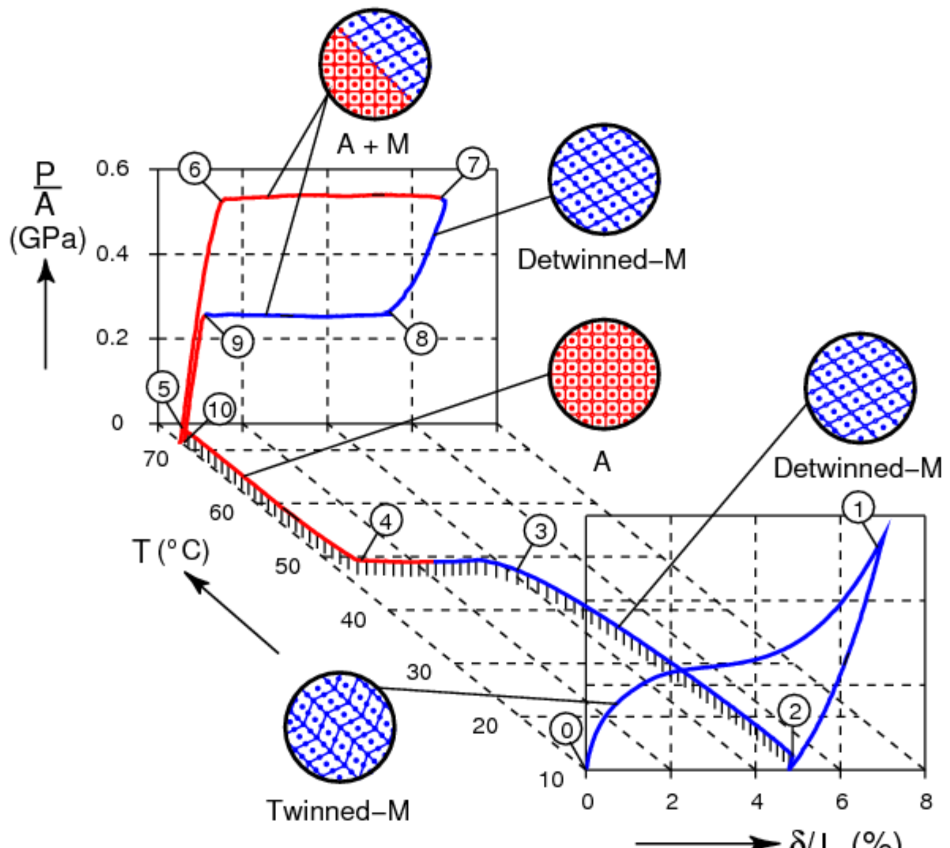
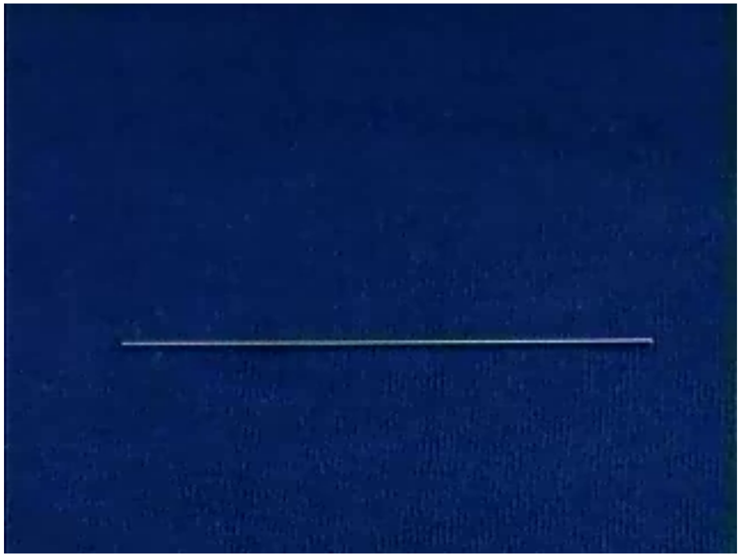
PHASE TRANSFORMATIONS IN SHAPE MEMORY ALLOYS



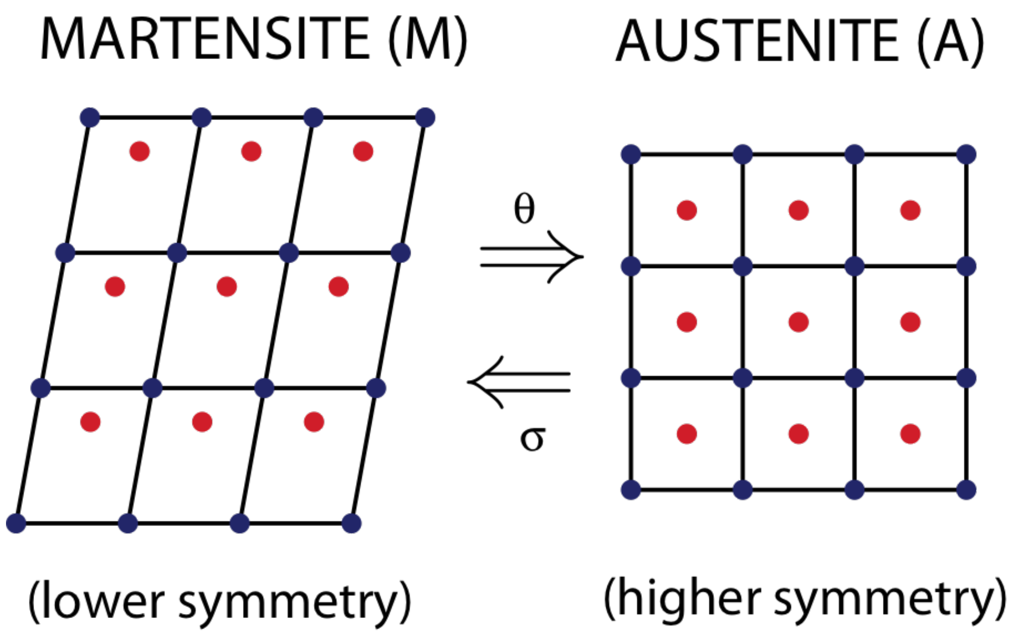
Tensile behavior of NiTi

(exhibiting the shape memory effect and pseudo–elasticity)

(J. Shaw 1997)

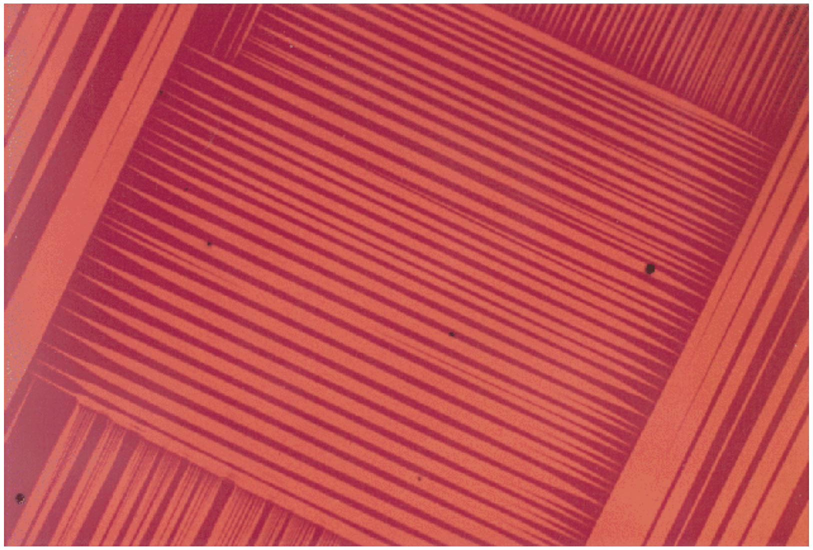


PHASE TRANSFORMATIONS: LATTICE INSTABILITIES



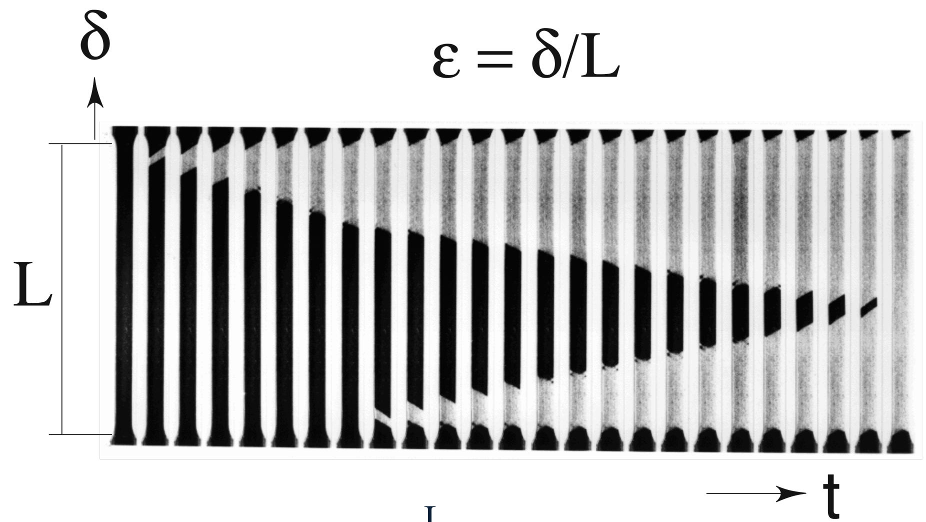
- **Shape memory behavior due to instabilities of the atomic lattice:**
- **At higher temperatures: austenitic (higher symmetry phase) is stable.**
- **At higher stresses: martensitic (lower symmetry phase) is stable.**
- **The consequence of this lattice-level instability shows all the way up to structural scale.**

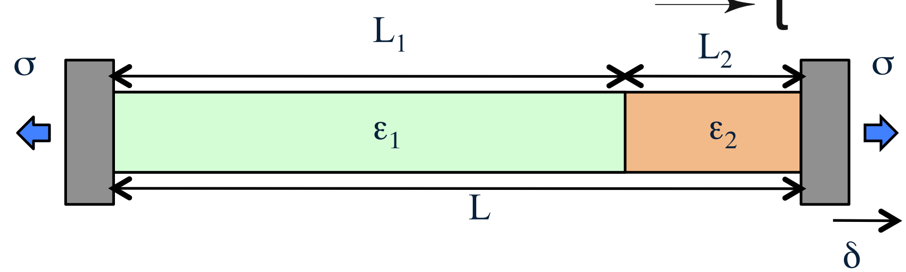
STRESS-INDUCED P.T. IN THIN STRIP STRECTCHING

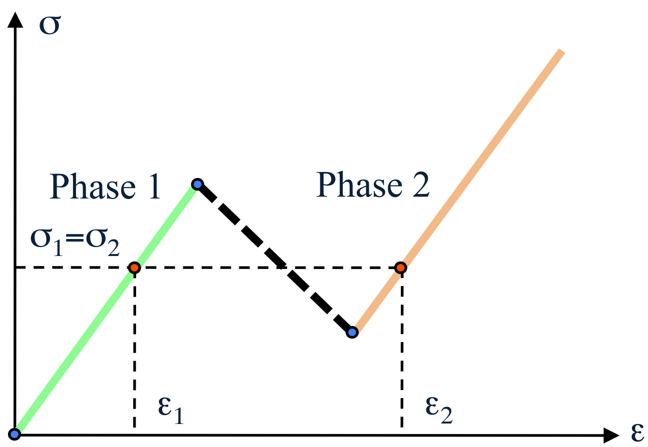


COEXISTING DIFFERENT PHASES IN CuAlNi (Chu & James 1995)

PROPAGATING INSTABILITY IN A NiTi STRIP (J. SHAW, PhD 1997)







