Methodology and micromechanical estimation of macroscopic elastic energy, coherence energy, and phase transition strains for SMA materials

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Dedicated to
Masters of Polish School of Mechanics

Bogdan Raniecki and Jan Rychlewski

(1938-2014)   (1934-2011)

Background information

In order to *correctly predict performance* of modern engineering materials, it is necessary to *understand their observed behavior* and *develop relevant physical/mathematical models* for description of such behavior.

The good theoretical model enables, for example, *efficient design* of engineering devices to take advantage of *functional* and/or *utility features* of specific advanced material.

Many sophisticated engineering materials rely on *phase transitions* taking place during their actual operation and/or during their manufacturing processes.
One of such materials are so called *Shape Memory Alloys* (SMA).

A very convenient and efficient theoretical environment for building *macroscopic constitutive models of advanced materials,* seems to be a framework of *non-equilibrium thermodynamics with internal state parameters*.

Kestin J. (1979) A course in Thermodynamics.
Horstemeyer M., Bammann D. (2010) Historical review of internal state variable theory for inelasticity, Int. J. Plast.
Ziółkowski A. (2015) Pseudoelasticity of Shape Memory Alloys, Theory and Experimental Studies, Elsevier.
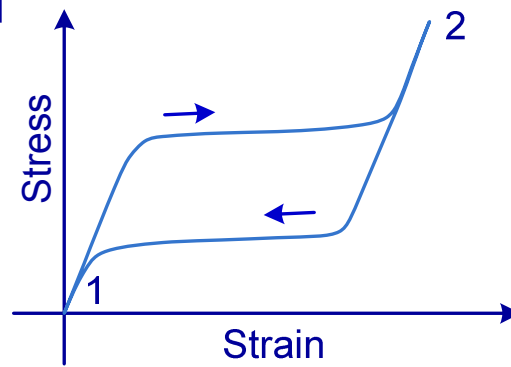*A. Ziółkowski*

Background information

Comprehensive information on various aspects of shape memory alloys from the perspective of continuum mechanics can be found in my book, "*Pseudoelasticity of Shape Memory Alloys Theory and Experimental Studies*"
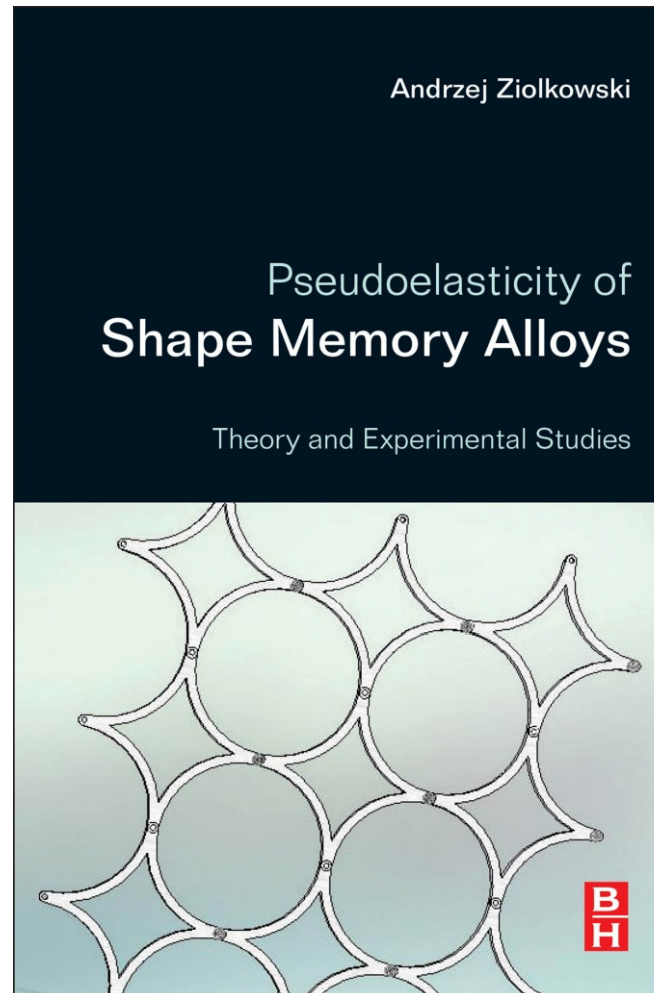
Ziółkowski A. (2015) Pseudoelasticity of Shape Memory Alloys, Theory and Experimental Studies, Butterworth-Heinemann, Elsevier. Title page photo originates from chapter Tarnita D. et al. "Orthopaedic Modular Implants Based on Shape Memory Alloys" in Biomedical Engineering – From Theory to Applications, www.intechopen.com.

Functional shape memory effects

F=0
1
$A_f < T$

Hot temperature
F>0
2

← Pseudoelasticity

Stress / Strain

1
2

Cold temp
2
F=0
1
Hot temp

F↓
2
2
cooling
3
4, F=0
F=0

4, F=0 → 5=1
heating

Strain / Temperature

3
4
5
2
1

← One way memory effect

Cold temp
2
F=0
1
Hot temp

cooling
heating

Strain / Temperature

Stress = 0
2
Hot
Cold
1
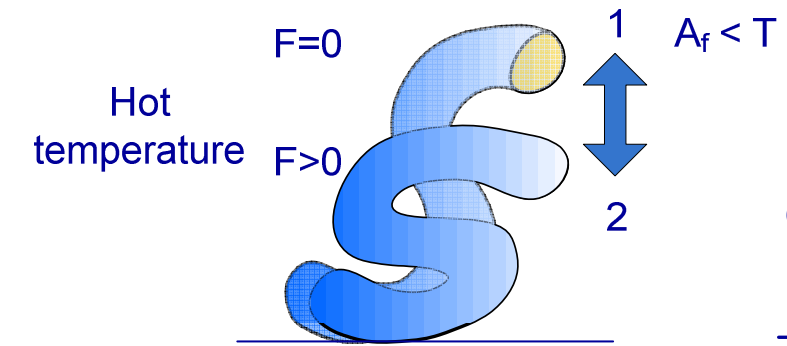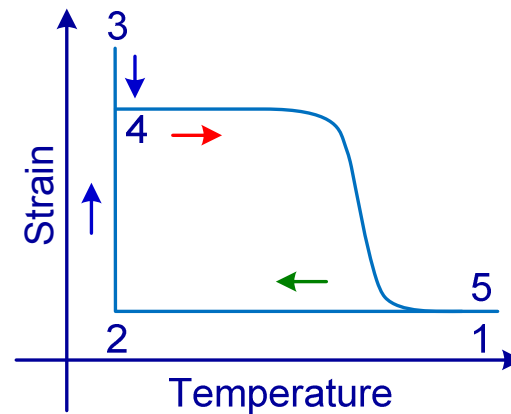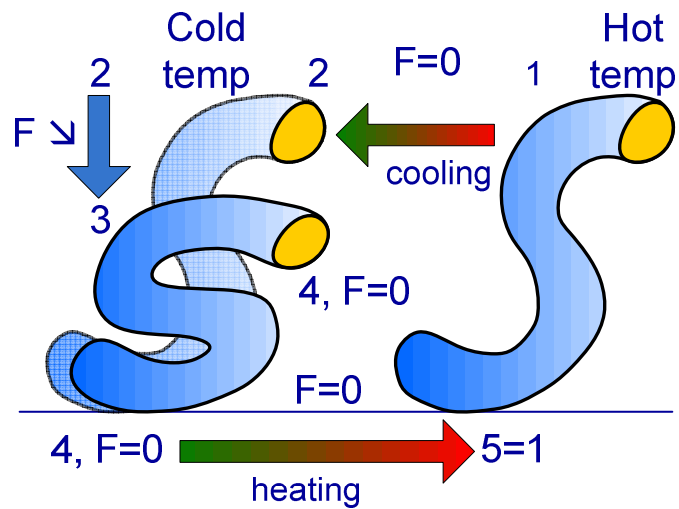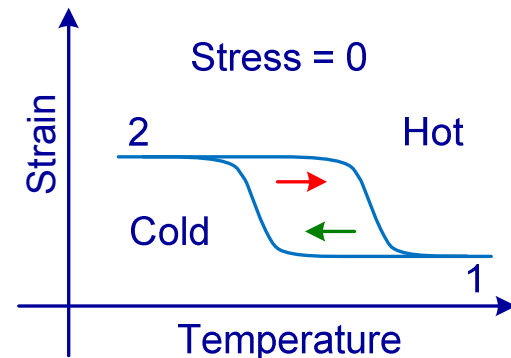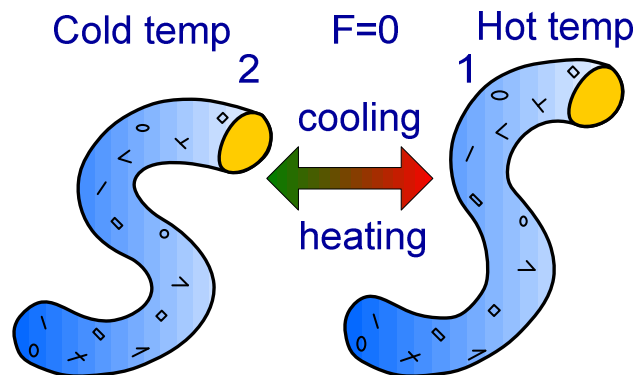
←Two way memory effect

Utility properties of shape memory alloys

Wide variety of metallic alloys exhibit shape memory effects. Three main groups attract special attention NiTi-based, Cu-based and Fe-based alloys – in view of their commercial success.

They exhibit wide variety of utility properties such as:
- stiffness (compliance)
- yield stress
- ultimate tensile strength
- elongation to failure
- fatigue resistance,
- corrosion resistance,
- wear
- forming properties

- cold working
- machinability fatigue resistance
- weldability
- easiness of chemical control
- biological compatibility
- critical stress for phase transition
- cost
- and many more

The specific utility features of some material frequently makes as important factor for its selection to be used in specific application as its functional properties.

Classification of research/development activities

The complicacy of research work efforts and involvement of different methods, techniques and equipment connected with gaining relevant knowledge/skills resulted in division of research activities into two main streams of *pure science* and *applied science*.

The following problems in the domain of SMA materials can be classified as belonging to *pure science*:

- acquiring knowledge on specific behavior of the specific material,
- efforts to discover processes undergoing in the material and understand their mechanisms,
- development of a theory of coherent phase transitions,
- gaining knowledge on kinetics of thermoelastic phase transformation,
- gaining knowledge on behavior of SMA materials under complex thermo-mechanical loadings,
- development of ab-initio numerical models of martensitic transformation
- discovery of criteria for forward and reverse phase transition
- and many others

Scientific Research = Seeking Truth about Nature,
Knowledge = Understanding of occurring phenomena,   Post truth = Lie
Wisdom = Capability of/and using of knowledge

Classification of research/development activities

The *applied science* problems in the case of SMA materials can embrace:

- development of manufacturing technologies in macro-, micro- and nano-scale. For example by alloying, powder sintering, magnetron sputtering,
- elaboration of thermo-mechanical processing routes for attaining required utility/functional properties,
- development of forming and/or joining technologies,
- elaboration of design methods and tools,
- design of engineering mechanisms and/or devices made with SMA materials,
- elaboration of steering algorithms for control of functional behavior,
- and many others

Classification of research/development activities

Schematic map of various thermomechanical treatments to obtain required properties of SMA materials – application oriented research.

Thermo-mechanical treatment (TMT) of SMA materials

Alloying

Annealing, aging, quenching (solution, homogenization recovery, recrystallization), Grains (size, shape, distribution), Precipitates ● (size, distribution, type, coherent, semi-coherent), – e.g. Ti_3Ni_4, Ti_2Ni_3, $TiNi_3$ Inclusions ● (size, distribution, affinity) – e.g. TiC, $Ti_4Ni_2O_x$, Trace elements ● – e.g. B, Ta, ...

