

\[ \phi(r; \theta) = A \left\{ \exp \left[ -2B \left( \frac{r}{\hat{r}(\theta)} - 1 \right) \right] - 2 \exp \left[ -B \left( \frac{r}{\hat{r}(\theta)} - 1 \right) \right] \right\} \]

\[ \hat{r}(\theta) = r_0 + r_\theta (\theta - 1) \]

<table>
<thead>
<tr>
<th></th>
<th>( r_0 )</th>
<th>( r_\theta )</th>
<th>( \beta )</th>
<th>( A )</th>
<th>mass</th>
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Multilattice (Cauchy-Born Kinematics)

\[ G_i \text{ – ref. lattice basis} \]
\[ X[\ell] \text{ – unit-cell ref. pos.} \]
\[ X[\ell_\alpha] \text{ – reference pos.} \]
\[ P[\alpha] \text{ – fractional pos.} \]
\[ \alpha = 0, 1, 2, 3 \]
Multilattice (Cauchy-Born Kinematics)

\begin{align*}
\mathbf{G}_i & \quad \text{ref. lattice basis} \\
\mathbf{X}[\ell] & \quad \text{unit-cell ref. pos.} \\
\mathbf{X} \left[ \ell_{\alpha} \right] & \quad \text{reference pos.} \\
\mathbf{P}[\alpha] & \quad \text{fractional pos.} \\
\alpha & = 0, 1, 2, 3
\end{align*}
Multilattice (Cauchy-Born Kinematics)

- $G_i$ – ref. lattice basis
- $X[\ell]$ – unit-cell ref. pos.
- $X[\ell]_\alpha$ – reference pos.
- $P[\alpha]$ – fractional pos.
  $$\alpha = 0, 1, 2, 3$$
- $S[\alpha]$ – sub-lat. ref. shifts
Multilattice (Cauchy-Born Kinematics)

$G_i$ – ref. lattice basis

$X[\ell]$ – unit-cell ref. pos.

$X^{\ell}_{\alpha}$ – reference pos.

$P[\alpha]$ – fractional pos.

\[ \alpha = 0, 1, 2, 3 \]

$S[\alpha]$ – sub-lat. ref. shifts
Multilattice (Cauchy-Born Kinematics)

\[ \mathbf{x}[\ell_\alpha] = \mathbf{F} \cdot (\mathbf{X}[\ell_\alpha] + \mathbf{S}[\alpha]) \]

- \( G_i \) – ref. lattice basis
- \( \mathbf{X}[\ell] \) – unit-cell ref. pos.
- \( \mathbf{X}[\ell_\alpha] \) – reference pos.
- \( \mathbf{P}[\alpha] \) – fractional pos.
  \( \alpha = 0, 1, 2, 3 \)
- \( \mathbf{S}[\alpha] \) – sub-lat. ref. shifts
- \( \mathbf{F} \) – uniform deformation

- \( \mathbf{g}_i \) – current lattice basis
- \( \mathbf{x}[\ell] \) – unit-cell current pos.
- \( \mathbf{x}[\ell_\alpha] \) – current pos.
**Multilattice Model & Stress-free Equilibrium**

$X^{[\ell]}$ — reference position vector of atom $\alpha$ in unit cell $\ell$

$S[\alpha]$ — displacement vector of atom $\alpha$ (sub-lattice)

$\alpha = 0, 1, 2, 3$

- Current position vector (Cauchy-Born kinematics, $\alpha = 0, 1, 2, 3$)

$$x^{[\ell]} = F \cdot (X^{[\ell]} + S[\alpha])$$

- Energy density

$$\tilde{W}(u; \theta) = \frac{1}{2V} \sum_{\alpha'} \sum_{[\ell]} \phi_{\alpha\alpha'} (r^{[\ell \ 0 \ \alpha']} ; \theta)$$

$$u \equiv \{F, S[1], S[2], S[3]\}, \quad r^{[\ell \ \alpha \ \alpha']} = \|x^{[\ell \ \alpha]} - x^{[\ell' \ \alpha']}\|$$
Multilattice Model & Stress-free Equilibrium