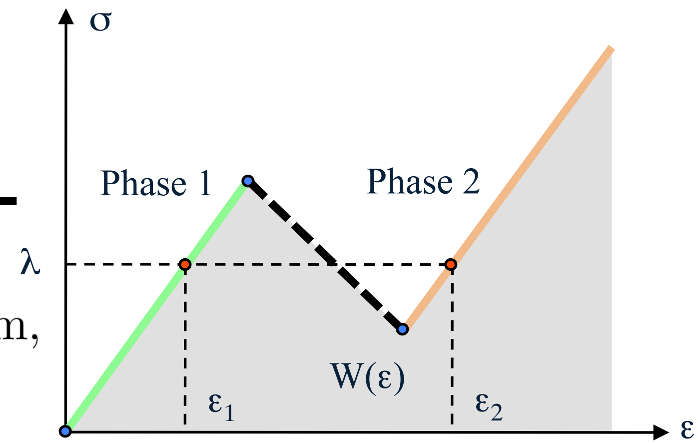
• **Stress is not a monotonically increasing function of strain, due to the presence of two different phases.**

• **The solution to the uniaxial stretching strip problem has discontinuities and is not unique.**

DISCONTINUOUS EQUILIBRIA IN THIN STRIP STRECTCHING

$$\boxed{\mathcal{E}(u,\lambda) = \int_0^L W(\varepsilon)dx - \lambda u(L);}$$ energy stored in bar where : $W(\varepsilon) \equiv \int_0^{\varepsilon} \sigma(\epsilon)\delta\epsilon$

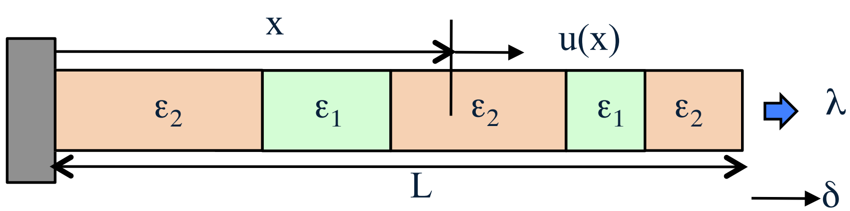
$$\varepsilon(x) = \frac{du}{dx};\ u(0) = 0,\ u(L) = \delta;$$ kinematics and b.c.

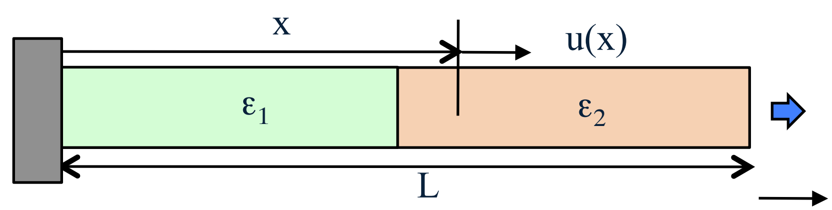


$$\mathcal{E}_{,u}\,\delta u = \int_0^L \left[\frac{dW(\varepsilon)}{d\varepsilon}\delta\varepsilon\right] dx - \lambda\delta u(L) = 0;$$ equilibrium,

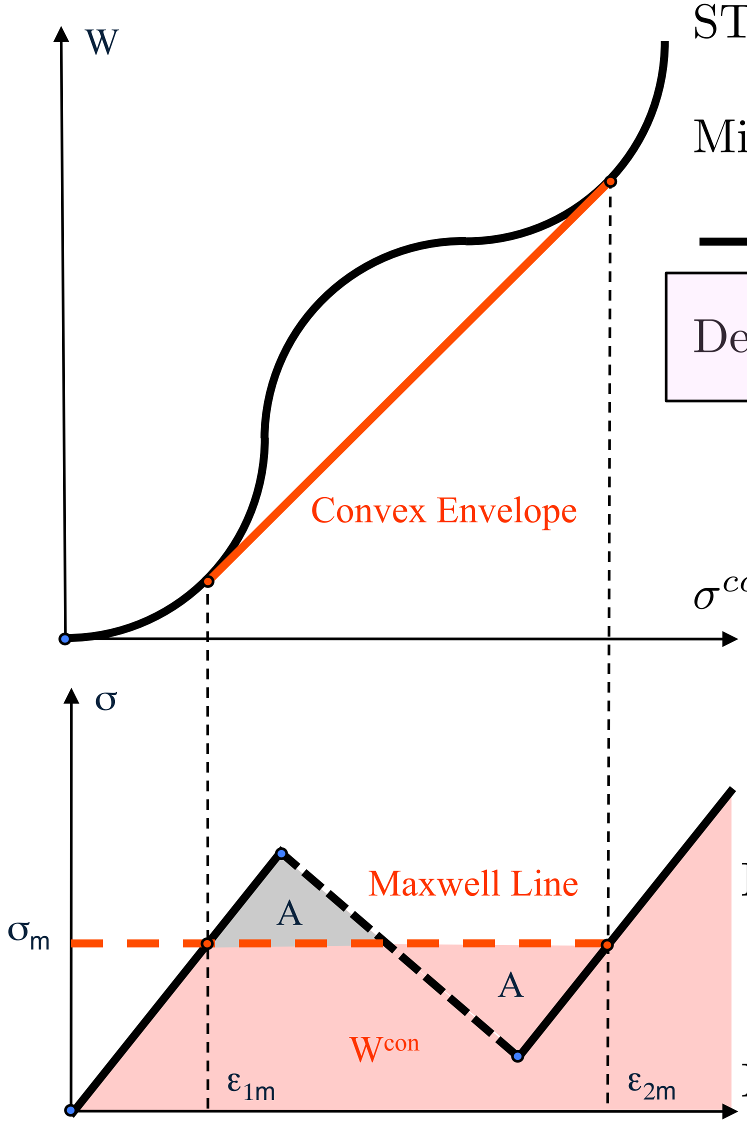
$$\Longrightarrow \boxed{\frac{dW(\varepsilon)}{d\varepsilon} \equiv \sigma(\varepsilon(x)) = \lambda;}$$ bar has constant stress λ,

Piecewise contant strain solution : $\sigma(\varepsilon_1) = \sigma(\varepsilon_2) = \lambda.$ SOLUTION IS NOT UNIQUE!





CONVEXIFIED ENERGY AND THE MAXWELL LINE SOLUTION



STABILITY : care in using $\mathcal{E}_{,uu}$ for $\varepsilon(x)$ discontinuous!

Minimum energy $\Longrightarrow$ propagating discontinuity at σ_m

---

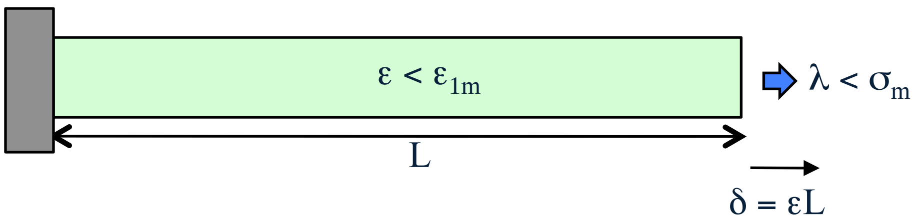
Define convex envelope of W : $W^{con}(\varepsilon) \equiv \int_0^{\varepsilon} \sigma^{con}(\epsilon) d\epsilon$

$$\sigma^{con}(\varepsilon) = \begin{cases} \sigma(\varepsilon) \text{ for : } 0 \leq \varepsilon \leq \varepsilon_{1m} \\ \sigma_m = \sigma(\varepsilon_{1m}) = \sigma(\varepsilon_{2m}) \text{ for : } \varepsilon_{1m} \leq \varepsilon \leq \varepsilon_{2m} \\ \sigma(\varepsilon) \text{ for : } \varepsilon_{2m} \leq \varepsilon < +\infty \end{cases}$$

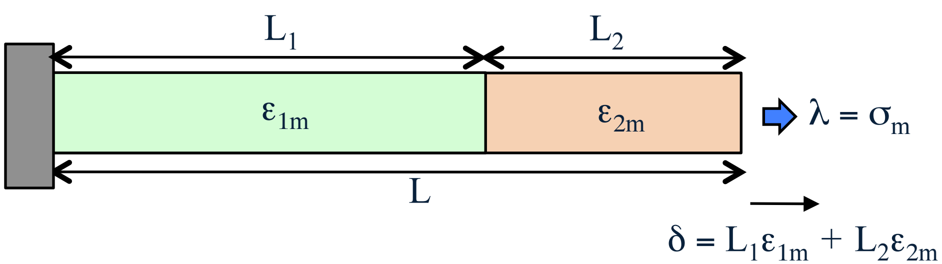
NOTE : $W^{con}(\varepsilon) = \begin{cases} W(\varepsilon) \text{ for : } 0 \leq \varepsilon \leq \varepsilon_{1m} \\ W(\varepsilon) \text{ for : } \varepsilon_{2m} \leq \varepsilon < +\infty \end{cases}$

Maxwell line : $\sigma_m \equiv \left[\int_{\varepsilon_{1m}}^{\varepsilon_{2m}} \sigma(\epsilon) d\epsilon \right] / \left[\varepsilon_{2m} - \varepsilon_{1m} \right]$

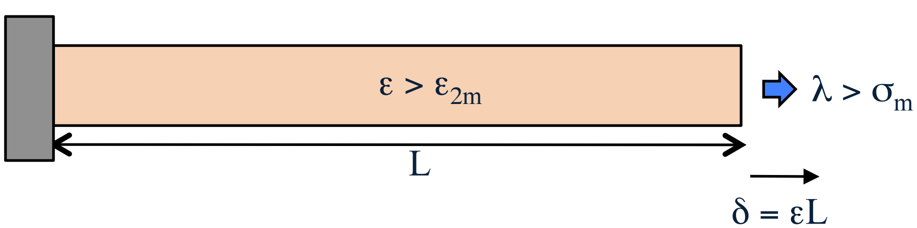
STABILITY OF THE MAXWELL LINE EQUILIBRIUM SOLUTION



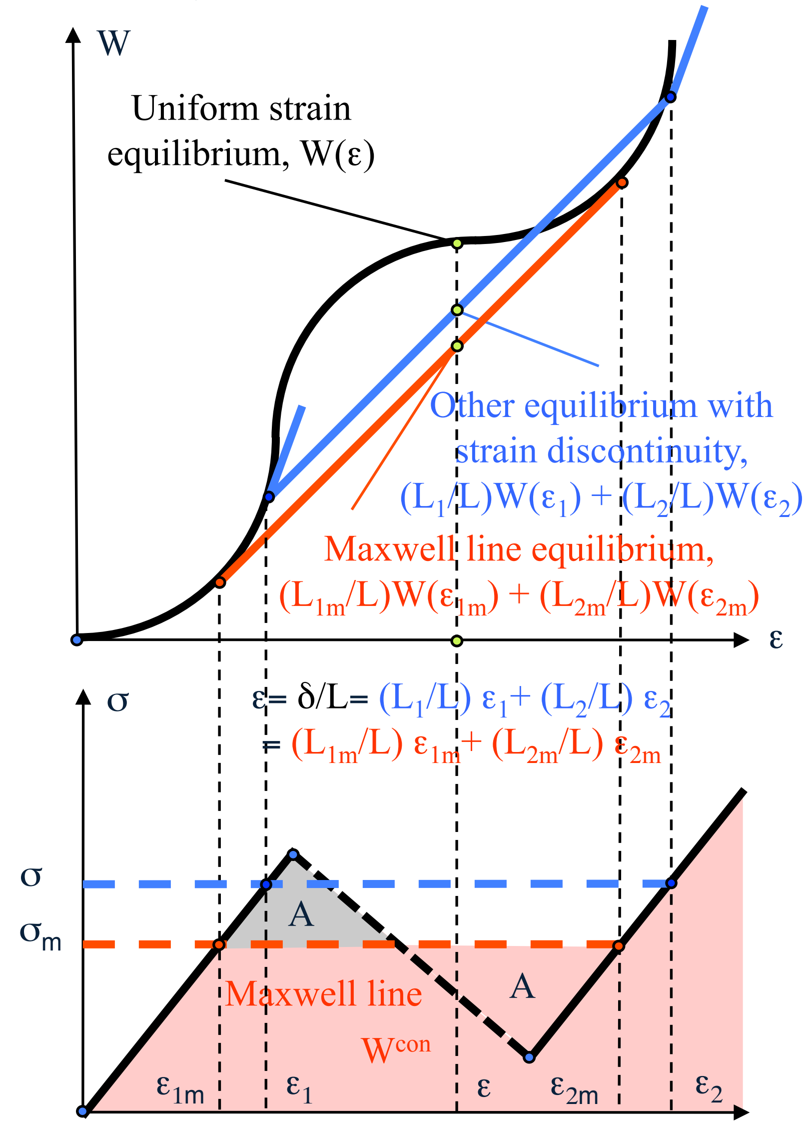
Uniform strain for $\delta/L < \varepsilon_{1m}$