Cold work, Hot work Dislocations, Vacancies, Stacking Faults (size, layout, distribution, patterns, ordering), Grains (shape, orientation), ...

Combined effects due to mutual couplings

Loading: (Stress, Temp)

Phase transformation (type, kinetics, charact. temperatures., heats of p.t., ...)

Shape memory alloys applications

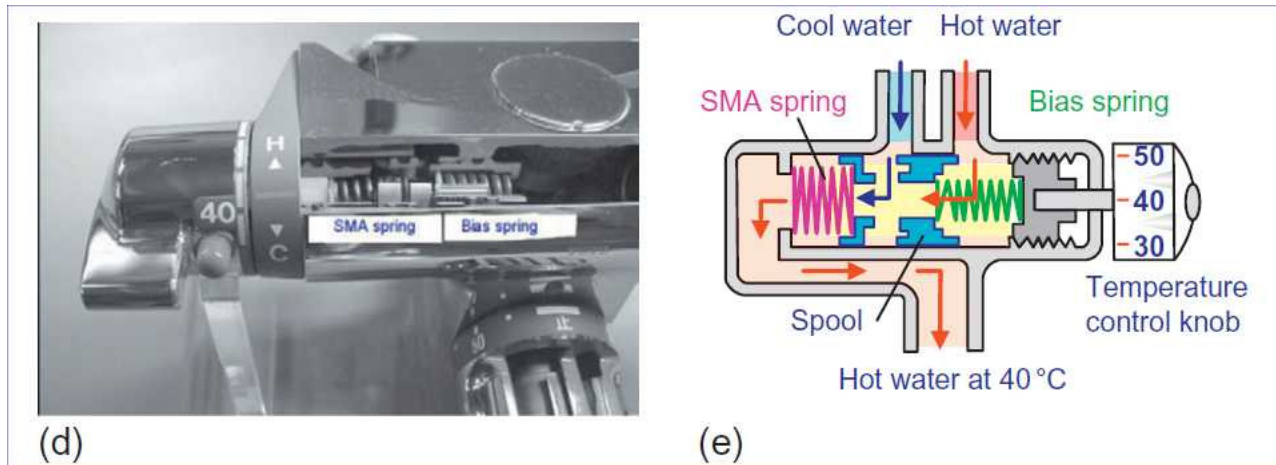Engineering applications of modern materials can be relatively simple or quite elaborate

Growing degree of complexity

(a) NiTi fishing line (0.045-0.085 mm) after Morris Co Ltd.; (b) orthodontic wire after Okhata (2011); (c) NiTi stent (Cordis SMART stent) exhibiting extreme crushing resistance after Stoeckel et al. (2009); (d), (e) water temperature regulator and scheme of operation principle za Suzuki (2011).

Figure after Ziółkowski A. (2015) Pseudoelasticity of Shape Memory Alloys, Theory and Experimental Studies

Shape memory alloys applications

Advanced technologically applications of SMA materials
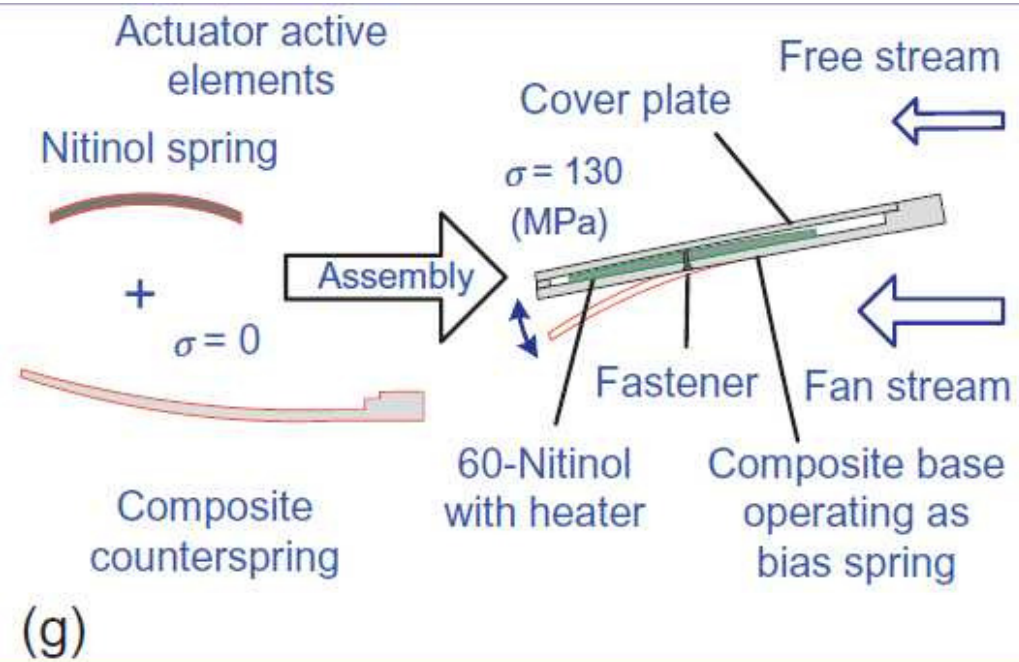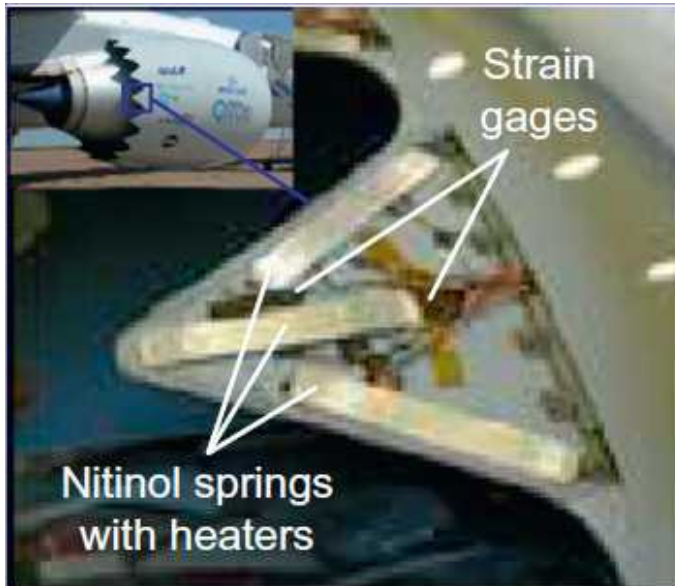
Variable geometry chevron for noise control of a jet engine and scheme of operation principle, after Mabe et al. (2006). Courtesy Boeing.

Festo BionicOpter, inspiration dragonfly flight, after Fig. 18. in Jani (2014)

Shape memory alloys applications

Concepts of advanced technologically applications of SMA materials

Prosthetic hand powered by SMA actuators, after Fig. 16. in Jani (2014)

Micro-gripper with SMA actuator, after Fig. 17. in Jani (2014)

(a) Micro-gripper design

(b) Micro-gripper fabricated sample and working principle
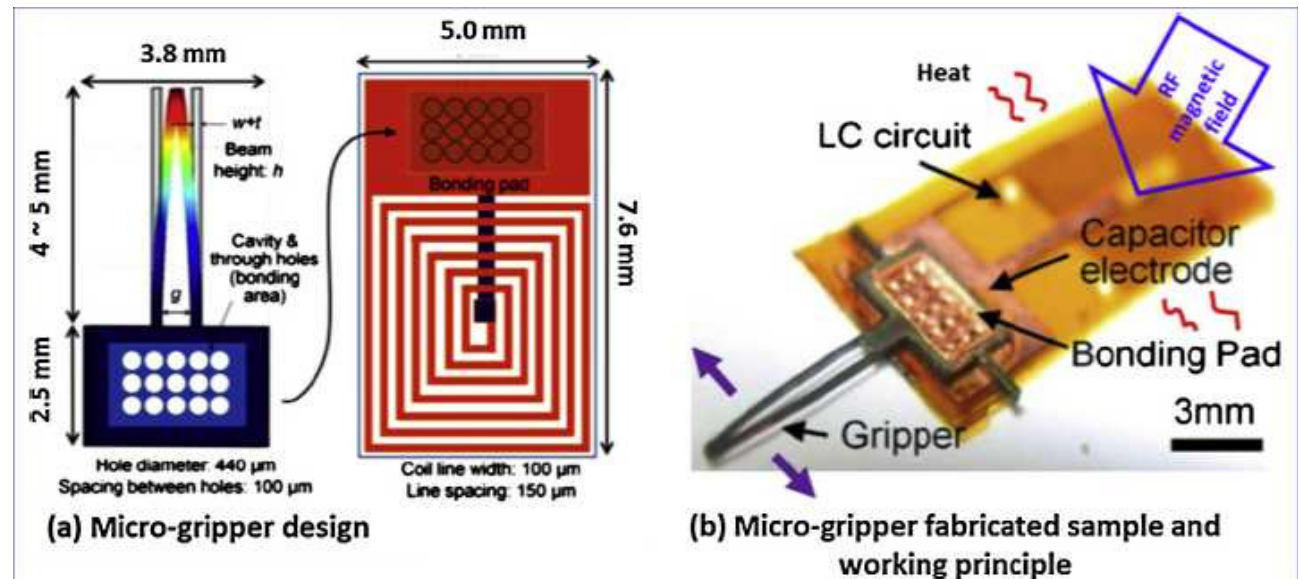
Scientific problem formulation

The key subject matter of the present work is development of *thermodynamic model of SMA materials behavior*. capable for simultaneous description of pseudoelasticity and one way memory effect.

The attention will be focused on *obtaining explicit form of Gibbs function* the most relevant for SMA materials. The methodology of micromechanics and homogenization will be employed.

The elaboration of thermodynamic model SMA materials and proposal of the most appropriate form of free enthalpy (Gibbs) function still constitutes at present an *open scientific problem*.

Proposal of possibly the most appropriate, explicit form of macroscopic Gibbs function of SMA materials makes vital contribution both in pure and applied science of SMA materials.

Generic features SMA materials behavior

Result of differential scanning calorimetry (DSC) test for Ni51at-Ti SMA.

Δu= 17.5 kJ/kg

Heat Flow (W/g)

305.38K

193.15K

250.19K

311.81K
17.32J/g

303.25K
268.56K 17.71J/g 319.19K

309.50K

Sample: NiTi_Japan_rod_400C_1h, Size: 17.1600 mg

Exo Up

Temperature (K)