- Equilibrium: 15 DOFs — 6 from $U = U^T$ and 9 from $S[\alpha]

\[ \frac{\partial \tilde{W}}{\partial u} = 0 \left\{ \begin{array}{c}
\frac{\partial \tilde{W}}{\partial S[1]} = 0, \\
\frac{\partial \tilde{W}}{\partial S[2]} = 0, \\
\frac{\partial \tilde{W}}{\partial S[3]} = 0.
\end{array} \right. \]

- Stability
  - Cauchy-Born stability (local energy minimizer):

\[ \delta u \frac{\partial^2 \tilde{W}}{\partial u \partial u} \delta u > 0; \quad \delta u = \{ \delta U, \delta S[1], \delta S[2], \delta S[3] \}, \quad \delta U = \delta U^T. \]

  - Phonon stability:

\[ \left( \omega^{(q)}(k) \right)^2 > 0, \quad \forall k, q. \]
- Hysteretic proper Martensitic transformation between $B2$ & $B19$
Transformation Parameters

$B2 \rightarrow B19$

Martensitic Transformation

- Experimental right stretch tensor

\[
\begin{bmatrix}
1.024 & 0.0106 & 0 \\
0.0106 & 1.024 & 0 \\
0 & 0 & 0.9491
\end{bmatrix}
\]

AuCd, \textit{(Chang, Read (1951))}

- Simulated right stretch tensor ($\theta = 1.0$)

\[
\begin{bmatrix}
1.042 & 0.0194 & 0 \\
0.0194 & 1.042 & 0 \\
0 & 0 & 0.9178
\end{bmatrix}
\]

CuAlNi, \textit{(Otsuka, Shimizu (1974))}

\[B19\]

- Simulated right stretch tensor ($\theta = 1.0$)

\[
\begin{bmatrix}
1.045 & 0.0173 & 0 \\
0.0173 & 1.045 & 0 \\
0 & 0 & 0.9224
\end{bmatrix}
\]

NiTi, \textit{(Otsuka et al. (1971))}
Computational Challenges

• Crystal structure stability
  – Robust stability criterion — phonon spectra
  – Efficient numerical evaluation of phonon spectra

• Efficient equilibrium path following
  – Reduced set of equations based on symmetry
  – Pseudo-arc-length method

• Determine behavior near bifurcation points
  – Identify all paths that emerge from a bifurcation point
  – Numerical implementation of asymptotic analysis
    - Projection operators
Direct Computation of Stability

- Compute all eigenvalues of
  \[ K = \frac{\partial^2 \tilde{W}}{\partial \mathbf{u}[^\ell][\alpha] \partial \mathbf{u}[^\ell][\alpha]}, \]  
  \((3MN \times 3MN)\)

  \(M\)—number of atoms per unit cell

  \(N\)—number of unit cells in crystal

\[
\begin{bmatrix}
* & * & * & \cdots \\
* & * & * & \cdots \\
* & * & * & \cdots \\
\vdots & \vdots & \vdots & \ddots \\
\end{bmatrix} \rightarrow \begin{bmatrix}
\lambda_1 \\
\lambda_2 \\
\lambda_3 \\
\vdots \\
\end{bmatrix}
\]

- Methods: SVD, LDU, Cholseky, Jacobi, Householder, etc.

- Time complexity: \(O\left([3MN]^3\right)\). Too slow for large \(N\)
Reduction to Block Diagonal Form

- In $3M \times 3M$ block form

\[
K = \begin{bmatrix}
\vdots \\
(K \begin{bmatrix} n-1 & n-1 \\ \alpha & \beta \end{bmatrix}) & (K \begin{bmatrix} n-1 & n \\ \alpha & \beta \end{bmatrix}) & (K \begin{bmatrix} n-1 & n+1 \\ \alpha & \beta \end{bmatrix}) \\
(K \begin{bmatrix} n & n-1 \\ \alpha & \beta \end{bmatrix}) & (K \begin{bmatrix} n & n \\ \alpha & \beta \end{bmatrix}) & (K \begin{bmatrix} n & n+1 \\ \alpha & \beta \end{bmatrix}) \\
(K \begin{bmatrix} n+1 & n-1 \\ \alpha & \beta \end{bmatrix}) & (K \begin{bmatrix} n+1 & n \\ \alpha & \beta \end{bmatrix}) & (K \begin{bmatrix} n+1 & n+1 \\ \alpha & \beta \end{bmatrix}) \\
\vdots
\end{bmatrix}
\]
Reduction to Block Diagonal Form