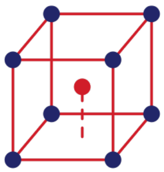
Discontinuous strain for $\varepsilon_{1m} < \delta/L < \varepsilon_{2m}$
Is the minimum energy equilibrium solution



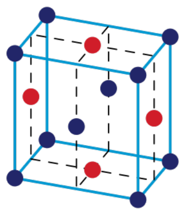
Uniform strain for $\delta/L > \varepsilon_{2m}$



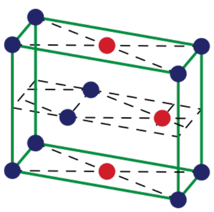
TEMPERATURE-INDUCED P.T.: LATTICE MODELS



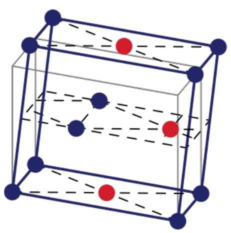
B2 - AUSTENITE FOR:
NiTi , AuCd, CuAlNi, NiAl



$L1_0$ - MARTENSITE FOR:
NiAl



B19 - MARTENSITE FOR:
AuCd, CuAlNi



B19' - MARTENSITE FOR:
NiTi

- **Some common SMA crystals have bi-atomic lattices.**
- **Their Austenitic (high symmetry) phase is cubic.**
- **Their Martensitic (low symmetry) phase can be tetragonal (e.g. $L1_0$ for NiAl), orthorhombic (e.g. B19 for AuCd, CuAlNi) or monoclinic (e.g. B19' for NiTi).**
- **Their shape memory effect will be modeled by using temperature-dependent atomic potentials.**
- **Using Cauchy-Born hypothesis, we derive the continuum energy density of the infinite, perfect, crystal $W(\mathbf{U},\mathbf{P},\theta)$, where U is the macroscopic stretch tensor, $\mathbf{P}$ shifts and θ is a temperature parameter.**
- **Martensitic phase transformations are identified as bifurcated equilibrium solutions emerging from the principal (austenitic) equilibrium path.**

JMPS, Elliott et al., **50**, 2002, p.2463; *IJSS*, Elliott et al., **39**, 2002, p.3845; *JMPS*, Elliott et al. I & II, **54**, 2006, p.161 & p.193

PHASE TRANSFORMATIONS: ATOMISTIC

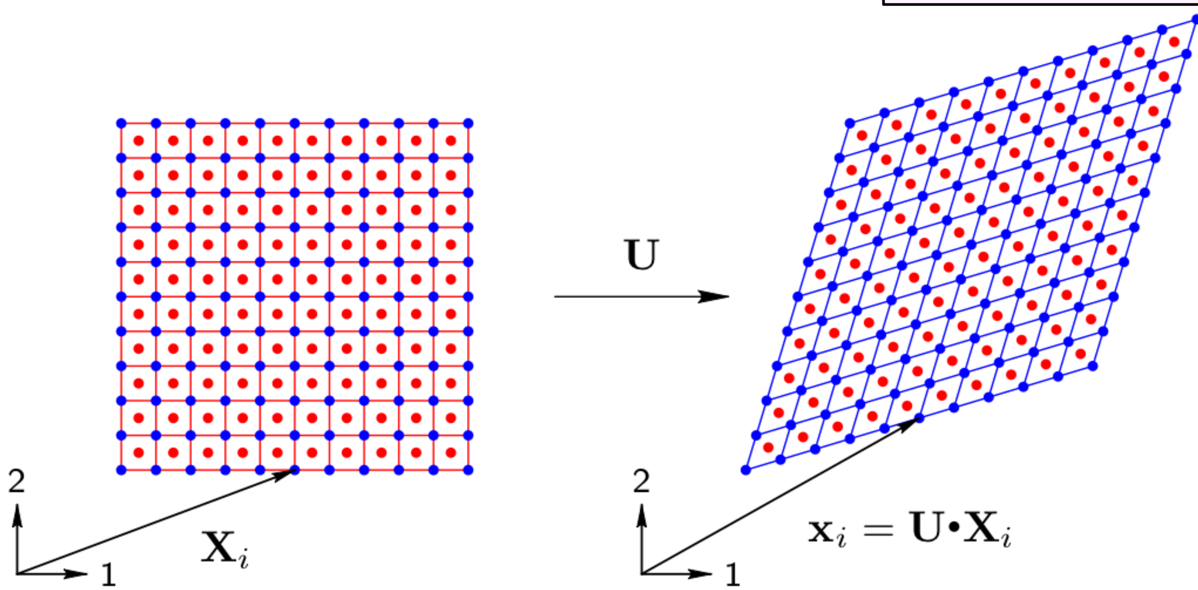
CAUCHY HYPOTHESIS – UNIFORM DEFORMATION

- Continuum-Lattice connection: $\mathbf{U}$ – symmetric right stretch tensor

$\mathbf{X}_i$ – reference position vector of atom i

$\mathbf{x}_i$ – current position vector of atom i

$$\mathbf{U} = \begin{bmatrix} U_{11} & U_{12} & U_{31} \\ U_{12} & U_{22} & U_{23} \\ U_{31} & U_{23} & U_{33} \end{bmatrix}$$



- Atomic separation

$$r_{ij} = \|\mathbf{x}_i - \mathbf{x}_j\| = \sqrt{(\mathbf{X}_i - \mathbf{X}_j)\bullet\mathbf{U}^2\bullet(\mathbf{X}_i - \mathbf{X}_j)}$$

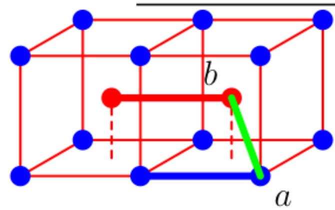
TEMPERATURE-DEPENDENT PAIR POTENTIALS

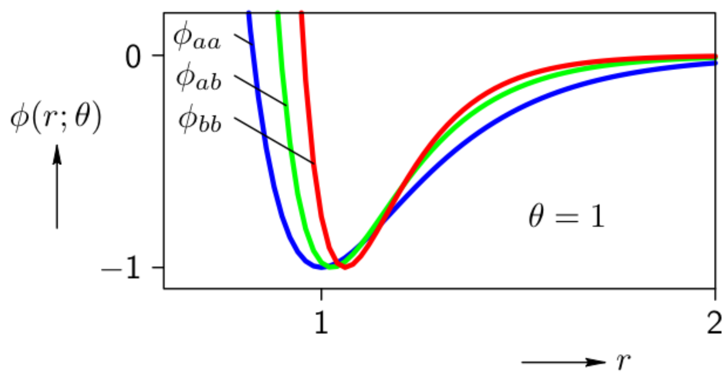
$$\phi(r;\theta) = A\left\{\exp\left[-2B\left(\frac{r}{r_0(\theta)}-1\right)\right] - 2\exp\left[-B\left(\frac{r}{r_0(\theta)}-1\right)\right]\right\}$$

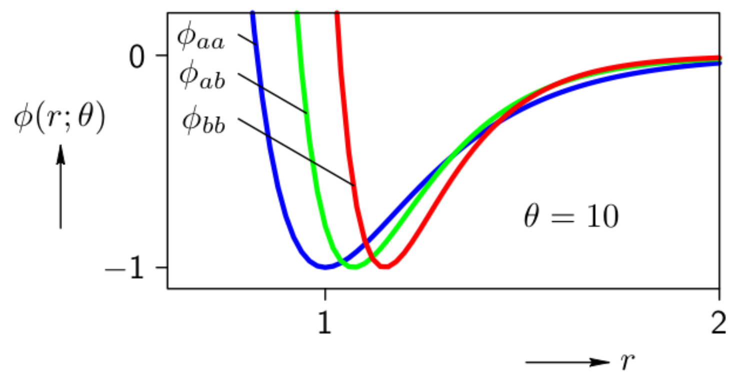
$$r_0(\theta) = r_0 + r_\theta\,(\theta - 1)$$

	r_0	r_θ	β	A	mass
aa	1	0	4	1	1
ab	1.026	0.005	5.5	1	N/A
bb	1.060	0.010	7	1	0.816

$$\theta = T/T_{ref}$$





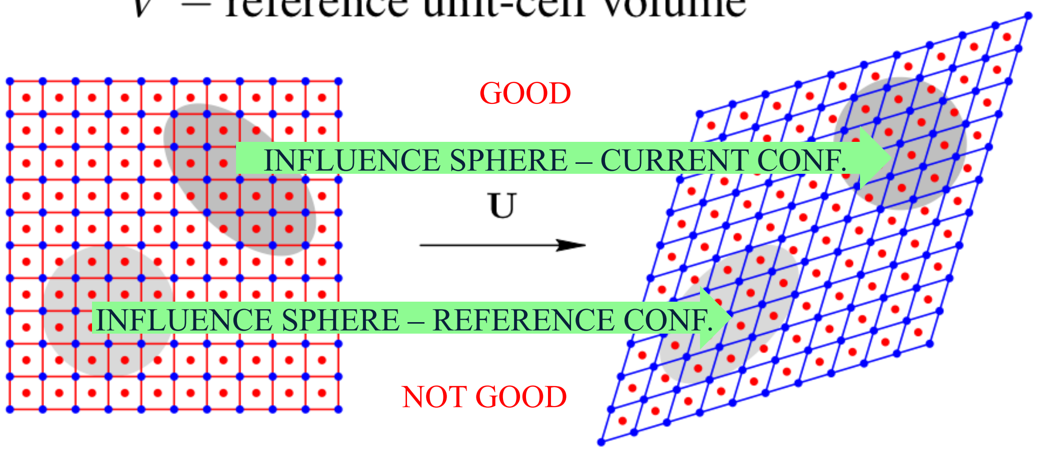


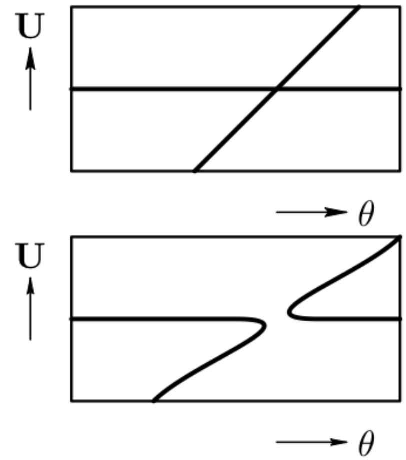
NOTE: Method easily generalized to much more general interaction potentials

CAUCHY HYPOTHESIS – EQUILIBRIUM AND STABILITY

$$W(\mathbf{U};\theta)=\frac{1}{2V}\left[\sum_i\left(\phi_{aa}(r_{aj};\theta)+\phi_{ab}(r_{bi};\theta)\right)+\sum_j\left(\phi_{bb}(r_{bj};\theta)+\phi_{ab}(r_{aj};\theta)\right)\right]$$

V – reference unit-cell volume





- Determine *stress-free* equilibrium solutions: (solve for 6 components of $\mathbf{U}$)

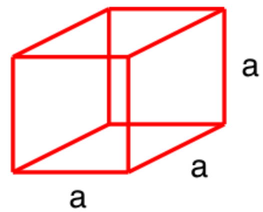
$$\frac{\partial W(\mathbf{U};\theta)}{\partial \mathbf{U}} = \mathbf{0},$$

- Stability (∞ wavelength): $\dfrac{\partial^2 W}{\partial \mathbf{U}\partial \mathbf{U}}$ is positive definite.