Universal V4.7A TA Instruments
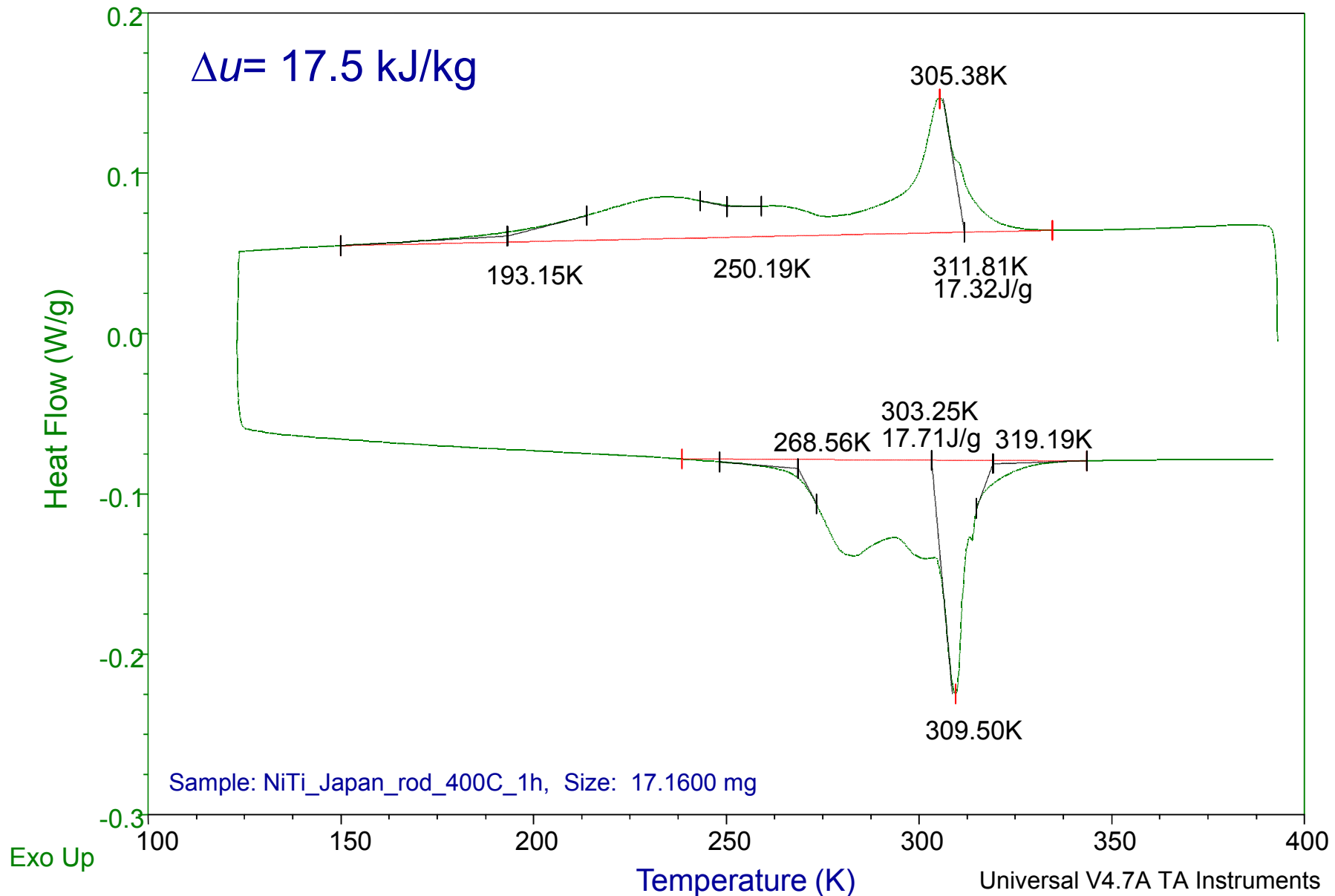
Generic features SMA materials behavior

(1) Chart stress $\leftrightarrow$ volume fraction of martensite (σ, z), (2) Chart strain $\leftrightarrow$ volume fraction of martensite (ε, z) for CuZnAl alloy simple tension, loading-unloading cycle. Volume fraction of martensitic phase determined from electrical resistivity measurements. Redrawn after (Vacher and Lexcellent, 1991).
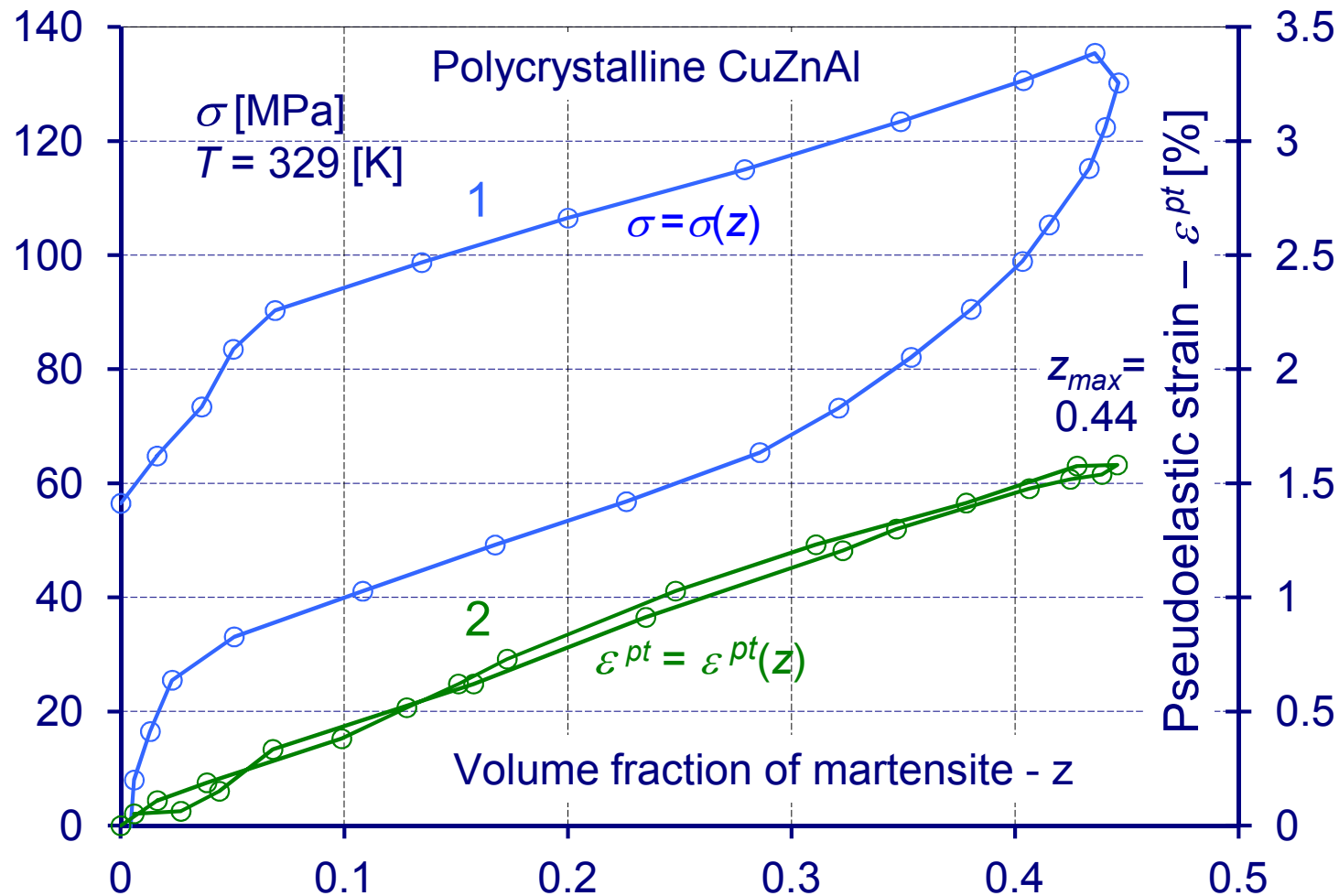
Measured:

$$\sigma(t), \varepsilon(t), \rho_{el}(t)$$

Calculated:

$$\rightarrow k\rho_{el}(t) = z(t)$$

$$z(t), \varepsilon(t), \sigma(t)$$

$$\rightarrow \varepsilon(z), \sigma(z)$$

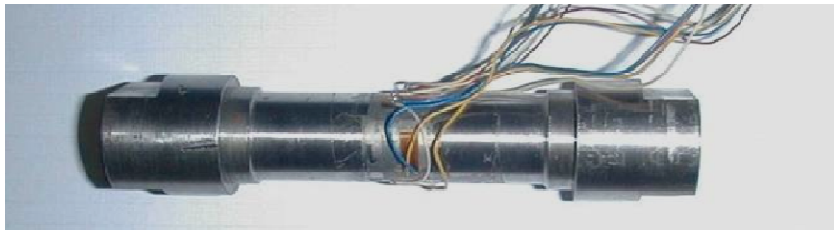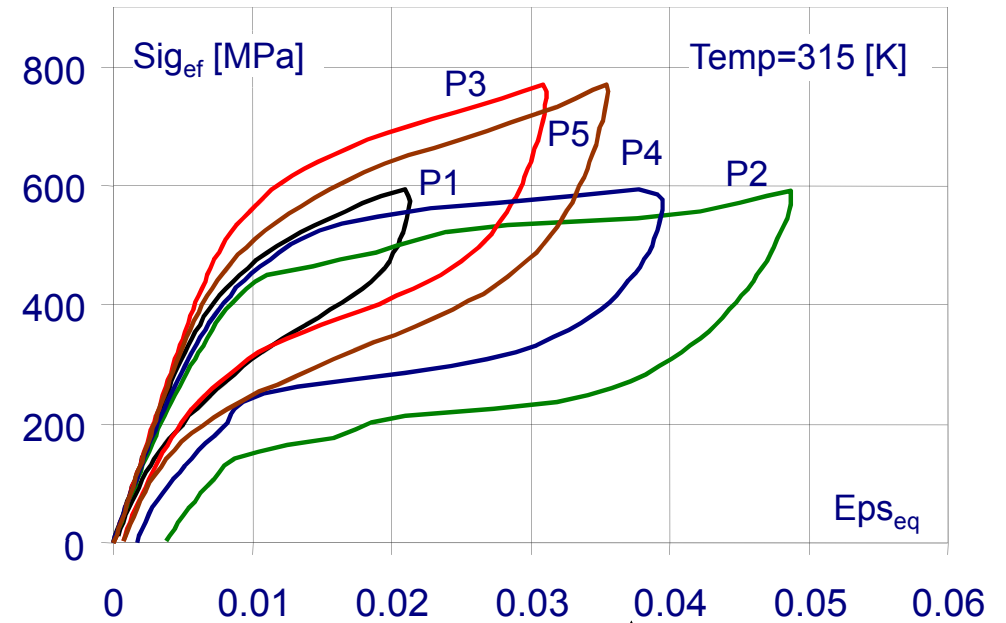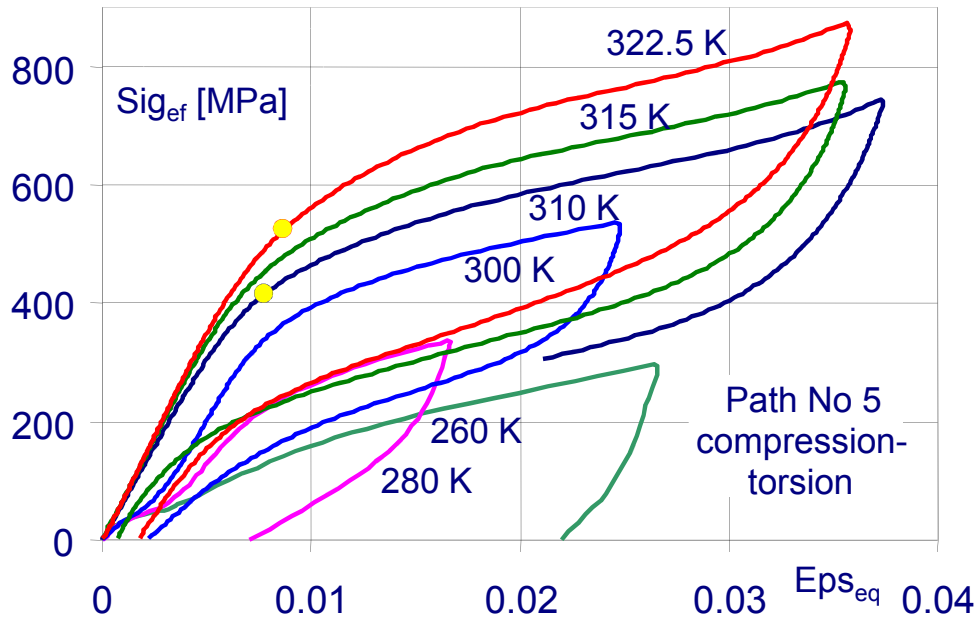$$\varepsilon^{pt}(z) = \varepsilon(z) - \frac{\sigma(z)}{E}$$

Conclusion:

$$\varepsilon^{pt} = z \cdot \gamma_{tn}$$

Conclusion can be inferred that macroscopic phase transformation strain is directly proportional to volume fraction of stress induced martensitic phase.

Generic features SMA materials behavior

Isothermal, mechanical behavior of NiTi submitted to *proportional paths of multiaxial, stress loadings* at higher temperatures.