- In $3M \times 3M$ block form

$$K = \begin{bmatrix}
\cdots \\
\begin{pmatrix} K & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} & \begin{pmatrix} K & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} & \begin{pmatrix} K & -1 & 1 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} \\
\begin{pmatrix} K^T & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} & \begin{pmatrix} K & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} & \begin{pmatrix} K & -1 & 1 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} \\
\begin{pmatrix} K^T & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} & \begin{pmatrix} K & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} & \begin{pmatrix} K & -1 & 1 \\
0 & 1 & 0 \\
0 & 0 & 0 \\
\end{pmatrix} \\
\cdots 
\end{bmatrix}$$

Translational periodicity (block-circulant matrix)
Reduction to Block Diagonal Form

- In $3M \times 3M$ block form

$$
K = \begin{bmatrix}
\cdots \\
\begin{pmatrix} K & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} K & 0 & 1 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} K & -1 & 1 \\ \alpha & \beta \end{pmatrix} \\
\begin{pmatrix} K^T & 0 & 1 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} K^T & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} K^T & 0 & 1 \\ -1 & \beta \end{pmatrix} \\
\begin{pmatrix} K^T & -1 & 1 \\ \alpha & \beta \end{pmatrix} & \begin{pmatrix} K^T & 0 & 1 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} K^T & 0 & 0 \\ \alpha & \beta \end{pmatrix}
\end{bmatrix}
$$

Translational periodicity (block-circulant matrix)

- block-Fourier transform

$$
\mathcal{K} = \begin{bmatrix}
\cdots \\
\begin{pmatrix} \mathcal{K}^{-1} & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} \mathcal{K}^{-1} & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} \mathcal{K}^{-1} & 0 & 0 \\ \alpha & \beta \end{pmatrix} \\
\begin{pmatrix} \mathcal{K} & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} \mathcal{K} & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} \mathcal{K} & 0 & 0 \\ \alpha & \beta \end{pmatrix} \\
\begin{pmatrix} \mathcal{K} & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} \mathcal{K} & 0 & 0 \\ 0 & \alpha & \beta \end{pmatrix} & \begin{pmatrix} \mathcal{K} & 0 & 0 \\ \alpha & \beta \end{pmatrix}
\end{bmatrix}
$$

- $3M \times 3M$ block diagonal form $\implies$ Time complexity: $O\left([3M]^3N\right)$. 

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Computational Challenges

- Crystal structure stability
  - Robust stability criterion — phonon spectra
  - Efficient numerical evaluation of phonon spectra

- Efficient equilibrium path following
  - Reduced set of equations based on symmetry
  - Pseudo-arc-length method

- Determine behavior near bifurcation points
  - Identify all paths that emerge from a bifurcation point
  - Numerical implementation of asymptotic analysis
    - Projection operators
Following Equilibrium Paths

Solve a *reduced* set of equilibrium equations, e.g.,

- **Cubic Phase**
  
  \[ U_{11} = U_{22} = U_{33} = a, \]
  \[ U_{12} = U_{23} = U_{31} = 0. \]

- **Tetragonal Phase**
  
  \[ U_{33} = c, \quad U_{11} = U_{22} = a, \]
  \[ U_{12} = U_{23} = U_{31} = 0. \]

- **Orthorhombic Phase**
  
  \[ U_{11} = a, \quad U_{22} = b, \quad U_{33} = c, \]
  \[ U_{12} = U_{23} = U_{31} = 0. \]

Advantages:

- Reduce computational effort
- **Eliminate singularities** near bifurcation points
Problem: following an equilibrium path around a turning point

- **Pseudo-arc-length method** (Riks method)
  - known solution $u(\theta_k)$
  - find solution $u(\theta_{k+1})$ a “distance” $\Delta$ away

- Augment equilibrium equations with “distance” constraint

$$\frac{\partial \tilde{W}(u(\theta_{k+1}); \theta_{k+1})}{\partial u} = 0, \quad ||u(\theta_{k+1}) - u(\theta_k)||^2 + (\theta_{k+1} - \theta_k)^2 = \Delta^2$$