THE SEVEN CRYSTAL SYSTEMS

$a = b = c$

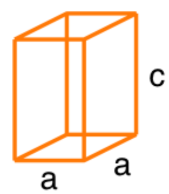
$\alpha = \beta = \gamma = 90^{o}$



Cubic

$a = b \neq c$

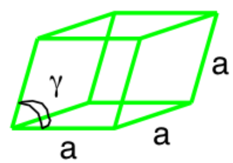
$\alpha = \beta = \gamma = 90^{o}$



Tetragonal

$a = b = c$

$\alpha = \beta = \gamma$

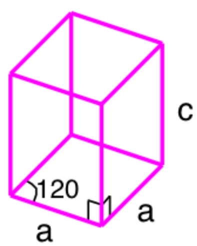


Rhombohedral

$a = b \neq c$

$\alpha = \beta = 90^{o}$

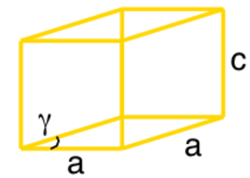
$\gamma = 120^{o}$



Hexagonal

$a = b \neq c$

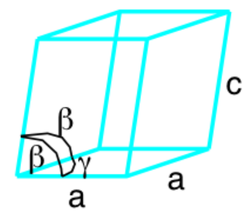
$\alpha = \beta = 90^{o} \neq \gamma$



Orthorhombic

$a = b \neq c$

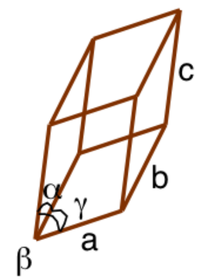
$\alpha = \beta \neq \gamma$



Monoclinic

$a \neq b \neq c \neq a$

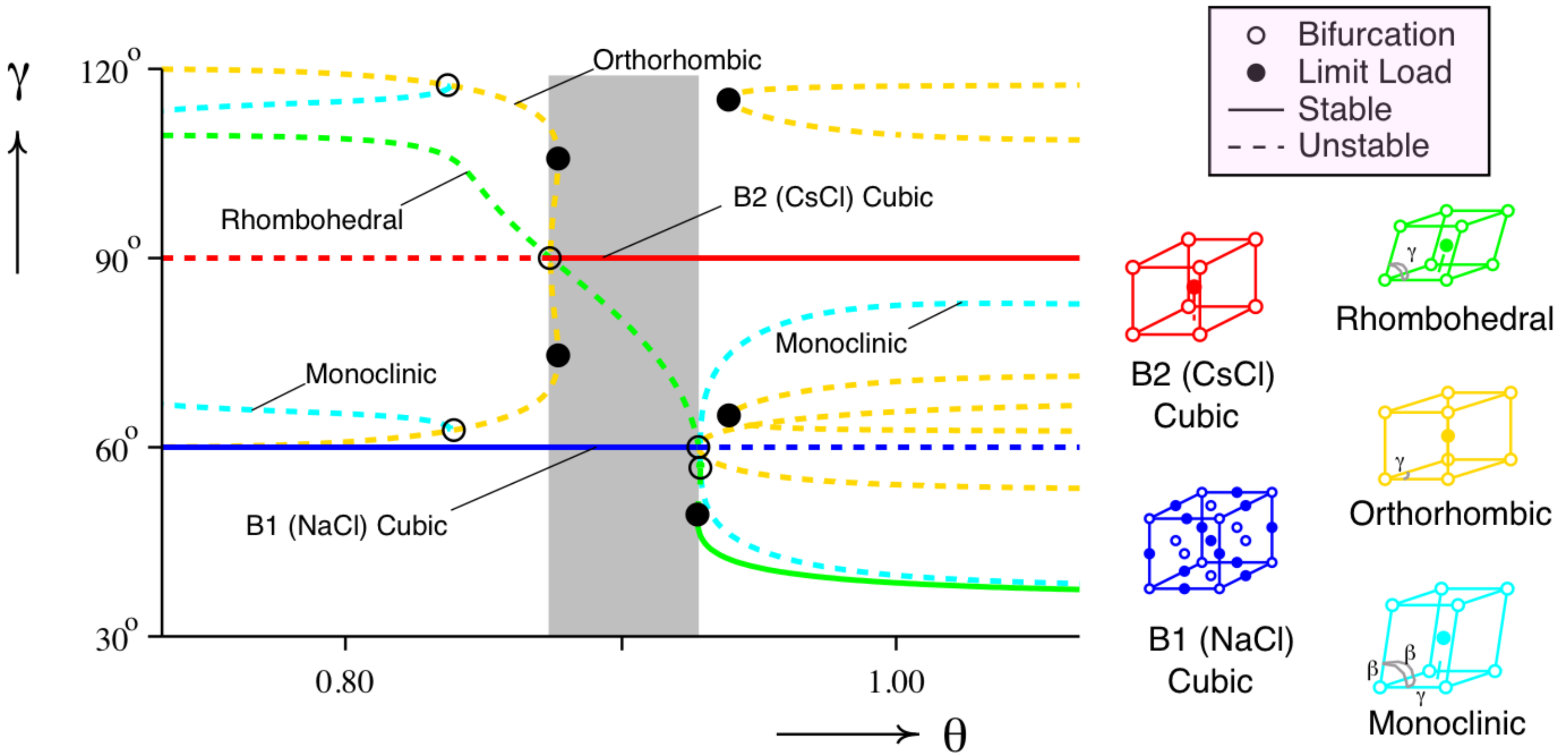
$\alpha \neq \beta \neq \gamma \neq \alpha$



Triclinic

CAUCHY HYPOTHESIS – FINAL RESULTS

$$\cos(\gamma) = U_{1k}U_{k2}$$

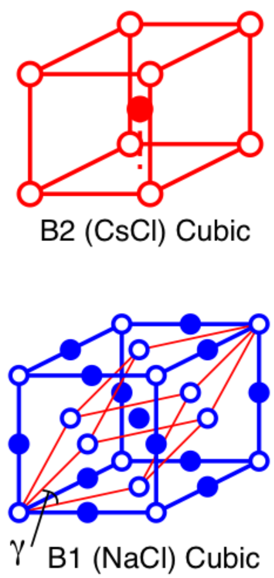


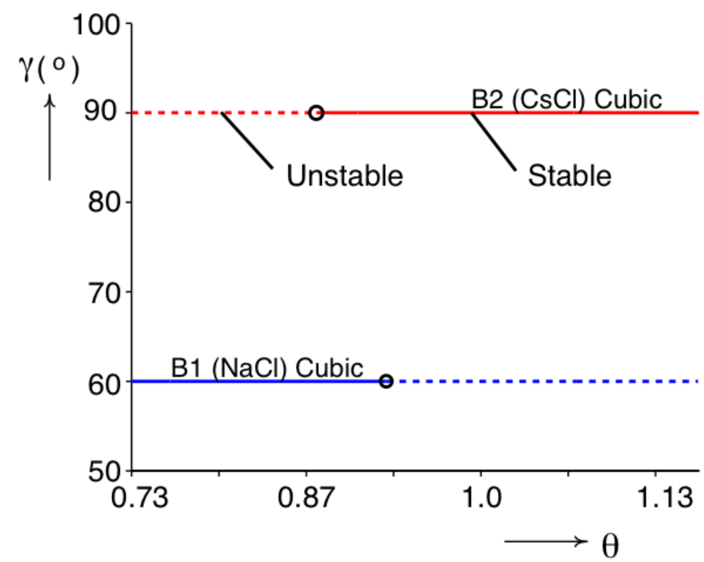
- Overlapping stable segments of $B2$ (CsCl) and $B1$ (NaCl) cubic phases
- Multiple bifurcation points require asymptotic techniques

CAUCHY HYPOTHESIS – PRINCIPAL SOLUTIONS (CUBIC)

Stress-Free Equilibrium Paths of Cubic Phases

$$\overset{0}{\mathbf{U}}_{B2}(\theta) = \lambda(\theta) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \overset{0}{\mathbf{U}}_{B1}(\theta) = \hat{\lambda}(\theta) \begin{bmatrix} 1 & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & 1 & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & 1 \end{bmatrix}.$$





NOTE: Two different cubic symmetry solutions exist. From the BCC B2 crystal one can obtain a FCC B1 crystal by applying a particular stretch tensor $\mathbf{U}$.

CAUCHY HYPOTHESIS – MODULI OF CUBIC SOLUTIONS

- Cubic material with principal solution $\overset{0}{\mathbf{U}}(\theta) = \lambda(\theta)\mathbf{I}$.

$$W(\mathbf{U};\theta) = W(\mathbf{M}^T \bullet \mathbf{U} \bullet \mathbf{M};\theta)$$

where $\mathbf{M}$ is in the octahedral symmetry group.

Thus,

$$\left.\begin{aligned} W &= W(U_{ii}, U_{jj}, U_{kk}, U_{ij}, U_{jk}, U_{ki};\theta) \\ &= W(U_{ii}, U_{jj}, U_{kk}, -U_{ij}, -U_{jk}, U_{ki};\theta) \\ &= W(U_{ii}, U_{jj}, U_{kk}, -U_{ij}, U_{jk}, -U_{ki};\theta) \\ &= W(U_{ii}, U_{jj}, U_{kk}, U_{ij}, -U_{jk}, -U_{ki};\theta) \end{aligned}\right\} \quad \begin{aligned} &\{i,j,k\} = Perm\{1,2,3\} \\ &\text{(no sum)} \end{aligned}$$

NOTE: For stability calculations most of the components of the energy's second derivatives $\partial^2 W/\partial U_{ij}\partial U_{kl}$ are related due to the cubic symmetry of the principal solution. Here $\mathbf{M}$ are the orthonormal matrices of the full octahedral symmetry group.

CAUCHY HYPOTHESIS – MODULI OF CUBIC SOLUTIONS

$$W(\overset{0}{\mathbf{U}}(\theta) + \mathbf{\Delta U}; \theta) = \overset{0}{L} + \overset{1}{L}_n \sum_i \Delta U_{ii}$$

$$+\frac{1}{2!}\left(\overset{2}{L}_{nn} \sum_i (\Delta U_{ii})^2 + \overset{2}{L}_{nn'} \sum_{i \neq j} (\Delta U_{ii} \Delta U_{jj}) + \overset{2}{L}_{ss} \sum_{i \neq j} 2(\Delta U_{ij})^2 \right)$$

$$+\frac{1}{3!}\left(\overset{3}{L}_{nnn} \sum_i (\Delta U_{ii})^3 + \overset{3}{L}_{nnn'} \sum_{i \neq j} 3((\Delta U_{ii})^2 \Delta U_{jj}) \right.$$

$$+\overset{3}{L}_{nn'n''} \sum_{i \neq j \neq k \neq i} (\Delta U_{ii} \Delta U_{jj} \Delta U_{kk}) + \overset{3}{L}_{nss} \sum_{i \neq j} 12(\Delta U_{ii} (\Delta U_{ij})^2)$$

$$\left. +\overset{3}{L}_{n'ss} \sum_{i \neq j \neq k \neq i} 6(\Delta U_{ii} (\Delta U_{jk})^2) + \overset{3}{L}_{ss's''} \sum_{i \neq j \neq k \neq i} 8(\Delta U_{ij} \Delta U_{ik} \Delta U_{jk}) \right)$$

$$+O\left(\mathbf{\Delta U}^4\right).$$

NOTE: Only 3 independent components of moduli !

$$\overset{2}{L}_{nn} = \frac{\partial^2 W}{\partial U_{11} \partial U_{11}}, \qquad \overset{2}{L}_{nn'} = \frac{\partial^2 W}{\partial U_{11} \partial U_{22}}, \qquad \overset{2}{L}_{ss} = \frac{\partial^2 W}{\partial U_{12} \partial U_{12}}$$