Pseudoelastic behavior is exhibited at higher temperatures

Path No 5 compression-torsion

322.5 K
315 K
310 K
300 K
260 K
280 K

Sig_{ef} [MPa]
Eps_{eq}

Temp=315 [K]

P3
P5
P4
P1
P2

Sig_{ef} [MPa]
Eps_{eq}

NiTi Tubular specimen

P1 - torsion,
P2 - tension,
P3 - compression,
P4 - tension-torsion,
P5 - compression-torsion

$\sqrt{3}\tau$
y=0
y=-11/16
$-\sigma_z=\tau$
y=11/16
$\sigma_z=\tau$
5   1   4
60°
3   2 σ_z
y=-1   y=1
y = cos(3θ)
θ–Lode angle

Raniecki B., Tanaka K., Ziółkowski A (2001) Testing and modeling of NiTi SMA at complex stress state – selected results of Polish-Japanese research cooperation. MSRI 2, 327-334.

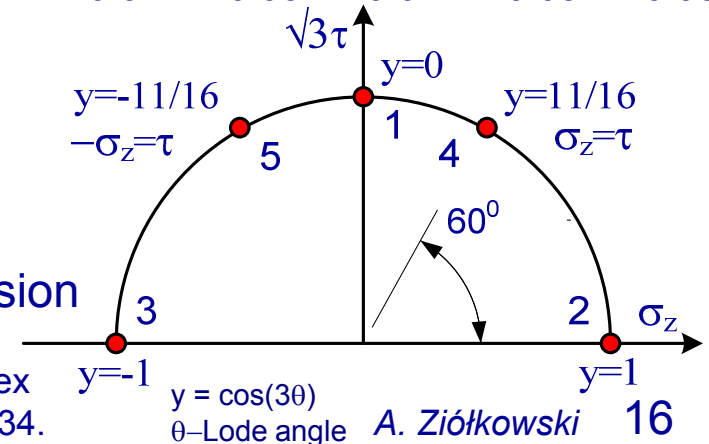*A. Ziółkowski*   16

Generic features SMA materials behavior

Isothermal, mechanical behavior of NiTi alloy submitted to *proportional paths of multiaxial, stress loadings* at lower temperatures.

Amplitude of residual transformation strain strongly depends on *loading path direction* in space of stress tensor components.
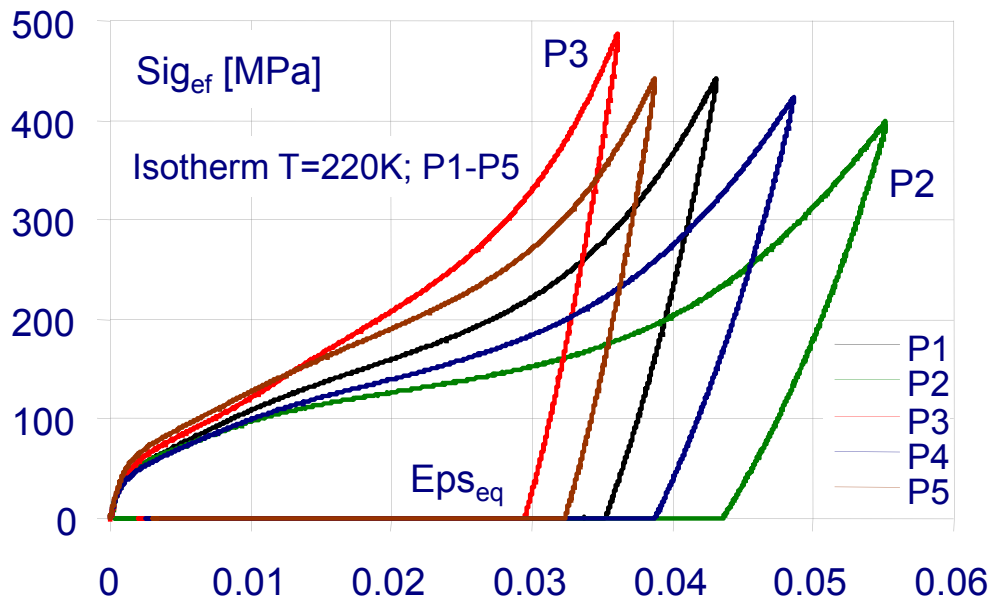
Upon heating the residual transformation strains disappear - *one way memory effect*.
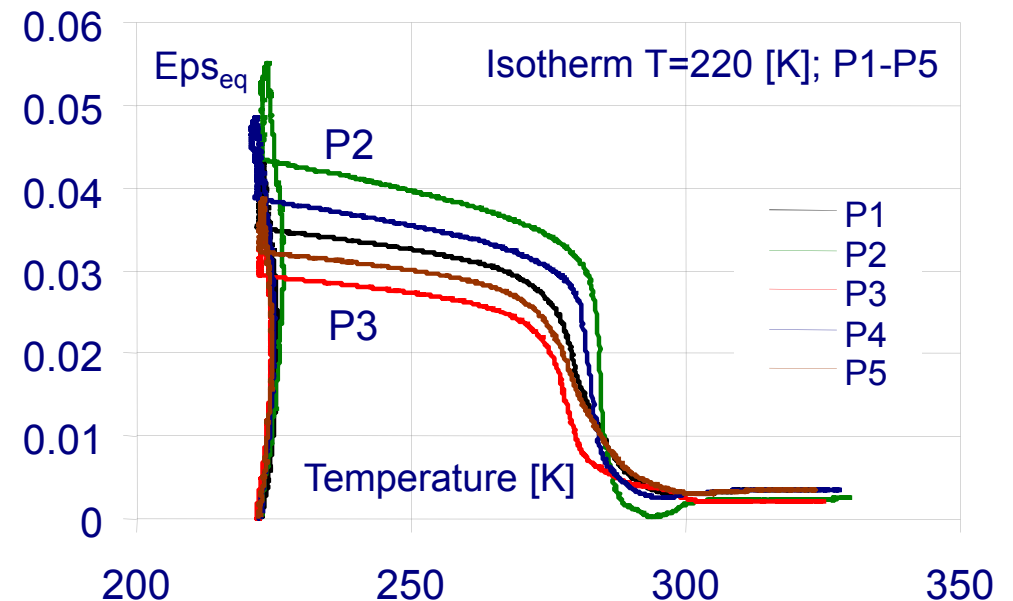
Generic features SMA materials behavior

Isostress behavior of NiTi submitted to one cycle of temperature loading at different values of *constant assisting stress*.

Strain transformation amplitude saturates at some level of assisting stress. It is due to full reorientation of martensitic phase.
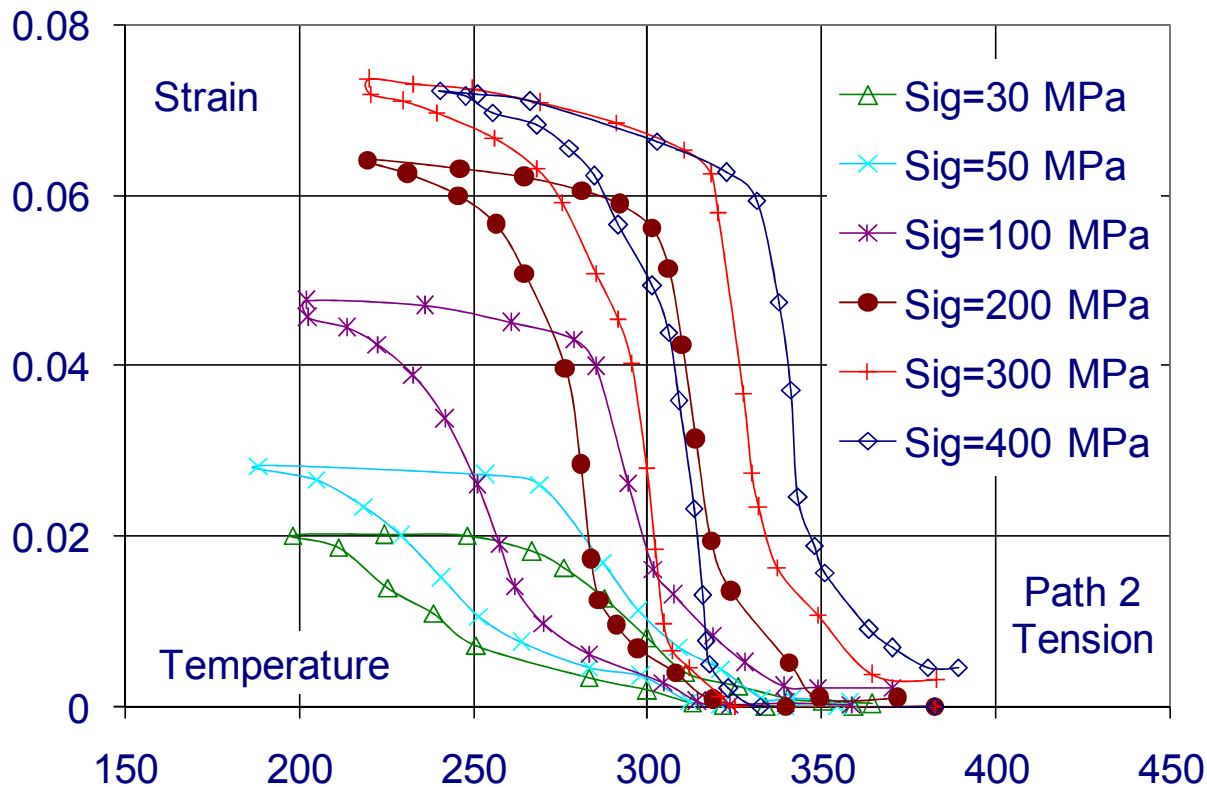
Amplitude of transformation strain strongly depends on the *value of assisting stress*.

Raw data after K. Tanaka, K. Kitamura, S. Miyazaki, Arch. Mech. 51, 1999
Elaboration Ziolkowski, Raniecki (unpublished).

Generic features SMA materials behavior

Isostress behavior of NiTi submitted to one cycle of temperature loading for *different directions of loading paths* (assisting stress σ_{ef}=50MPa).

Strain transformation amplitude saturates at some level of assisting stress.
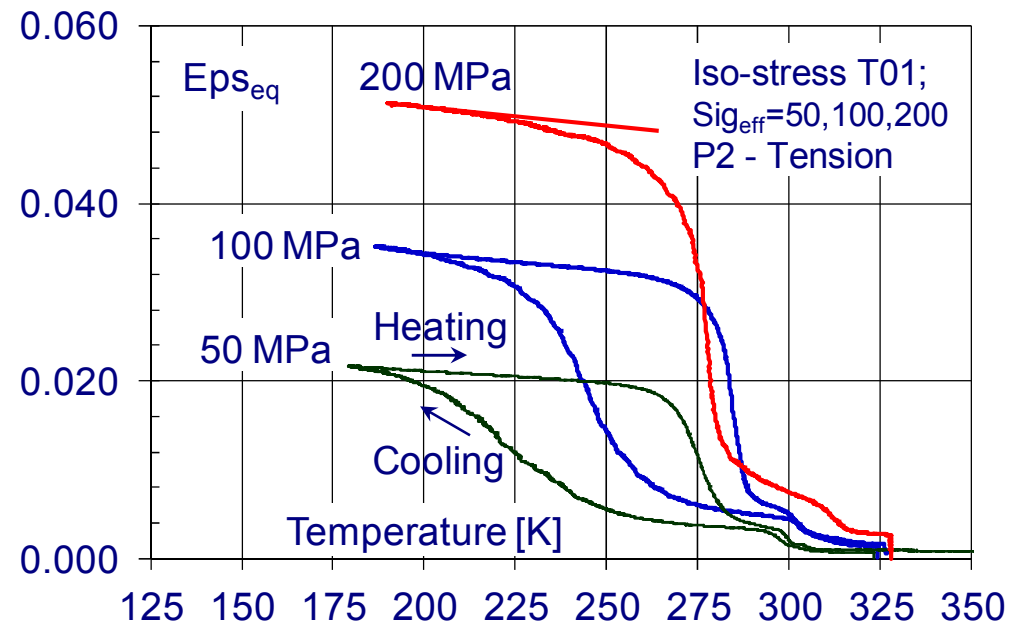
Amplitude of residual transformation strain strongly depends on *loading path direction* in space of stress tensor components.