- solve for $\theta_{k+1}$ and $u(\theta_{k+1})$ simultaneously

- Also adaptively change $\Delta$ near turning points
Computational Challenges

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Asymptotic Bifurcation Analysis

- At a multiple bifurcation point, \((u_c, \theta_c)\):
  \[
  \frac{\partial^2 \tilde{W}}{\partial u^2} \bigg|_c \text{ is singular with a null space of dimension } H \geq 2.
  \]

- Following Triantafyllidis & Peek (1992), (bifurcation amplitude parameter \(\xi\))

  \[
  \theta(\xi) = \theta_c + \theta_1 \xi + \theta_2 \frac{\xi^2}{2} + O(\xi^3),
  \]
  \[
  u(\xi) = u(\theta(\xi)) + \left( \sum_{I=1}^{H} \alpha_I u^I \right) \xi + \left( \sum_{I,J=1}^{H} \alpha_I \alpha_J u^{IJ} \right) \frac{\xi^2}{2} + O(\xi^3),
  \]

  where \(\left\{ \frac{1}{u}, \ldots, H \right\} u \) is an O.N. basis for the null space of \(\frac{\partial^2 \tilde{W}}{\partial u^2} \bigg|_c\).

Transcritical bifurcation

Symmetric bifurcation
Substitute into equilibrium equations $\frac{\partial \tilde{W}}{\partial u} = 0$, expand, and collect L.O.T.

- For symmetric bifurcation:
  \[
  \left( \frac{\partial^3 \tilde{W}}{\partial u^3} \bigg|_c \right)_{IJKL} \equiv 0
  \]

  \[
  \sum_{J,K,L=1}^H \alpha_J \alpha_K \alpha_L \mathcal{E}_{IJKL} + 3\theta_2 \sum_{J=1}^H \alpha_J \mathcal{E}_{IJ\theta} = 0,
  \]

  \[
  \sum_{I=1}^H (\alpha_I)^2 = 1.
  \]

  \[
  \mathcal{E}_{IJ\theta} \equiv \left( \frac{d}{d\theta} \left( \frac{\partial^2 \tilde{W}(\tilde{u}(\theta); \theta)}{\partial \tilde{u} \partial \tilde{u}} \right) \right) \bigg|_{IJ\tilde{u}},
  \]

  \[
  \mathcal{E}_{IJKL} \equiv \frac{\partial^4 \tilde{W}}{\partial u^4} \bigg|_{IJKL\tilde{u} \tilde{u} \tilde{u} \tilde{u}} + \frac{\partial^3 \tilde{W}}{\partial u^3} \bigg|_{IJ\tilde{u}} \left( JKL \tilde{v} \tilde{u} + KLJ \tilde{v} \tilde{u} + LJK \tilde{v} \tilde{u} \right)
  \]

- Fredholm alternative guarantees a unique $IJ \tilde{v}$
Numerical Asymptotic Bifurcation Analysis

\[ \text{Need} \quad IJ \overline{v} : \quad \frac{\partial^2 \tilde{W}}{\partial u^2} \bigg|_c IJ \overline{v} = - \frac{\partial^3 \tilde{W}}{\partial u^3} \bigg|_c IJ \overline{u}u \]

- Generate an O.N. basis for \( \mathbb{R}^n \) by diagonalizing \( \frac{\partial^2 \tilde{W}}{\partial u^2} \bigg|_c \in \mathbb{R}^n \times \mathbb{R}^n \)

\[ \mathcal{N} = \text{Span} \left\{ \frac{1}{u}, \ldots, H_u \right\}, \quad \mathcal{N}^\perp = \text{Span} \left\{ \frac{1}{v}, \ldots, n-H_v \right\} \]

- Projection operator \([Q_{IJ}] = [I_{Ij}] : \mathbb{R}^n \mapsto \mathcal{N}^\perp\)

\[ Q \frac{\partial^2 \tilde{W}}{\partial u^2} \bigg|_c Q^T Q_{IJ} \overline{v} = -Q \frac{\partial^3 \tilde{W}}{\partial u^3} \bigg|_c IJ \overline{u}u \]

\[ \begin{array}{cc} & \text{non-singular} \\ \end{array} \]