CAUCHY HYPOTHESIS – CRITICAL POINTS ON B2, B1

- Identify critical points, $\left.\frac{\partial^2 W}{\partial \mathbf{U} \partial \mathbf{U}}\right|_c : \overset{(I)}{\mathbf{U}} = 0.$ $\qquad I = 1, \ldots, H$
- $\overset{(I)}{\mathbf{U}}$ is the I^{th} eigenvector of $\left.\frac{\partial^2 W}{\partial \mathbf{U} \partial \mathbf{U}}\right|_c$, with eigenvalue 0.

$$\begin{bmatrix} \overset{2}{L}{}^c_{nn} & \overset{2}{L}{}^c_{nn'} & \overset{2}{L}{}^c_{nn'} & 0 & 0 & 0 \\ \overset{2}{L}{}^c_{nn'} & \overset{2}{L}{}^c_{nn} & \overset{2}{L}{}^c_{nn'} & 0 & 0 & 0 \\ \overset{2}{L}{}^c_{nn'} & \overset{2}{L}{}^c_{nn'} & \overset{2}{L}{}^c_{nn} & 0 & 0 & 0 \\ 0 & 0 & 0 & \overset{2}{L}{}^c_{ss} & 0 & 0 \\ 0 & 0 & 0 & 0 & \overset{2}{L}{}^c_{ss} & 0 \\ 0 & 0 & 0 & 0 & 0 & \overset{2}{L}{}^c_{ss} \end{bmatrix} \begin{bmatrix} U_{11} \\ U_{22} \\ U_{33} \\ 2U_{12} \\ 2U_{23} \\ 2U_{31} \end{bmatrix}^{(I)} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

- Thus,

$$\det\left(\left.\frac{\partial^2 W}{\partial \mathbf{U} \partial \mathbf{U}}\right|_c \right) = \left(\overset{2}{L}{}^c_{nn} + 2\overset{2}{L}{}^c_{nn'} \right) \left(\overset{2}{L}{}^c_{nn} - \overset{2}{L}{}^c_{nn'} \right)^2 \left(\overset{2}{L}{}^c_{ss} \right)^3 = 0.$$

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

- Expansion of $\mathbf{U}$ and θ near θ_c. (ξ – bifurcation amplitude)

($\overset{(I)}{\mathbf{U}}$– eigenvectors in the null-space of $W^c{}_{,\mathbf{UU}}$)

$$\mathbf{U}(\xi) = \overset{0}{\mathbf{U}}(\theta(\xi)) + \xi \left(\sum_{I=1}^{H} \alpha_I \overset{(I)}{\mathbf{U}} \right) + O(\xi^2) \, ; \quad \theta(\xi) = \theta_c + \xi\theta_1 + \frac{\xi^2}{2}\theta_2 + O(\xi^3) \, .$$

- Equilibrium equations: $\boldsymbol{\alpha}$ – tangent vector, $\mathcal{E}$ – higher order derivatives of W

$$\text{if} \quad \theta_1 \neq 0 \text{ (asymmetric)} : \quad \sum_{J,K=1}^{H} \alpha_J \alpha_K \mathcal{E}_{IJK} + 2\theta_1 \sum_{J=1}^{H} \alpha_J \mathcal{E}_{IJ\theta} = 0,$$

or

$$\text{if} \quad \theta_1 = 0 \text{ (symmetric)} : \quad \sum_{J,K,L=1}^{H} \alpha_J \alpha_K \alpha_L \mathcal{E}_{IJKL} + 3\theta_2 \sum_{J=1}^{H} \alpha_J \mathcal{E}_{IJ\theta} = 0.$$

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

- Initial stability depends on the eigenvalues of B_{IJ}.

$$B_{IJ} = \begin{cases} \theta_1 \mathcal{E}_{IJ\theta} + \displaystyle\sum_{K=1}^{H} \alpha_K \mathcal{E}_{IJK} & \text{if } \theta_1 \neq 0 \text{ (asymmetric)}, \\ \theta_2 \mathcal{E}_{IJ\theta} + \displaystyle\sum_{K,L=1}^{H} \alpha_K \alpha_L \mathcal{E}_{IJKL} & \text{if } \theta_1 = 0 \text{ (symmetric)}. \end{cases}$$

$$\mathcal{E}_{IJK} \equiv \left. \frac{\partial^3 W}{\partial U_{ij} \partial U_{kl} \partial U_{mn}} \right|_c \overset{(I)}{U}_{ij} \overset{(J)}{U}_{kl} \overset{(K)}{U}_{mn},$$

$$\mathcal{E}_{IJKL} \equiv \left(\left(\left(\left. \frac{\partial^4 W}{\partial U_{ij} \partial U_{kl} \partial U_{mn} \partial U_{qr}} \right|_c \overset{(J)}{U}_{kl} \right) \overset{(K)}{U}_{mn} \right) \overset{(L)}{U}_{qr} + \dots \right) \overset{(I)}{U}_{ij},$$

$$\mathcal{E}_{IJ\theta} \equiv \left. \left(\frac{d}{d\theta} \left(\frac{\partial^2 W(\overset{0}{U}(\theta); \theta)}{\partial U_{ij} \partial U_{kl}} \right) \right) \right|_c \overset{(I)}{U}_{ij} \overset{(J)}{U}_{kl}.$$

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

$$\left(\frac{\partial^2 W}{\partial \mathbf{U}\partial\theta}\bigg|_c\right) : \overset{(I)}{\mathbf{U}} = \begin{cases} = 0 & \text{bifurcation} \\ \neq 0 & \text{limit load} \end{cases} \qquad I = 1, \ldots, H$$

- Case I. $\boxed{\overset{2}{L}{}^c_{nn} + 2\overset{2}{L}{}^c_{nn'} = 0}$, multiplicity of $H = 1$

$$\overset{(1)}{\mathbf{U}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

$$\left(\frac{\partial^2 W}{\partial \mathbf{U}\partial\theta}\bigg|_c\right) : \overset{(1)}{\mathbf{U}} = 3 \left.\frac{\partial \overset{1}{L}_n}{\partial\theta}\right|_c \neq 0$$

$\Longrightarrow$ Limit Load.

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

- Case II. $\boxed{\overset{2}{L}{}^{c}_{nn} = \overset{2}{L}{}^{c}_{nn'}}$, multiplicity of $H = 2$

$$\overset{(1)}{\mathbf{U}} = \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \overset{(2)}{\mathbf{U}} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

$$\left(\left. \frac{\partial^2 W}{\partial \mathbf{U} \partial \theta} \right|_c \right) : \overset{(I)}{\mathbf{U}} = \left. \frac{\partial \overset{1}{L}_n}{\partial \theta} \right|_c \left(\sum_{i=1}^{3} \overset{(I)}{U}_{ii} \right) = 0$$

$\Longrightarrow$ Bifurcation.

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

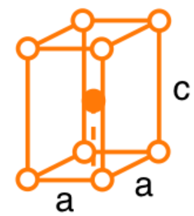
Case II. $\boxed{\overset{2}{L}{}^{c}_{nn} = \overset{2}{L}{}^{c}_{nn'}}$,

$H = 2 \Rightarrow$ a max of $2^H - 1 = 3$, asymmetric $(\theta_1 \neq 0)$, bifurcated paths,

---

$$\mathbf{U} = \begin{bmatrix} c & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{bmatrix}, \quad \begin{bmatrix} a & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & a \end{bmatrix}, \quad \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{bmatrix}.$$

$$\boldsymbol{\alpha} = \quad (1,0) \qquad (0,1) \qquad (-1,-1)$$



Tetragonal

All 3 bifurcated paths are *initially* unstable.

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

- Case III. $\boxed{\overset{2}{L}{}^{c}_{ss} = 0}$, multiplicity $H = 3$

$$\overset{(1)}{\mathbf{U}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \quad \overset{(2)}{\mathbf{U}} = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad \overset{(3)}{\mathbf{U}} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

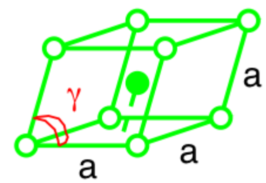
$$\left(\left. \frac{\partial^2 W}{\partial \mathbf{U} \partial \theta} \right|_c \right) : \overset{(I)}{\mathbf{U}} = \left. \frac{\partial \overset{1}{L}_n}{\partial \theta} \right|_c \left(\sum_{i=1}^{3} \overset{(I)}{U}_{ii} \right) = 0$$

$\Longrightarrow$ Bifurcation.

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

Case III. $\overset{2}{L}{}^{c}_{ss} = 0$,

$H = 3 \Rightarrow$ a max of $2^H - 1 = 7$ bifurcated paths.



a) Four, asymmetric ($\theta_1 \neq 0$), bifurcated paths,

$$\mathbf{U} = \begin{bmatrix} a & \zeta & \zeta \\ \zeta & a & \zeta \\ \zeta & \zeta & a \end{bmatrix}, \quad \begin{bmatrix} a & \zeta & \zeta \\ \zeta & a & -\zeta \\ \zeta & -\zeta & a \end{bmatrix}, \quad \begin{bmatrix} a & \zeta & -\zeta \\ \zeta & a & \zeta \\ -\zeta & \zeta & a \end{bmatrix}, \quad \begin{bmatrix} a & -\zeta & \zeta \\ -\zeta & a & \zeta \\ \zeta & \zeta & a \end{bmatrix}.$$

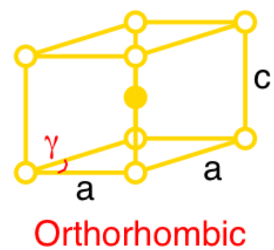
$$\boldsymbol{\alpha} = (-1,-1,-1)/\sqrt{3} \quad (-1,1,1)/\sqrt{3} \quad (1,-1,1)/\sqrt{3} \quad (1,1,-1)/\sqrt{3}$$

All 4 rhombohedral bifurcated paths are *initially* unstable.

CAUCHY HYPOTHESIS – LSK ASYMPTOTICS

Case III. $\boxed{\overset{2}{L}{}^{c}_{ss} = 0}$,
$H = 3 \Rightarrow$ a max of $2^H - 1 = 7$ bifurcated paths.

b) Three, symmetric ($\theta_1 = 0; \theta_2 \neq 0$), bifurcated paths,



$$\mathbf{U} = \begin{bmatrix} c & 0 & 0 \\ 0 & a & \zeta \\ 0 & \zeta & a \end{bmatrix}, \quad \begin{bmatrix} a & 0 & \zeta \\ 0 & c & 0 \\ \zeta & 0 & a \end{bmatrix}, \quad \begin{bmatrix} a & \zeta & 0 \\ \zeta & a & 0 \\ 0 & 0 & c \end{bmatrix}.$$

$$\boldsymbol{\alpha} = \quad (1,0,0) \qquad (0,1,0) \qquad (0,0,1)$$

All 3 orthorhombic bifurcated paths' *initial* stability depends on W.