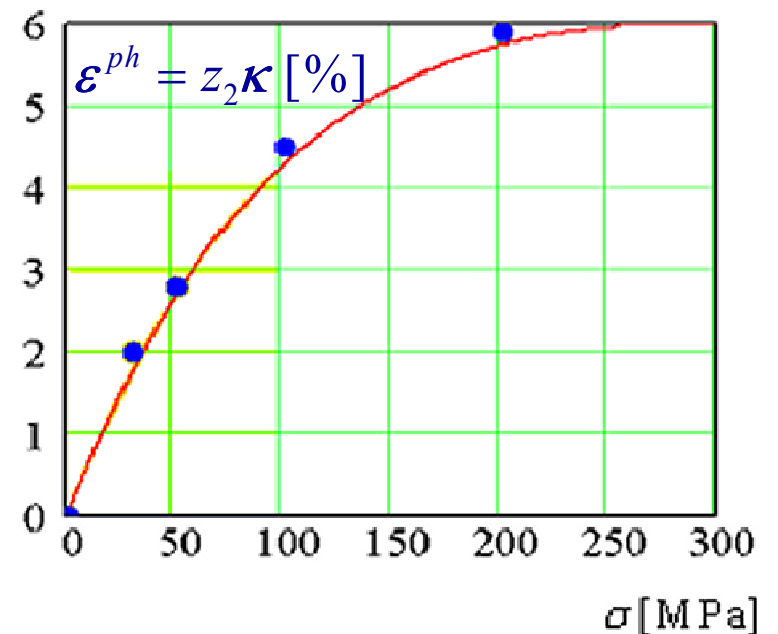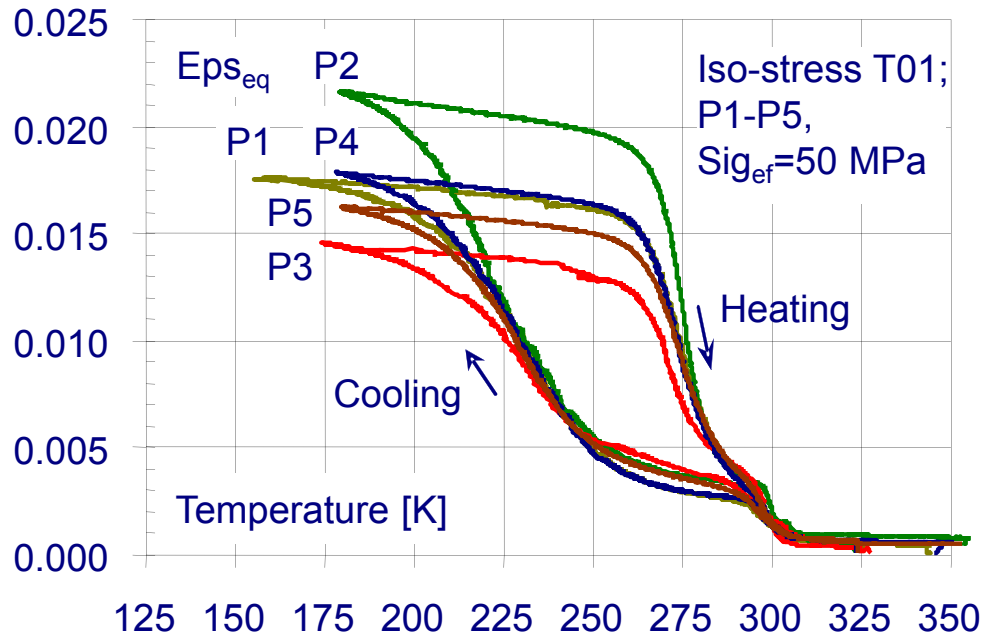# Generic features SMA materials behavior

Behavior of NiTi alloy submitted to CCW and CW loading programs composed of *two isothermal* and *two izostress segments*. These testing programs can be regarded as counterparts of *working cycles of heat machines*, heat engine (CW - clockwise cycle) and heat pump (CCW - counterclockwise cycle).
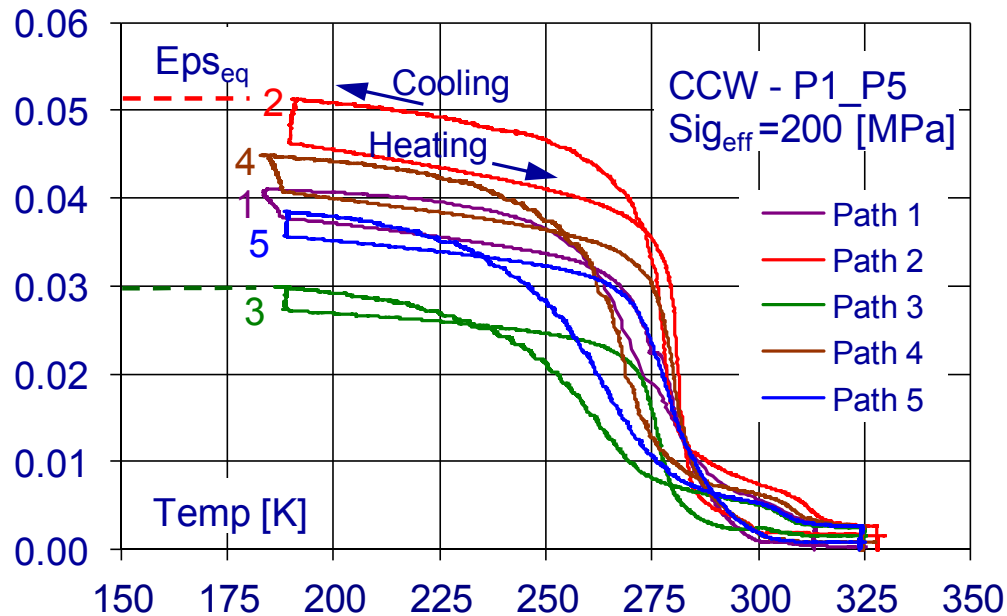
Thermomechanical tests for five multiaxial paths of loadings with maximum loading stress of 200 [MPa] in couterclockwise direction – CCW,
(σ_{ef}=0↗200MPa,T=325K)→(σ_{ef}=200,T=325↘190)
→(σ_{ef}=200↘0,T=190)→(σ=0 MPa,T=190↗325K).
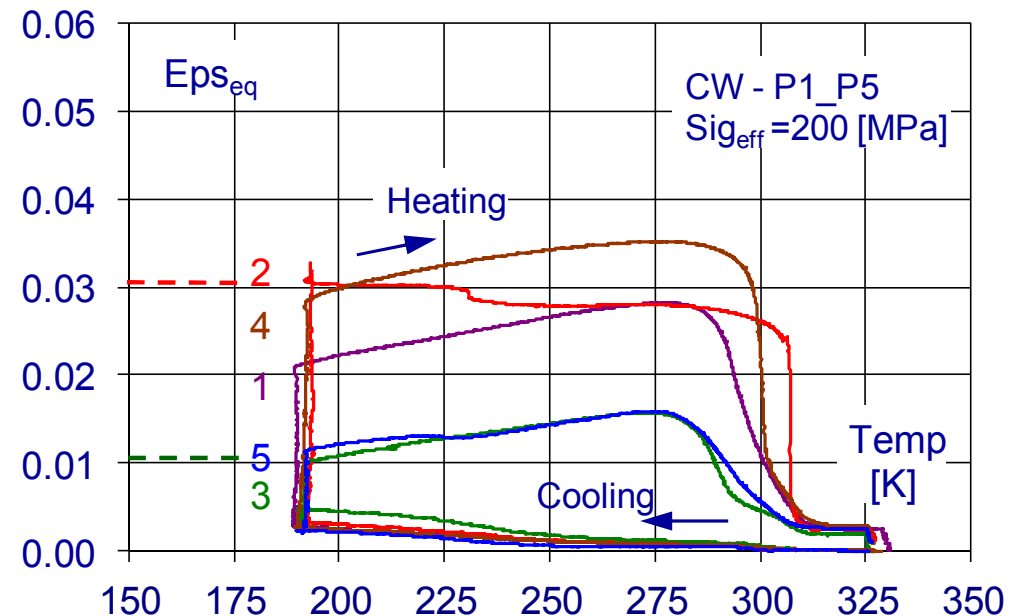
Thermomechanical tests for five multiaxial paths of loadings with maximum loading effective stress of 200 [MPa] in clockwise direction – CW,
(σ_{ef}=0MPa,T=325↘190K)→(σ_{ef}=0↗200,T=190)→
(σ_{ef}=200,T=190↗325)→(σ_{ef}=200↘0MPa,T=325K).

Generic features SMA materials behavior

The NiTi alloy submitted to CW and CCW testing programs revealed the effect of *strong dependence of strain magnitude on the order of consecutive purely thermal and purely mechanical (multiaxial) loading segments*.

When NiTi alloy goes from the state (σ_{ef}=0MPa,T=325K) to the state (σ_{ef}=200MPa,T=190K), when submitted to loading segments in the order of *CW cycle*, then the *strain effect* is nearly *two times smaller*, in comparison to the strain effect when the state (σ_{ef}=200,T=190) is reached by the material in the order of loading segments of *CCW cycle*. This effect is exhibited in the case of each direction of multiaxial, mechanical loading path. For example in the case of path No 1 (torsion) process (σ_{ef}=0,T=325)$\rightarrow$(0,190)$\rightarrow$(200,190) – CW half cycle, leads to equivalent strain ε_{eq}=~2%, while process (σ_{ef}=0,T=325)$\rightarrow$ (200,325)$\rightarrow$(200,190) – CCW half cycle, leads to equivalent strain ε_{eq}=~4%.

Research on the impact of *history of thermomechanical loadings* on SMA materials *deformation effects at lower temperatures* - when the material is in martensitic state, constitutes at present *open scientific problem*

Generic features SMA materials behavior

The NiTi alloy preloaded mechanically at low temperatures, to obtain oriented martensitic phase, *exhibits large thermostriction effect*, – below reverse p.t. temperature. Upon temperature cycling the *strain diminishes and grows in response to increase and decrease* of the sample temperature. The size of the effect strongly depends on maximum value of mechanical pre-load applied to the NiTi material (amount of oriented martensite). In the case $Ni_{50at\%}$-Ti alloy, pre-loaded up to 500 MPa, the strain varies by about 0.6 [%] upon temperature variation amplitude of 75 degrees. Research on *thermostriction effect* of SMA materials constitutes at present *open scientific problem*.