- Solving gives

\[ IJ \overline{v} = -Q^T \left[ Q \frac{\partial^2 \tilde{W}}{\partial u^2} \bigg|_c Q^T \right]^{-1} Q \frac{\partial^3 \tilde{W}}{\partial u^3} \bigg|_c IJ \overline{u}u. \]

\[ \begin{array}{ccc} & n \times (n-H) & (n-H) \times (n-H) & (n-H) \times 1 \\ \end{array} \]

\[ \begin{array}{c} n \times 1 \\ \end{array} \]
Numerical Asymptotic Bifurcation Analysis

- $E_{IJ\theta}$, $\nu$, and $E_{IKKL}$ are obtained numerically
- All bifurcating equilibrium paths are found by solving

$$\sum_{J,K,L=1}^{H} \alpha_J \alpha_K \alpha_L E_{IKKL} + 3 \theta_2 \sum_{J=1}^{H} \alpha_J E_{IJ\theta} = 0, \quad \sum_{I=1}^{H} (\alpha_I)^2 = 1.$$ 

- In general there are $(3^H - 1)/2$ pairs of solutions $(\alpha_I, \theta_2)$ and $(-\alpha_I, \theta_2)$
- Each pair of solutions corresponds to one symmetric equilibrium path

Symmetric bifurcation

Symmetric bifurcation

\begin{align*}
I \\
\uparrow u \\
\theta_2/2 \\
\alpha_I \\
0 u(\theta) \\
\theta \\
\end{align*}
Example of Degree Two Bifurcation

- Bifurcation of degree two \((H = 2)\) at \(B\)
Example of Degree Two Bifurcation

- Bifurcation of degree two \( (H = 2) \) at \( \mathcal{B} \)

- Basis for \( \mathcal{N} \) (translation of certain crystal planes)

\[
\begin{align*}
1\mathbf{u} &= \begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0.6931 & 0 & 0 & 0.7203 & 0 & 0 & 0.0271 & 0
\end{bmatrix}, \\
2\mathbf{u} &= \begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0.0271 & 0 & 0 & 0.7203 & 0 & 0 & 0.6931 & 0
\end{bmatrix}
\end{align*}
\]

- Resulting bifurcation equations \( (\theta_1 = 0) \)

\[
-4849.2(\alpha_1)^3 - 19421(\alpha_1(\alpha_2)^2) + 3\theta_2(0.02425\alpha_1) = 0,
-19421((\alpha_1)^2\alpha_2) - 4849.2(\alpha_2)^3 + 3\theta_2(0.02425\alpha_2) = 0.
\]

- Solutions (four pairs)

\[
\begin{align*}
B19(1) & : \quad \alpha_1 = 1, \quad \alpha_2 = 0, \quad \theta_2 = 66654, \\
B19(2) & : \quad \alpha_1 = 0, \quad \alpha_2 = 1, \quad \theta_2 = 66654, \\
\text{Cmmm}(1) & : \quad \alpha_1 = 1, \quad \alpha_2 = 1, \quad \theta_2 = 333607, \\
\text{Cmmm}(2) & : \quad \alpha_1 = 1, \quad \alpha_2 = -1, \quad \theta_2 = 333607.
\end{align*}
\]
Verification of Asymptotic Results

- Compare numerical and asymptotic results

![Graph showing comparison between numerical and asymptotic results]
Summary & Conclusions

Numerical techniques for bifurcation investigation of atomistic material models

- Phonon spectra — important measure of crystal stability
  - Block-Fourier transform allows efficient phonon spectra computation
  - Time complexity $O((3M)^3 N)$: linear in number of unit cells

- Efficient methods for following equilibrium paths
  - Reduce the number of equations by invoking symmetry
  - Pseudo-arc-length method

- Analyze behavior near bifurcation points
  - Numerically assisted asymptotic bifurcation investigation
Summary & Conclusions

• Used these computational techniques to study a new atomistic model
  – Temperature-dependent atomic-potentials
  – Cauchy-Born kinematics — uniform deformation & internal shifts

• Identified a **hysteretic proper Martensitic transformation**
  – Cubic austenite phase (*B*2 CsCl-type crystal)
  – Orthorhombic martensite phase (*B*19 crystal structure)
  – These structures are experimentally observed in SMA’s such as AuCd, CuAlNi, and NiTiCu.