CAUCHY HYPOTHESIS – FOLLOWING EQUILIBRIUM PATHS

Procedure

- **Cubic Phase**

$$U_{11} = U_{22} = U_{33} = a,$$
$$U_{12} = U_{23} = U_{31} = 0.$$

Solve: $\boxed{\dfrac{\partial W}{\partial a} = 0.}$

- **Rhombohedral Phase**

$$U_{11} = U_{22} = U_{33} = a,$$
$$U_{12} = U_{23} = U_{31} = \zeta.$$

Solve: $\boxed{\dfrac{\partial W}{\partial a} = 0, \quad \dfrac{\partial W}{\partial \zeta} = 0.}$

- **Orthorhombic Phase**

$$U_{33} = c, \quad U_{11} = U_{22} = a,$$
$$U_{12} = \zeta, \quad U_{23} = U_{31} = 0.$$

Solve: $\boxed{\dfrac{\partial W}{\partial a} = 0, \quad \dfrac{\partial W}{\partial c} = 0, \quad \dfrac{\partial W}{\partial \zeta} = 0.}$

- **Monoclinic Phase**

$$U_{33} = c, \quad U_{11} = U_{22} = a,$$
$$U_{12} = \zeta, \quad U_{23} = U_{31} = \rho.$$

Solve: $$\boxed{\begin{array}{ll} \dfrac{\partial W}{\partial a} = 0, & \dfrac{\partial W}{\partial \zeta} = 0, \\ \dfrac{\partial W}{\partial c} = 0, & \dfrac{\partial W}{\partial \rho} = 0. \end{array}}$$

CAUCHY HYPOTHESIS – FOLLOWING EQUILIBRIUM PATHS

- For each path prescribe the appropriate amplitude parameter ξ,

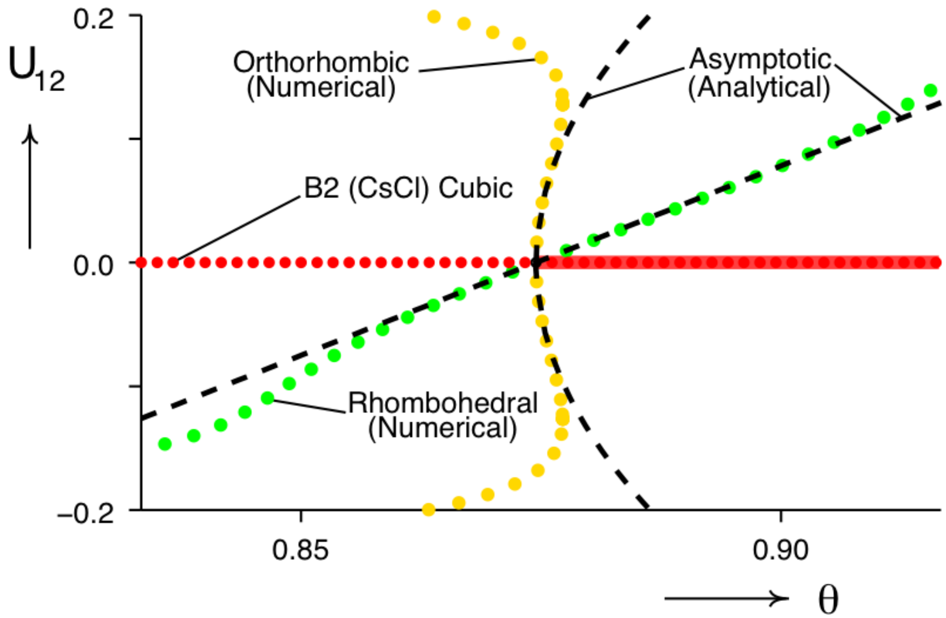
$$
\begin{array}{lll}
\text{Cubic} & \rightarrow & \xi = U_{11} = a, \\
\text{Rhombohedral} & \rightarrow & \xi = U_{12} = \zeta, \\
\text{Orthorhombic} & \rightarrow & \xi = U_{12} = \zeta, \\
\text{Monoclinic} & \rightarrow & \xi = U_{31} = \rho.
\end{array}
$$

- Incremental Newton-Raphson method is used to find solutions.
- Arc-length (Δd) technique is used to accommodate limit loads.

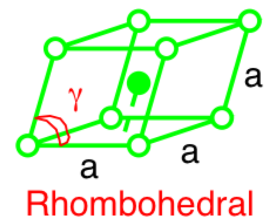
$$
\begin{array}{lll}
\text{Cubic} & \rightarrow & (\Delta d)^2 = (\Delta\theta/\theta^*)^2 + (\Delta a)^2, \\
\text{Rhombohedral} & \rightarrow & (\Delta d)^2 = (\Delta\theta/\theta^*)^2 + (\Delta a)^2 + (\Delta\zeta)^2, \\
\text{Orthorhombic} & \rightarrow & (\Delta d)^2 = (\Delta\theta/\theta^*)^2 + (\Delta a)^2 + (\Delta\zeta)^2 + (\Delta c)^2, \\
\text{Monoclinic} & \rightarrow & (\Delta d)^2 = (\Delta\theta/\theta^*)^2 + (\Delta a)^2 + (\Delta\zeta)^2 + (\Delta c)^2 + (\Delta\rho)^2.
\end{array}
$$

CAUCHY HYPOTHESIS – VERIFICATION AT TRIPLE POINT

$$\text{Shear modulus } \overset{2}{L}{}^{c}_{ss} = 0$$

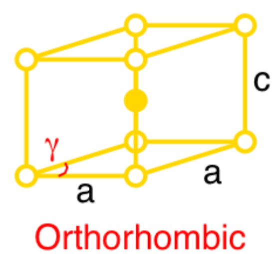


- 4 Rhombohedral paths



Initially unstable regardless of W

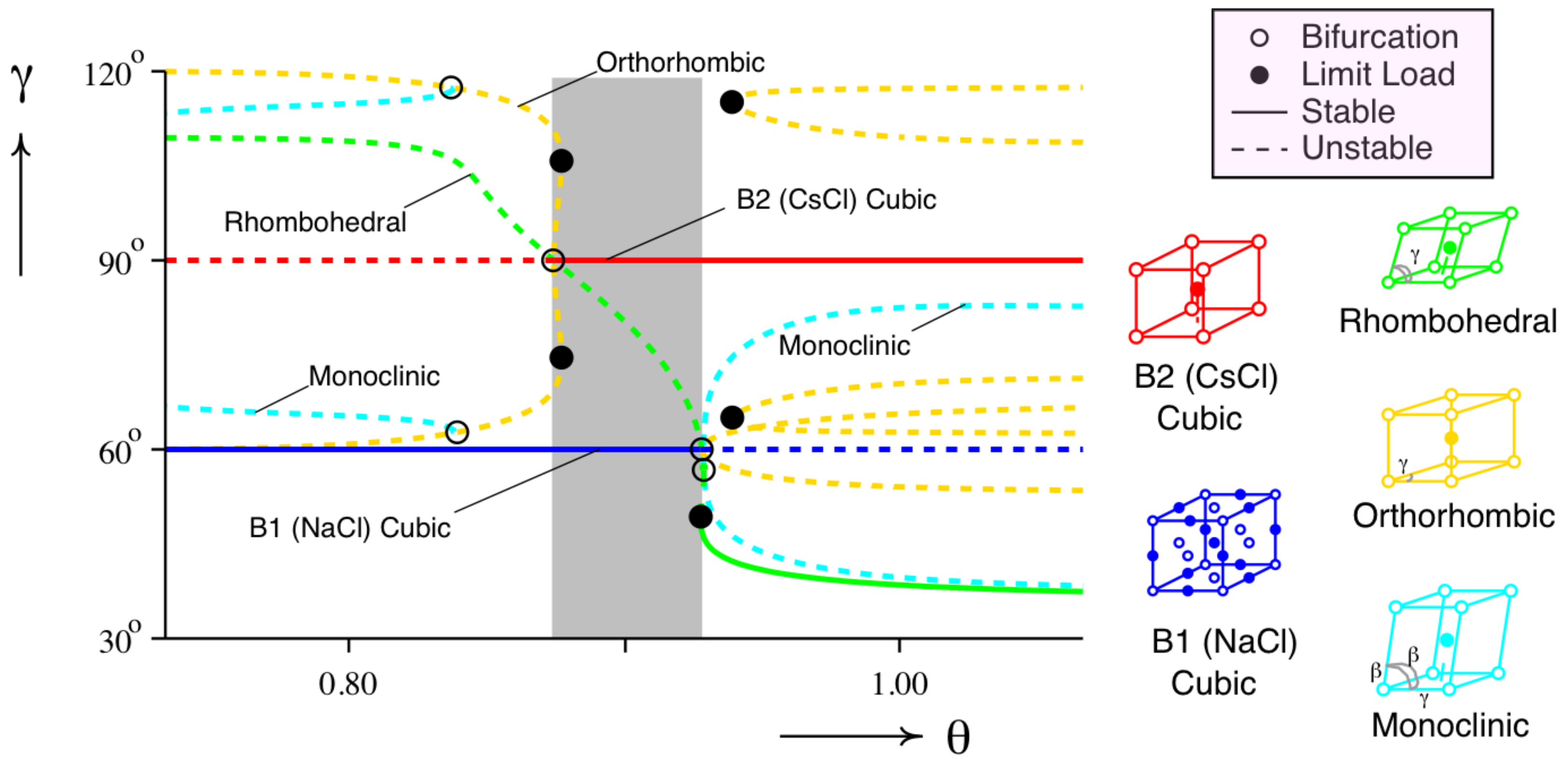
- 3 Orthorhombic paths



Initial stability depends on *W*

CAUCHY HYPOTHESIS – REVIEW OF FINAL RESULTS

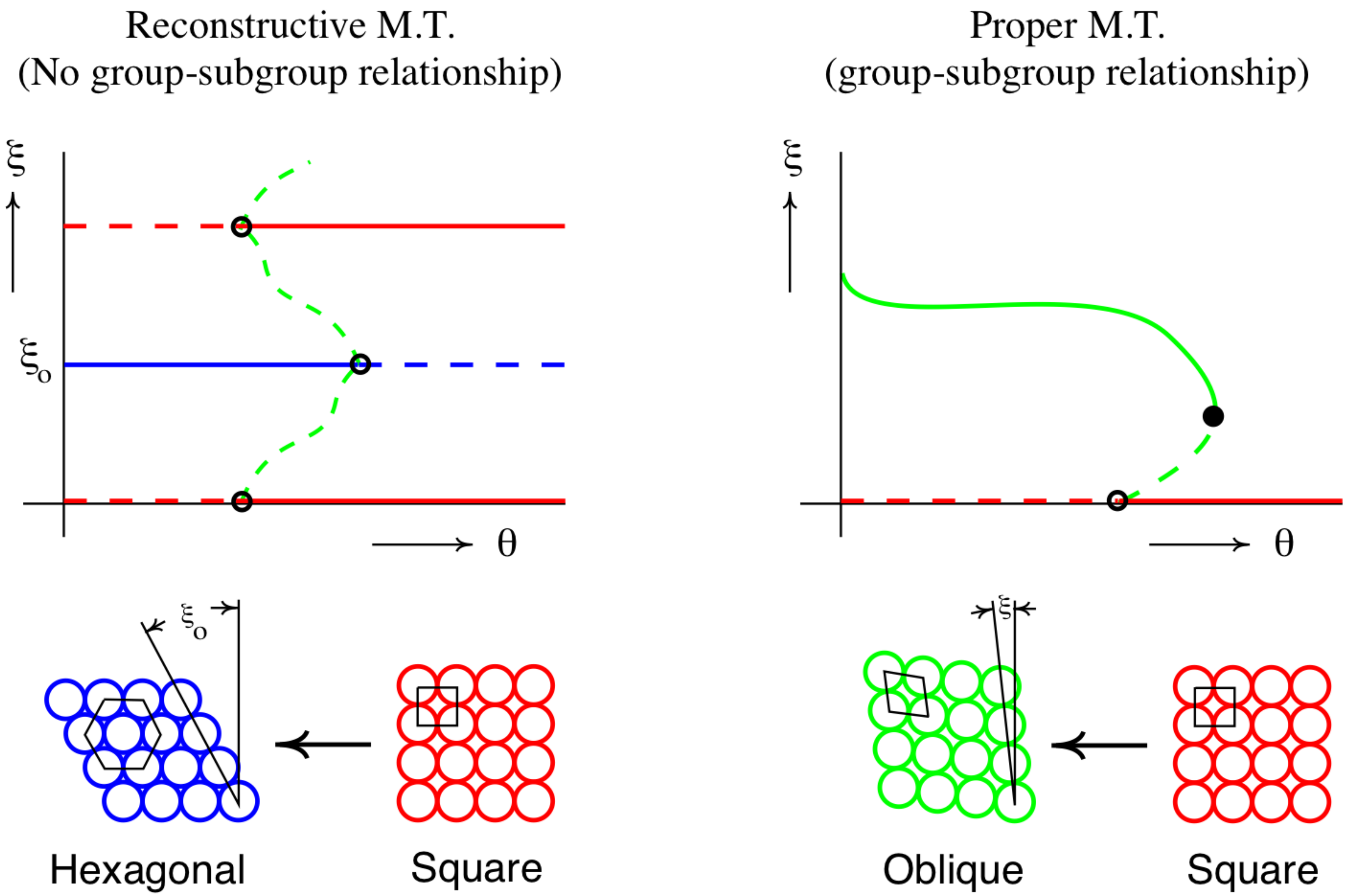
$$\cos(\gamma) = U_{1k}U_{k2}$$



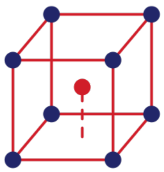
• **NOTE: Cauchy hypothesis predicts that only cubic configurations are stable and hence only reconstructive phase transformations found. Model is inadequate for proper M. T. s.**