Samples of $Ni_{50at\%}$-Ti alloy were cooled under assisting stress of 20 MPa, from temperature 110°C to – 65°C, i.e. below M_f^0 temperature. At temperature –65°C they were loaded isothermally to maximum effective stress of 20, 130, 200 and 500 MPa respectively, and unloaded to 20 MPa. Finally the samples were heated from temperature –65°C to 110°C with assisting stress of 20 MPa. During heating segment the intermediate temperature cycle was executed (–40 →+25→ –40 →+25 C < $A_s^{2\text{-}1}$=54°C).
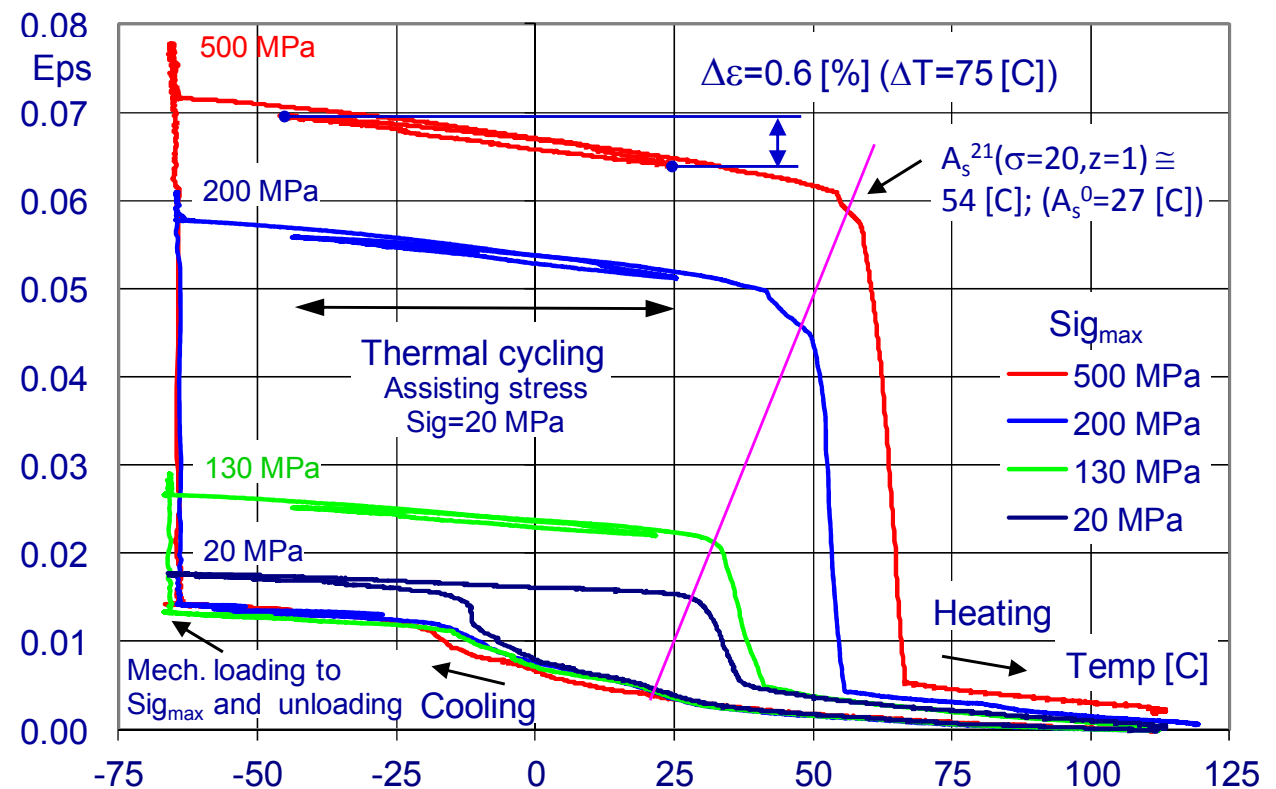
Generic features of SMA materials behavior

Macroscopic thermo-mechanical behavior of SMA materials in stress-strain temperature coordinates. Not to scale. (a) one-way memory effect; (b) pseudoelasticity with internal hysteresis loops and plastic slip deformation.
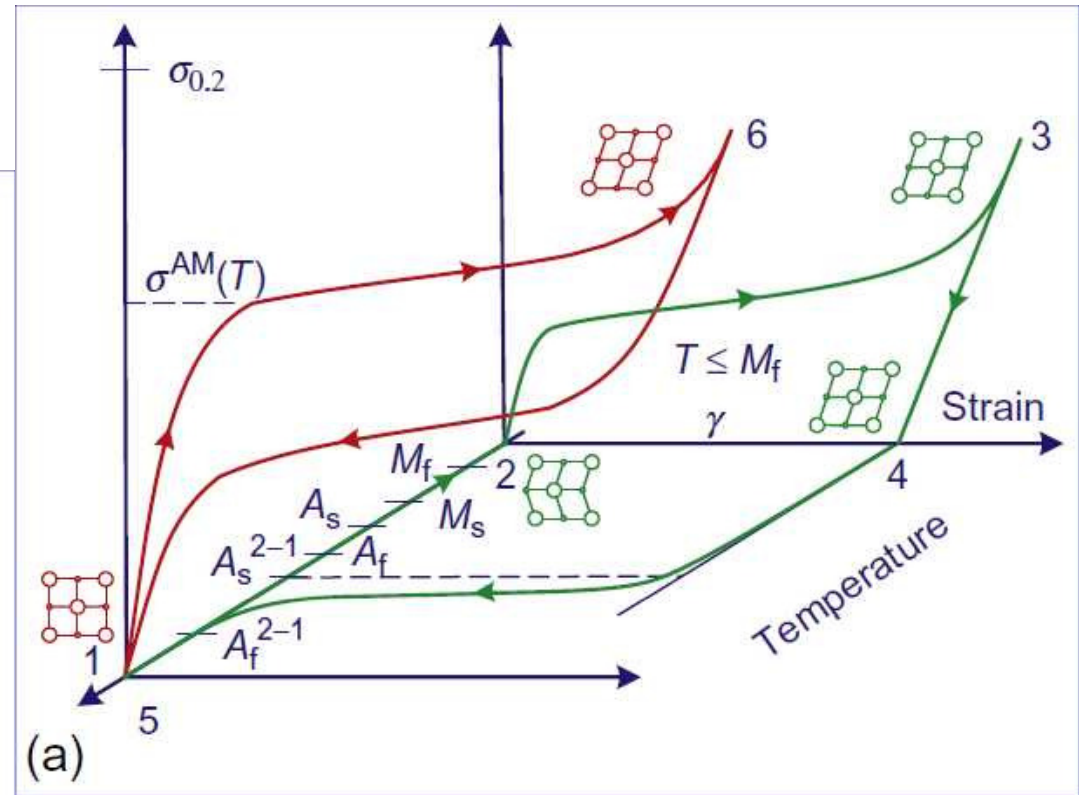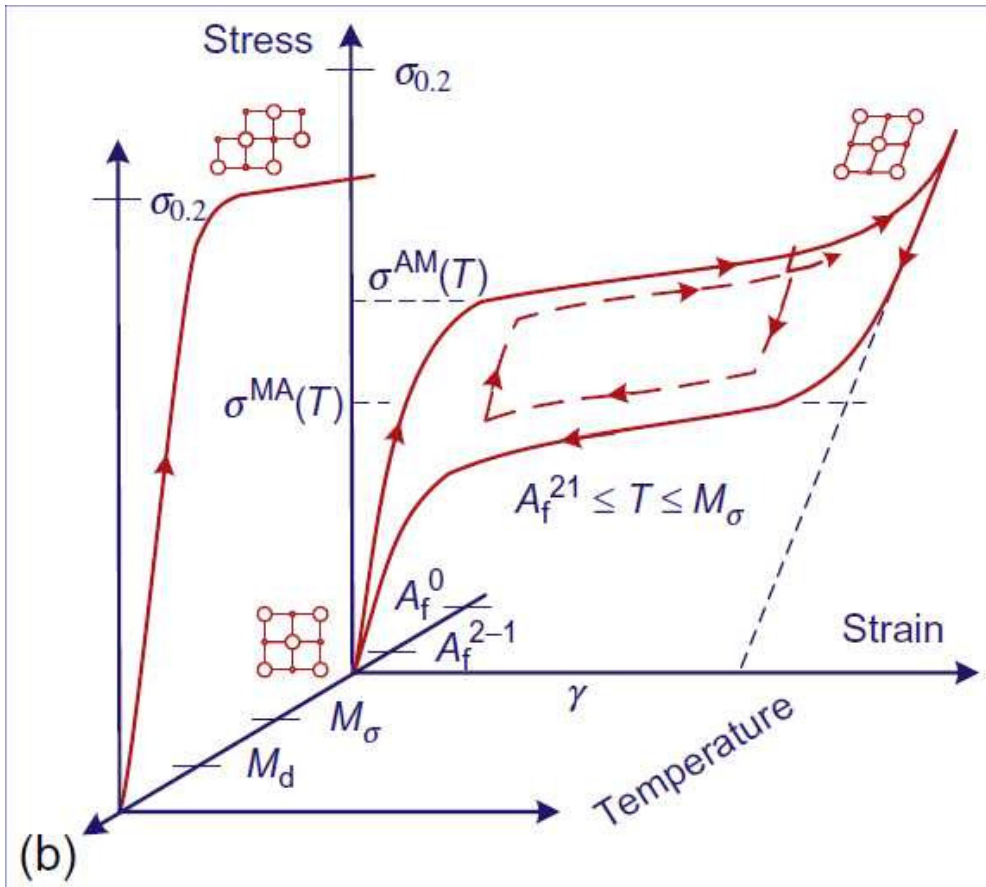
Thermodynamic fundamentals

As it was found out that the physical mechanism underlying SMA effects are phase transitions, apparatus of thermodynamics seems to be the most appropriate/natural tool for their description.

Considerable portion of phenomena exhibited by SMA materials can be described using *equilibrium thermodynamics*.
The development of equilibrium thermodynamics was practically ended at the turn of the 19th and 20th centuries. Probably as the crowning gem of development works on equilibrium thermodynamics there can be recognized, the masterpiece of Willard Gibbs "On the equilibrium of heterogeneous substances" published in the years 1876-1878, where Gibbs introduced the concept of *chemical potential*.
The work was translated into German in 1892 and into French in 1899.
The development of *non-equilibrium thermodynamics* was started in XX century and is continuously subject of intensive research works. Many streams of non-equilibrium thermodynamics exist.

The methodology of *non-equilibrium thermodynamics with internal state parameters* will be used here.

Muller I. (2007) History of Thermodynamics, Springer (excellent book on what thermodynamics and its underlying philosophy).
Horstenmeyer M., Bammann D (2010) Historical review of internal state variable thermodynamics for inelasticity, Int. J. Plast.
Kestin J. (1979) A course in Thermodynamics.

Thermodynamic fundamentals

For description of thermodynamic processes taking place in the material there must be introduced relevant *thermodynamic parameters/variables*, e.g. temperature (T), pressure (p), volume (V).

Two classes can be distinguished among them: *intensive thermodynamic parameters*, which *do not change* when the amount (mass/number of moles) of the material undergoing thermodynamic process is changed, e.g. temperature T or pressure p, and *extensive thermodynamic parameters*, which *change linearly proportionally* with the amount (mass) of the processed material, e.g. volume V, or entropy S.

There can be distinguished conjugate pairs of extensive and intensive parameters (*thermodynamic forces and thermodynamic fluxes*) e.g. $p \leftrightarrow V$, $T \leftrightarrow S$, $\pi \leftrightarrow z$ etc.

It proved useful to introduce various *thermodynamic functions* for convenient description of *thermodynamic properties/state* of a substance/material. The most commonly used are: *internal energy U, enthalpy H, free energy* F (Helmholtz function), or *free enthalpy* G (Gibbs function) defined as follows

$$H \equiv U + pV, \quad F \equiv U - TS, \quad G \equiv U - TS + pV; \quad \leftarrow U = U(T,V)$$

See also: Hillert M. (2008) Phase Equilibriums, Phase Diagrams and Phase Transformations, Cambridge University Press

Thermodynamic fundamentals

Formalism of thermodynamics can serve probably as a model field where preserving strict mathematical precision plays a key role, where "*devil is in details*".

Even *minor/trivial imprecision* can cost long hours of seeking error, and neglecting perceptiveness can *push/lead one into onerous and costly operations* and beyond (on top) of that to relatively poor quality results.

There can be listed several sources of arising difficulties and motivations for choosing as it could seem initially eccentric path/methodological approach, e.g.:

- thermodynamic function expressed in terms of a *set of some variables* is *much more useful/convenient* than when it is expressed, in mathematically completely equivalent manner, with different set of variables,

- partial derivatives of thermodynamic functions determined with *different variables kept constrained* (constant) have completely *different physical meaning*,

- some of the thermodynamic variables can be *experimentally measured or constrained directly/easily*, for example temperature T or volume V, while the other *actually cannot be directly experimentally measured* (or when measurement is possible it is quite difficult/thus expensive), for example entropy S or internal energy $U.$

Thermodynamic fundamentals

In order to be able to evaluate the instantaneous values of thermodynamic parameters/states of a material submitted to various thermodynamic processes *both* the so called *thermal equation of state* and *caloric equation of state* must be known explicitly. Naturally they must be determined in some program of experimental tests. How this can be done?

Thermal equations of state $p=p(T,V)$?

$$\text{measurement} \rightarrow p(T,V); \quad (\sigma = E[\varepsilon + \alpha(T - T_0)])$$

Caloric equation of state $U=U(T,V)$?

$$dU(T,V) = \left(\partial U / \partial T\right)_V dT + \left(\partial U / \partial V\right)_T dV$$

$$\text{measurement} \rightarrow C_v(T,V) \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

$$\text{measurement} \rightarrow C_p(T,V) \rightarrow \frac{(C_p - C_V)}{\left(\partial V / \partial T\right)_p} = \left(\frac{\partial U}{\partial V}\right)_T \leftarrow \overbrace{\left(\frac{\partial U}{\partial T}\right)_p}^{\equiv C_p} - \overbrace{\left(\frac{\partial U}{\partial T}\right)_V}^{\equiv C_V} = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Formula for differentiation of a composed function

$$Z = Z(X(Y,W),Y)$$

$$\left(\frac{\partial Z}{\partial Y}\right)_W = \left(\frac{\partial Z}{\partial Y}\right)_X + \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_W$$

$$Z = U, Y = T, X = V, W = p \downarrow$$

Thus, after experimental determination of relations $p(T,V)$, $C_v(T,V)$ and $C_p(T,V)$ finally internal energy $U=U(T,V)$ can be determined by integration

$$U(T,V) = \int_{U_0}^{U} dU(T,V)$$

$$\frac{\partial U}{\partial T} = ???$$

Can internal energy function be determined more effectively?

Thermodynamic fundamentals

I and II Law of thermodynamics (balance of energy and definition of entropy)

$$dU = dQ + dW; \quad dQ = TdS, \quad dW = -pdV$$

leads to *Gibbs equation*

$$dU(S,V) = \overbrace{T\,dS}^{I\,L.T.} + \underbrace{(-p)dV}_{dW}, \quad dU(S,V) = \overbrace{\left(\frac{\partial U}{\partial S}\right)_V}^{\equiv T} dS + \overbrace{\left(\frac{\partial U}{\partial V}\right)_S}^{\equiv -p} dV$$

(with $\underbrace{T\,dS}_{dQ(II\,L.T.)}$)

Gibbs equation reveals that when *internal energy* function is known in *explicit form U=U(S,V)* as function of *entropy and volume* (thermodynamic fluxes) then conjugated with them temperature and pressure (thermodynamic forces) can be straightforwardly calculated by simple differentiation ($T\leftrightarrow S$, $p\leftrightarrow V$).

Internal energy function *U=U(S,V)* is called *fundamental relation (equation of state)*. This specific form of *U* earned the special name because when its explicit form is known then *all thermodynamic properties* of a material can be unveiled from this *single relation*.

The *fundamental relation* can be treated as a kind of *DNA of a material*.

Internal energy function expressed in terms of *S* and *V* is called *thermodynamic potential* and *S* and *V* are called *natural (canonic) variables* for *U*.

Thermodynamic fundamentals

When thermal $p(T,V)$ and caloric $U(T,V)$ equations of state are known explicitly then by integration of Gibbs equation there can be obtained relation for entropy expressed in terms of temperature and volume $S=S(T,V)$.

$$dS = (1/T)(dU + pdV), \quad dU/T = (C_v/T)dT + [(\partial p/\partial T)_V - (p/T)]dV$$

$$\rightarrow dS(T,V) = (C_v/T)dT + (\partial p/\partial T)_V dV \quad S(T,V) = \int_{S_0}^{S} dS(T,V) \quad C_v \equiv (\partial U/\partial T)_V$$

Next upon inverting this relation temperature can be expressed in terms of entropy and volume $\rightarrow T(S,V)$. When relation $T=T(S,V)$ is known then *fundament equation of state* for internal energy can be obtained $U(S,V)=U(T(S,V),V)$.

Gibbs relation also allows to determine fundamental relations for other popular thermodynamic functions, and in this manner identify their *natural variables*, e.g. for free energy F it is,

$$F \equiv U - TS, \quad dF = dU - TdS - SdT = -SdT - pdV = dF(T,V)$$

Fundamental relations of other popular thermodynamic functions are:

$$H = H(S,P), F = F(T,V), G = F(T,p)$$

Mixed second order derivatives do not depend on order of differentiation. This leads to relations between first derivatives which are known as *Maxwell relations, e.g.*

$$\partial(-\partial F/\partial T)/\partial V = (\partial S/\partial V)_T = (\partial p/\partial T)_V = \partial(-\partial F/\partial V)/\partial T$$

Thermodynamic fundamentals

Profound understanding of *Gibbs equation* and resulting from it *Maxwell relations* together with capability of using this knowledge is worth fortune in *applied sciences*. Let us return again to experimental determination of *caloric equation*.

$$\left(\frac{\partial Z}{\partial Y}\right)_W = \left(\frac{\partial Z}{\partial Y}\right)_X + \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_W$$

$$dU(T,V) = \left(\partial U / \partial V\right)_T dV + \left(\partial U / \partial T\right)_V dT$$

$$Z = U, Y = V, X = S, W = T \downarrow$$

$$p(T,V) \rightarrow -p + T\left(\partial p / \partial T\right)_V = \left(\partial U / \partial V\right)_T \quad \leftarrow \left(\frac{\partial U}{\partial V}\right)_T = \underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{=-p} + \underbrace{\left(\frac{\partial U}{\partial S}\right)_V}_{=T} \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{=(\partial p / \partial T)_V}$$

$$C_v = C_v(T)$$

$$\left.\begin{array}{l} p = p(T,V) \rightarrow T(\partial^2 p / \partial T^2)_V = (\partial C_v / \partial V)_T \end{array}\right\} \rightarrow C_v(T,V) = \left(\partial U / \partial T\right)_V$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T = \frac{\partial}{\partial T}(-p + T\left(\frac{\partial p}{\partial T}\right)_V)_V = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

$$U(T,V) = \int_{U_0}^{U} dU(T,V); \quad dU = C_v dT + [-p + T\left(\partial p / \partial V\right)_T] dV$$

Upon use of thermodynamic equivalence relations internal energy *U=U(T,V)* can be determined upon experimental measurement of *p(T,V)* and $C_v(T)$ only instead of measurement of *p(T,V)*, $C_v(T,V)$ and $C_p(T,V)$. This leads to *huge costs and time savings*.

See also: Muller I. (2007) History of Thermodynamics, Springer.

Experiment and theory - mutual coupling

In order to demonstrate how development of *theoretical thermodynamic model* helps in understanding the material behavior, task for *pure science*, let us discuss an illustrative example of cauotchouc rubber behavior.

In accordance with *Gibbs equation*

$$TdS = dU - PdL \quad (dQ = dU - dW),$$

$$P(T,L) = (\partial U / \partial L)_T - T(\partial S / \partial L)_T,$$

Thus, it can be said that the load *P* has an *energetic and entropic* part.

Maxwell compatibility condition requires that

$$dF = -SdT + PdL \quad \leftarrow F(T,L) = U - TS$$

$$\partial^2 F / \partial T \partial L = \partial^2 F / \partial L \partial T \implies$$

$$-(\partial S / \partial L)_T = (\partial P / \partial T)_L$$
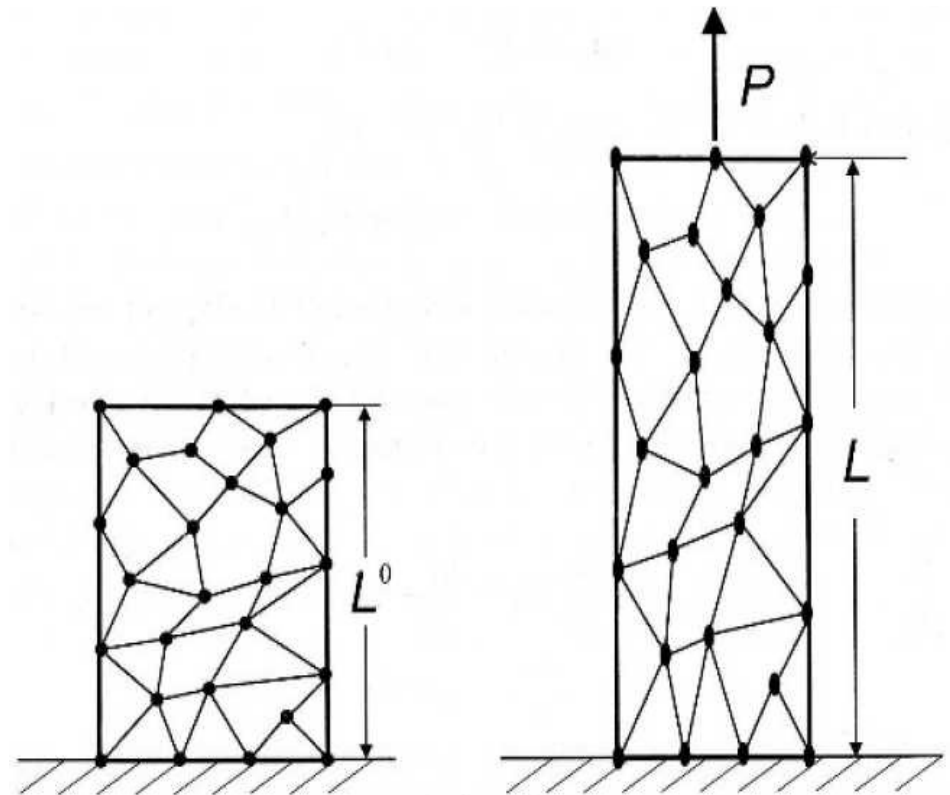
A rubber bar in the unstretched and stretched configurations,
cf. Rubber and Rubber balloons.
Muller, Strehlow (2004)

Experiment and theory - mutual coupling

Entropic part of the tension load may be identified with the slope of tangent to easily obtainable experimentally $P(T)$ curve of a bar with fixed length L. The energetic part can be identified as ordinate intercept of that tangent with Y axis.

Therefore in rubber internal energy U *does not depend on L.*

$$P = \cancel{(\partial U / \partial L)_T} - T(\partial S / \partial L)_T ,$$

$$(P = \cancel{(\partial U / \partial L)_T} + T(\partial P / \partial T)_L)$$

Elastic force in rubber is entropy induced, while internal energy *does not play* role in rubber elasticity.

This fact was first noticed in 1935 by K. Meyer and C. Ferri.