• **NOTE: Stability results based on continuum energy minimization are incomplete, since they ignore perturbations with wavelengths of the order of interatomic distances.**

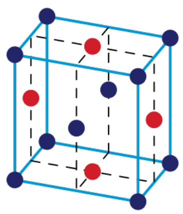
CAUCHY HYPOTHESIS – REVIEW OF FINAL RESULTS



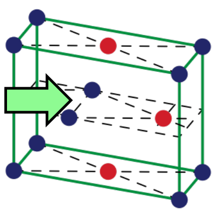
CAUCHY HYPOTHESIS – HOW TO IMPROVE



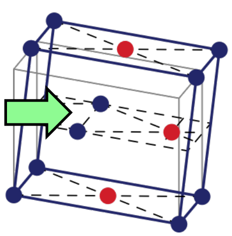
B2 - AUSTENITE FOR:
NiTi , AuCd, CuAlNi, NiAl



$L1_0$ - MARTENSITE FOR:
NiAl



B19 - MARTENSITE FOR:
AuCd, CuAlNi



B19' - MARTENSITE FOR:
NiTi

- **Simple Cauchy hypothesis predicts stable B1 and B2 equilibrium paths at given temperature but not the martensitic phases for AuCd, CuAlNi or NiTi.**

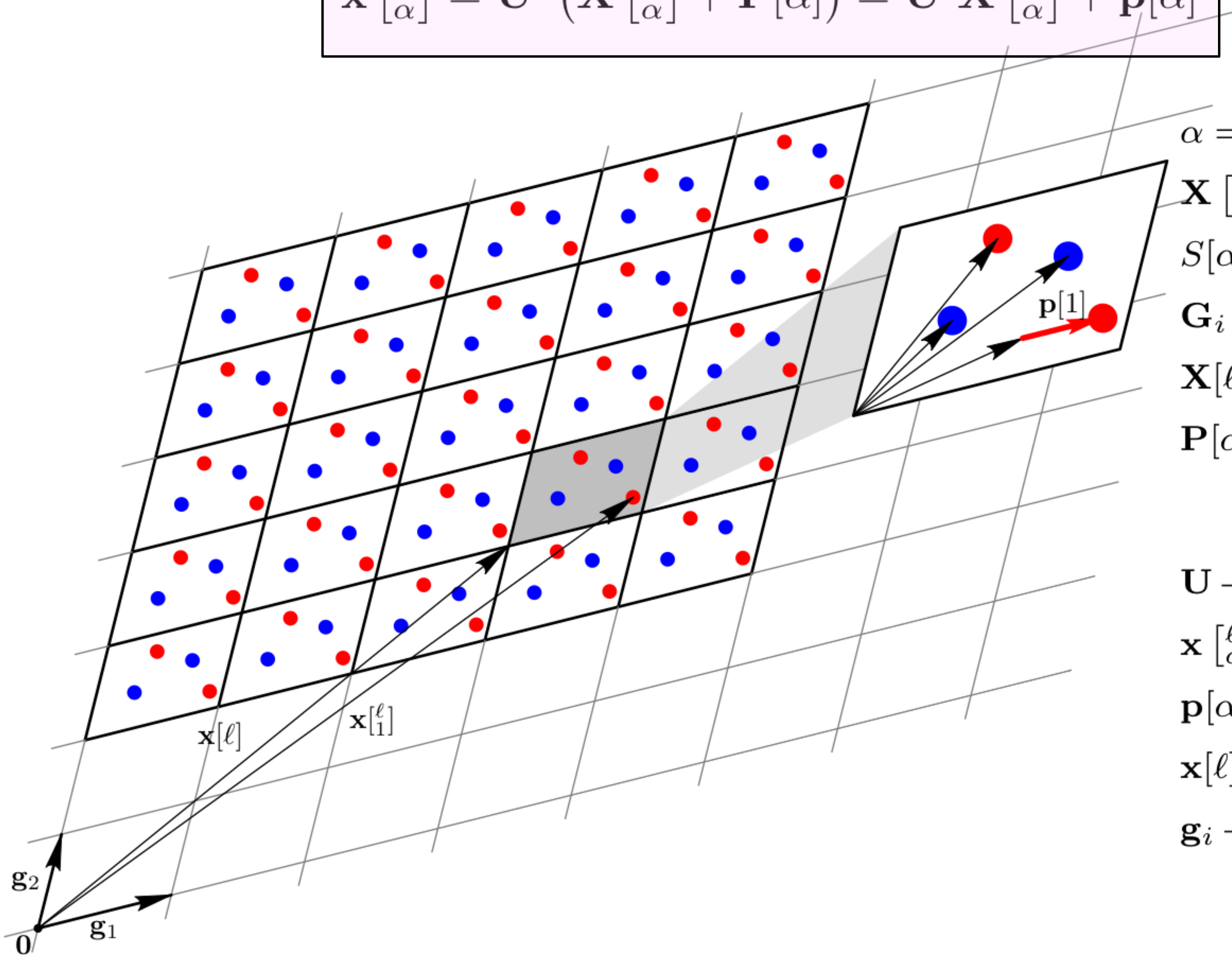
- **Reason: Proper martensitic transformations of interest (B19, B19') involve internal shifts. Consequently models with more d.o.f. are needed to describe the equilibrium paths (Cauchy-Born hypothesis) which allow internal shifts in addition to a macroscopic stretch tensor U.**

- **Stability calculations need to consider bounded perturbations of all possible wavelengths with respect to interatomic distances. Consequently phonon spectra calculations (the discrete analogue of the Bloch wave calculations for the continuum periodic solids of the previous lecture) need to be considered.**

- **Phonon spectra calculations are used to determine the minimum number of d.o.f. needed for the Cauchy-Born calculations.**

CAUCHY-BORN HYPOTHESIS (INTERNAL SHIFTS)

$$\mathbf{x}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} = \mathbf{U}\bullet\left(\mathbf{X}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} + \mathbf{P}[\alpha]\right) = \mathbf{U}\bullet\mathbf{X}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} + \mathbf{p}[\alpha]$$



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

$\mathbf{X}\begin{bmatrix}\ell\\ \alpha\end{bmatrix}$ – reference pos.

$S[\alpha]$ – fractional pos.

$\mathbf{G}_i$ – ref. lattice basis

$\mathbf{X}[\ell]$ – unit-cell ref. pos.

$\mathbf{P}[\alpha]$ – sub-lat. ref. shifts

$\mathbf{U}$ – uniform deformation

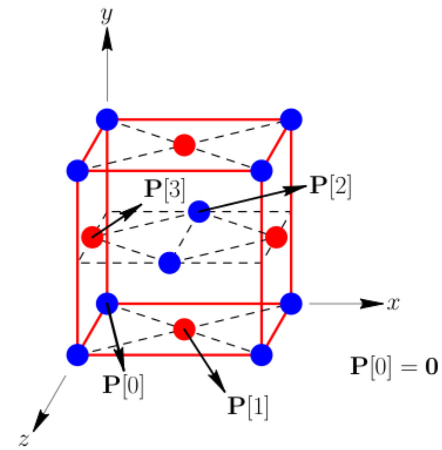
$\mathbf{x}\begin{bmatrix}\ell\\ \alpha\end{bmatrix}$ – current pos.

$\mathbf{p}[\alpha]$ – sub-lat. current pos.

$\mathbf{x}[\ell]$ – unit-cell current pos.

$\mathbf{g}_i$ – current lattice basis

CAUCHY-BORN HYPOTHESIS: ENERGY DENSITY



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

$$\mathbf{x}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} = \mathbf{U}\bullet\left(\mathbf{X}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} + \mathbf{P}[\alpha]\right)$$

- Atomic separation

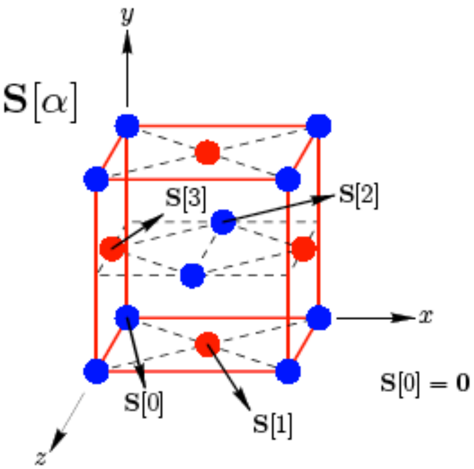
$$r\begin{bmatrix}\ell & \ell'\\ \alpha & \alpha'\end{bmatrix} = \left\|\mathbf{x}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} - \mathbf{x}\begin{bmatrix}\ell'\\ \alpha'\end{bmatrix}\right\|$$

- Energy density

$$\widetilde{W}(\mathbf{U},\ \mathbf{P}[1],\ \mathbf{P}[2],\ \mathbf{P}[3];\theta) = \frac{1}{2V}\sum_{\alpha'}\sum_{\left[\substack{\ell\\ \alpha}\right]}\phi_{\alpha\alpha'}\left(r\begin{bmatrix}\ell & 0\\ \alpha & \alpha'\end{bmatrix};\theta\right)$$

CAUCHY-BORN HYPOTHESIS: EQUILIBRIUM & STABILITY

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



$$\frac{\partial \widetilde{W}}{\partial \mathbf{u}} = \mathbf{0} \begin{cases} \dfrac{\partial \widetilde{W}}{\partial \mathbf{U}} = \mathbf{0}, \\ \dfrac{\partial \widetilde{W}}{\partial \mathbf{S}[1]} = \mathbf{0}, \quad \dfrac{\partial \widetilde{W}}{\partial \mathbf{S}[2]} = \mathbf{0}, \quad \dfrac{\partial \widetilde{W}}{\partial \mathbf{S}[3]} = \mathbf{0}. \end{cases}$$

- Stability for perturbations of ∞ wavelength):
  - Cauchy-Born stability (local energy minimizer):

$$\delta\mathbf{u} \frac{\partial^2 \widetilde{W}}{\partial \mathbf{u} \partial \mathbf{u}} \delta\mathbf{u} > 0; \qquad \delta\mathbf{u} = \{\delta\mathbf{U}, \delta\mathbf{S}[1], \delta\mathbf{S}[2], \delta\mathbf{S}[3]\}, \ \delta\mathbf{U} = \delta\mathbf{U}^T.$$

PHONON STABILITY FOR INFINITE, PERFECT LATTICE

- Linearized equations of motion about equilibrium:

$$m_\alpha \ddot{\mathbf{u}} \begin{bmatrix} \ell \\ \alpha \end{bmatrix} = - \sum_{\begin{bmatrix} \ell' \\ \alpha' \end{bmatrix}} \mathbf{K} \begin{bmatrix} \ell & \ell' \\ \alpha & \alpha' \end{bmatrix} \bullet \mathbf{u} \begin{bmatrix} \ell' \\ \alpha' \end{bmatrix},$$

m_α – mass of atom α,

$\mathbf{u} \begin{bmatrix} \ell \\ \alpha \end{bmatrix}$ – displacement of atom α in unit cell ℓ,

$\mathbf{K} \begin{bmatrix} \ell & \ell' \\ \alpha & \alpha' \end{bmatrix}$ – stiffness between atoms $\begin{bmatrix} \ell \\ \alpha \end{bmatrix}$ and $\begin{bmatrix} \ell' \\ \alpha' \end{bmatrix}$ calculated from the atomic potentials.

- Initial conditions:

$$\mathbf{u} \begin{bmatrix} \ell \\ \alpha \end{bmatrix} \Big|_{t=0} = \mathbf{u}^0 \begin{bmatrix} \ell \\ \alpha \end{bmatrix}, \quad \dot{\mathbf{u}} \begin{bmatrix} \ell \\ \alpha \end{bmatrix} \Big|_{t=0} = \dot{\mathbf{u}}^0 \begin{bmatrix} \ell \\ \alpha \end{bmatrix}.$$

- Stability (in the sense of Lyapunov):

$$\left\| \mathbf{u}^0 \begin{bmatrix} \ell \\ \alpha \end{bmatrix} \right\|, \left\| \dot{\mathbf{u}}^0 \begin{bmatrix} \ell \\ \alpha \end{bmatrix} \right\| < \epsilon \quad \Longrightarrow \quad \left\| \mathbf{u} \begin{bmatrix} \ell \\ \alpha \end{bmatrix} \right\|, \left\| \dot{\mathbf{u}} \begin{bmatrix} \ell \\ \alpha \end{bmatrix} \right\| < \delta(\epsilon).$$

PHONON STABILITY FOR INFINITE, PERFECT LATTICE

- Phonon (normal mode) solutions: (a–lattice spacing, $M = 4$ -atoms/unit-cell)

$$\mathbf{u}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} = \mathbf{\Delta u}^{(q)}[\alpha]\exp\left\{-i\left(\mathbf{k}\bullet\mathbf{X}\begin{bmatrix}\ell\\ \alpha\end{bmatrix} + \omega^{(q)}(\mathbf{k})t\right)\right\},$$

$$\mathbf{k} - \text{wave number vector}, \mathbf{k} \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right)^3;$$

$$q - \text{phonon index}, q = 1, 2, \ldots, 3M;$$

$$\omega^{(q)}(\mathbf{k}) - \text{phonon frequency};$$

$$\mathbf{\Delta u}^{(q)}[\alpha] - \text{amplitude vector}.$$

- Phonon-stability:

$$\left(\omega^{(q)}(\mathbf{k})\right)^2 > 0, \text{for all } \mathbf{k}, \text{ and all } q.$$

NOTE: Here a is the interatomic distance of the cubic lattice

PHONON STABILITY FOR INFINITE, PERFECT LATTICE

- Block-diagonalize $\mathbf{K}\begin{bmatrix} \ell & \ell' \\ \alpha & \alpha' \end{bmatrix}$ by taking the Fourier transform

$$m\ddot{u}(\mathbf{x},t) = -Ku(\mathbf{x},t)$$

becomes

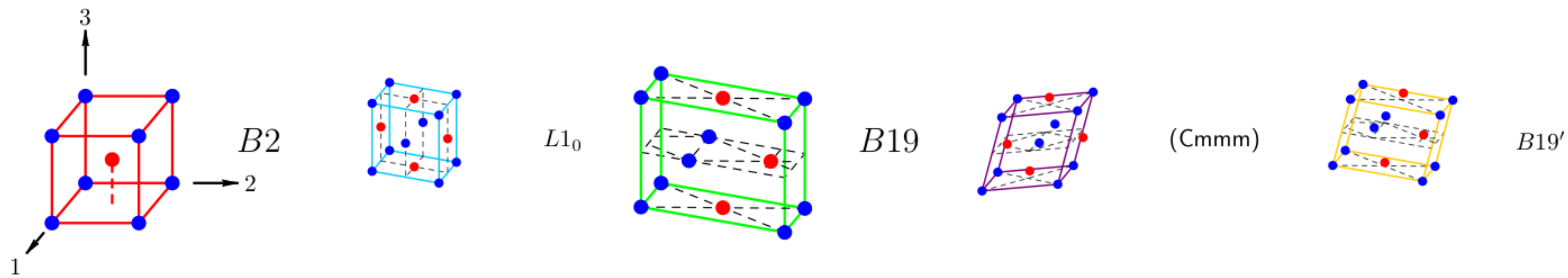
$$\ddot{v}(\mathbf{k},t) = -\mathbb{K}v(\mathbf{k},t)$$

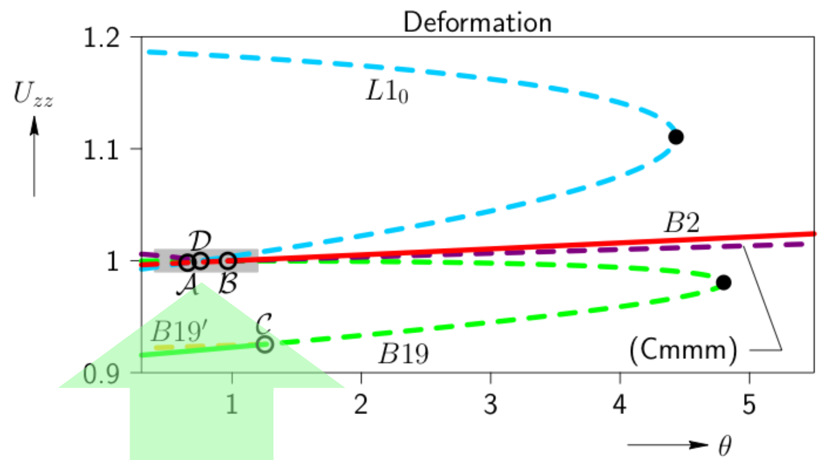
- Dynamical matrices — $3M \times 3M$

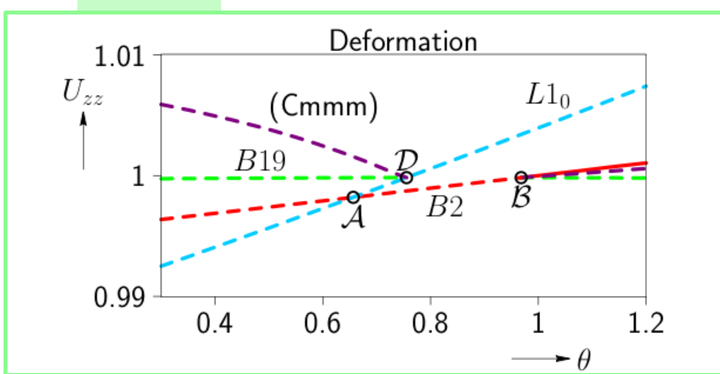
$$\mathbb{K}_p^j\begin{bmatrix} \mathbf{k} & \\ \alpha & \alpha' \end{bmatrix} = \frac{1}{\sqrt{m_\alpha m_{\alpha'}}}\sum_{\ell'} G^{jk}K_{kp}\begin{bmatrix} 0 & \ell' \\ \alpha & \alpha' \end{bmatrix}\exp\left\{-i\mathbf{k}\bullet\left(\mathbf{X}\begin{bmatrix} \ell' \\ \alpha' \end{bmatrix} - \mathbf{X}\begin{bmatrix} 0 \\ \alpha \end{bmatrix}\right)\right\}.$$

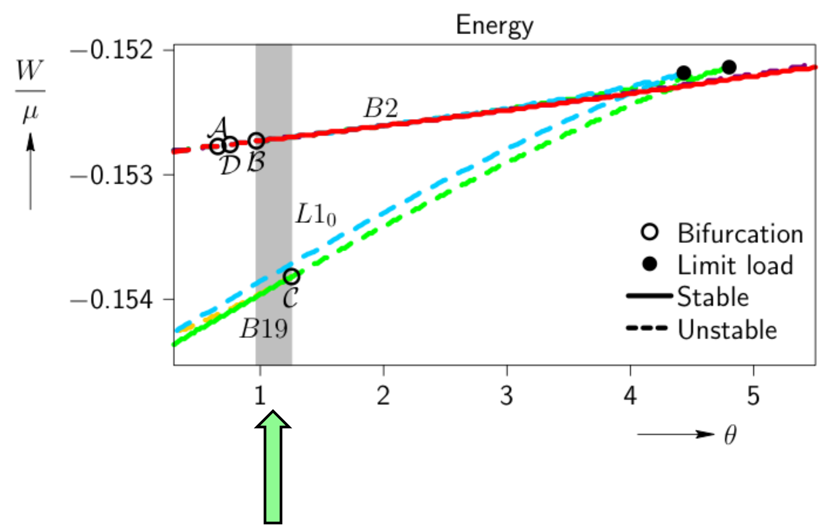
- The $\left(\omega^{(q)}(\mathbf{k})\right)^2$, are the $3M$ eigen-values of $\mathbb{K}_p^j\begin{bmatrix} \mathbf{k} & \\ \alpha & \alpha' \end{bmatrix}$ for each $\mathbf{k}$.
- Numerically use a uniform grid in $\mathbf{k}$ domain ($[-\frac{\pi}{a}, \frac{\pi}{a})^3$)

CAUCHY-BORN & PHONON STABILITY RESULTS









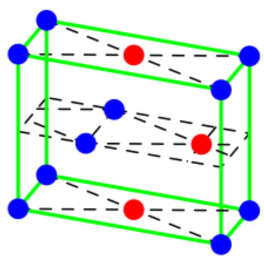
Proper martensitic transformation

COMPARISON OF CALCULATIONS WITH EXPERIMENTS

$$B2 \Longrightarrow B19$$

Martensitic Transformation

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



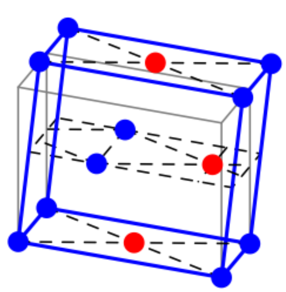
$B19$

$$\mathbf{U} = \begin{bmatrix} 1.026 & 0.0099 & 0 \\ 0.0099 & 1.026 & 0 \\ 0 & 0 & 0.9501 \end{bmatrix}$$

AuCd, (*Ohba (1990), Vivet (1998)*)

$$\mathbf{U} = \begin{bmatrix} 1.042 & 0.0195 & 0 \\ 0.0195 & 1.042 & 0 \\ 0 & 0 & 0.9178 \end{bmatrix}$$

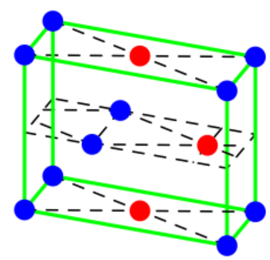
CuAlNi, (*Bhatacharya, James (1999)*)



$B19'$

$$\mathbf{U} = \begin{bmatrix} 1.024 & 0.058 & 0.0427 \\ 0.058 & 1.024 & 0.0427 \\ 0.0427 & 0.0427 & 0.9563 \end{bmatrix}$$

NiTi, (*Knowles and Smith (1981)*)



$B19$

$$\mathbf{U} = \begin{bmatrix} 1.045 & 0.0173 & 0 \\ 0.0173 & 1.045 & 0 \\ 0 & 0 & 0.9227 \end{bmatrix}$$

- **A 4-atom Cauchy-Born lattice model finds a B19 phase with a stable segment which overlaps with the stable segment of the B2 phase.**
- **Results indicate a hysteretic, proper martensitic transformation in this bi-atomic lattice model.**
- **Reasonable agreement with experiments.**

WHAT HAVE LEARNED FROM THIS APPLICATION

- **Usefulness** of LSK aymptotics to a) **guide** the nonlinear calculations **near critical points** and b) serve as a **check** of the numerical calculations.

- Important **concept of scale**. There are **global** (long wavelength) and **local** (of the order of unit cell dimensions) **instabilities**. One has to check for **both**!

- Important concept of **phonon spectra** (same as **Bloch wave** representation but for discrete systems) can **check** stability of an **infinite periodic system** by analyzing **only one unit cell**.

- Analytical methods are **indispensable** for effective and intelligent numerical calculations

- Work presented explains only thermal behavior of SMA's. Stress influence on SMA's more complicated, and **has already been studied** using **same** ideas.

- **Ultimate goal**: **understand** reasons for phase transformations and **design** materials at the atomic scale.