Pressure in ideal gas is also entropy induced that is why sometimes rubber is called "ideal gas among solids".
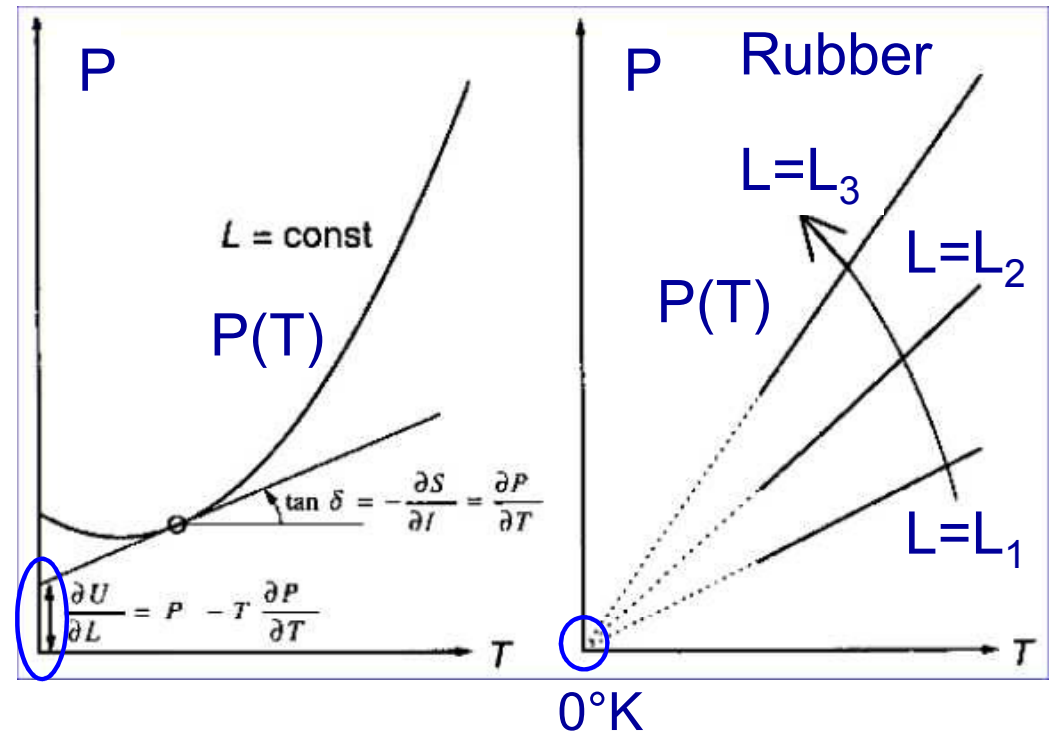
Left: P-T curve for a generic material,
Right: P-T curves for rubber.
Tangent allows to separate/identify *entropic* and *energetic* parts of force.
After Muller, History of thermodynamics.

Experiment and theory - mutual coupling

It would be very difficult task to unambiguously decide, which physical phenomenon actually is responsible for elastic properties of cauotchouc gum without *well coordinated theoretical works* (development of constitutive model of cauotchouc gum behavior) *and experimental works* (execution of well planned program of experimental tests) in order to obtain decisive evidences.

Discussed example of cauotchouc gum and explanation of its specific behavior makes an excellent example of operation of II Law of Thermodynamics and expressed by it law of nature, which can be worded as follows,

CONTINUOS MUTUAL BATTLE OF ENERGY versus ENTROPY

Spontaneously system always tries to take configuration with highest value of entropy (*spontaneous process* results in preservation or *increase of entropy* of the system).
Entropy can decrease, but only on the cost of execution of work over the system (*non-spontaneous process*).

Problem formulation – Gibbs free energy function for SMA's

In the mainstream macroscopic thermodynamic theories of SMA materials usually it is conjectured that representative volume element (RVE) – macroelement of SMA material is in general a conglomerate of two phases austenitic and martensitic ($n=2$). Usually it is accepted that each phase can be treated as linear thermoelastic material. Accordingly the *fundamental equation* for SMA materials *macroelement* is frequently *heuristically* adopted in the following form,

$$g(T,\boldsymbol{\sigma},z) = u_1^0 - Ts_1^0 + z(u_2^0 - Ts_2^0) + c_p[\Delta T - T\ln(T/T_0)]$$

$$- \tfrac{1}{2}\boldsymbol{\sigma}\cdot\boldsymbol{M}\boldsymbol{\sigma}/\rho - \boldsymbol{\sigma}\cdot\boldsymbol{\alpha}(T-T_0)/\rho - \boldsymbol{\sigma}\cdot\boldsymbol{\varepsilon}^{pt}/\rho + \phi^{coh}$$

$$\boldsymbol{\varepsilon}^{pt} = z\boldsymbol{\kappa},\ \ \boldsymbol{\kappa} \equiv \rho\,\partial g^{ult}/\partial\boldsymbol{\sigma},\ \ \rho\,g^{ult}(\boldsymbol{\sigma}) = \boldsymbol{\sigma}\cdot\boldsymbol{\kappa},$$

$$\phi^{coh} = \phi_2^{st}z_2 + \phi_{it}z_1z_2,\ \ \phi_{it} = \phi_{12} - Ts_{12};\ \ \phi_2^{st} = \Delta u_2^{st} - T\Delta s_2^{st}$$

Are the terms appearing in the Gibbs function mutually consistent?

See: Raniecki B., Lexcellent C. (1998) Thermodynamics of isotropic pseudoelasticity in shape memory alloys, Eur.J.Mech., A/Solids.

Problem formulation – Gibbs free energy function for SMA's

Gibbs potential for SMA materials

$$g(T,\boldsymbol{\sigma},z) = (u_1^0 - Ts_1^0) - z\,\pi_0^f(T) + c_p[\Delta T - T\ln(T/T_0)]$$

$$-\boldsymbol{\sigma}\cdot\boldsymbol{\varepsilon}^{th}/\rho - g^{el} - \boldsymbol{\sigma}\cdot\boldsymbol{\varepsilon}^{pt}/\rho + \phi^{coh}$$

Are the terms appearing in the Gibbs function mutually consistent?

$(u_1^0 - Ts_1^0) - z\,\pi_0^f(T)$ free energy of RVE in two-phase state at zero micro-scopic stresses $(\breve{\sigma}(x) = 0)$ – "chemical" free energy

$\pi_0^f(T) \equiv \Delta u^0 - T\Delta s^0 = -\Delta G_{chem}$

$c_p[\Delta T - T\ln(T/T_0)]$ term connected with heat capacity

$\boldsymbol{\sigma}\cdot\boldsymbol{\varepsilon}^{th}/\rho$ $(\boldsymbol{\varepsilon}^{th} = \boldsymbol{\alpha}\,\Delta T)$ term connected with thermal expansion

g^{el} $(\tfrac{1}{2}\boldsymbol{\sigma}\cdot\boldsymbol{M}\boldsymbol{\sigma}/\rho)$ complementary elastic energy

$\boldsymbol{\sigma}\cdot\boldsymbol{\varepsilon}^{pt}$ $(\boldsymbol{\varepsilon}^{pt} = z\,\boldsymbol{\kappa}(h))$ work on phase transition strains

$\rho\,g^{ult} \equiv \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}$ potential of ultimate phase transition eigenstrains

ϕ^{coh} $(\phi_2^{st}z_2 + \phi_{it}z_1z_2)$ coherency energy (necessary for assuring continuity of displacement field in RVE)

$\Delta T = (T - T_0)$

$\Delta u^0 = u_1^0 - u_2^0,\ \ \Delta s^0 = s_1^0 - s_2^0,\ \ \phi_{it} = (\phi_{12} - T\cdot s_{12}),\ \ \phi_2^{st} = (\Delta u_2^{st} - T\cdot\Delta s_2^{st})$

Problem formulation – state parameters

SMA macroelement in prevailing time remains in a state of *constrained thermodynamic equilibrium.*

The following thermodynamic variables were found useful in description of SMA materials behavior:

external state variables:

T, $\boldsymbol{\sigma}$, ε temperature, stress or strain,

internal state variables:

z_α volume fractions of phases,

$\{\boldsymbol{h}\}$ set of hidden parameters; describing the evolution of microstructure geometry

$\boldsymbol{\kappa}_\alpha$ *ultimate phase strains*; depending on hidden variables $\boldsymbol{\kappa}_\alpha(\boldsymbol{h})$.

It is convenient to introduce denotations for some sets of variables:

$$\mathrm{Y}_{\mathrm{h}}^{\mathrm{T}\sigma} \equiv \{T, \boldsymbol{\sigma}, \boldsymbol{h}\}, \quad \mathrm{Y}_{\mathrm{h}}^{\sigma} \equiv \{\boldsymbol{\sigma}, \boldsymbol{h}\}, \quad \mathrm{Y}_{\mathrm{h}}^{\mathrm{T}\varepsilon} \equiv \{T, \varepsilon, \boldsymbol{h}\}, \quad \mathrm{Y}_{\mathrm{h}}^{\varepsilon} \equiv \{\varepsilon, \boldsymbol{h}\}$$

Problem formulation – Gibbs free energy function for SMA's

Thermal equations of state for SMA material

$$\varepsilon \equiv -\rho \, \partial g(T,\boldsymbol{\sigma},z) / \partial \boldsymbol{\sigma} = \boldsymbol{M}\,\boldsymbol{\sigma} + \boldsymbol{\alpha}\,\Delta T + \varepsilon^{pt} \left.\begin{array}{c} \\ \\ \end{array}\right\}$$

$$\varepsilon^{e} \equiv \varepsilon - \varepsilon^{th} - \varepsilon^{pt} \qquad\qquad \boldsymbol{\sigma} = \boldsymbol{L}\,\varepsilon^{e}$$

$$s \equiv -\partial g(T,\boldsymbol{\sigma},z) / \partial T = s_1^0 + c_p \ln(T/T_0) - (1-z)\,\Delta s^0 + \boldsymbol{\alpha}\cdot\boldsymbol{\sigma}/\rho$$

Thermodynamic *driving force of phase transition*

$$\pi^{1-2} \equiv \partial g(T,\boldsymbol{\sigma},z) / \partial z = (\pi_0^f - \phi_2^{st}) - (1-2z)\,\phi_{it} + \boldsymbol{\kappa}\cdot\boldsymbol{\sigma}/\rho$$

The information, which is *not contained in Gibbs function* and necessary for correct description of SMA materials behavior is for example:
- *evolution of volume fraction of martensite*, i.e. kinetics of martensitic phase transition $z = z(\sigma, T)$,
- *evolution of phase transformation eigenstrains* $\boldsymbol{\kappa} = \boldsymbol{\kappa}(\sigma, T)$.

Notation

$$\boldsymbol{1} \leftrightarrow \delta_{ij}, \ (\boldsymbol{I})_{klmn} \leftrightarrow 0.5(\delta_{km}\delta_{\ln} + \delta_{kn}\delta_{lm}), \ (!\alpha) \rightarrow \text{no summation over index}$$

$$(\boldsymbol{A}^T)_{kl} = A_{lk} \text{ or } (\boldsymbol{A}^T)_{klmn} = A_{mnkl}, \ \boldsymbol{A}^{-1} \text{ inverse of } \boldsymbol{A} \, (A_{kl}^{-1} A_{lm} = \delta_{km} \text{ or } A_{klmn}^{-1} A_{mnpr} = I_{klpr}),$$

$$\boldsymbol{AB} \rightarrow A_{kl}B_{lm} \text{ or } A_{klmn}B_{mnpr}, \ \boldsymbol{A}\cdot\boldsymbol{B} \rightarrow A_{ij}B_{ij}, \, tr(\boldsymbol{AB}) \rightarrow A_{ij}B_{ji}$$

Problem formulation – Micromechanical experimental motivation

Martensitic phase transition kinetics at microscale and appearing microstructures.
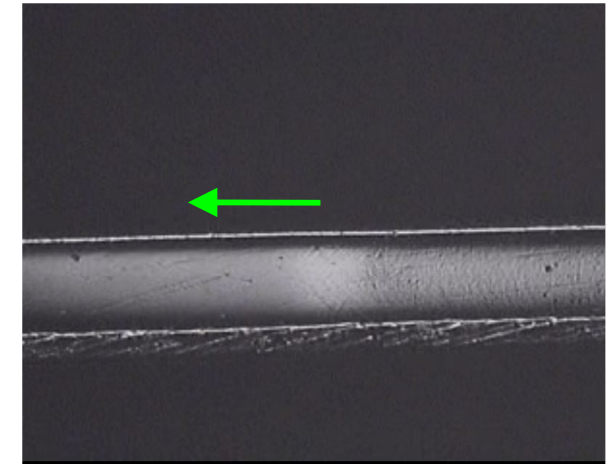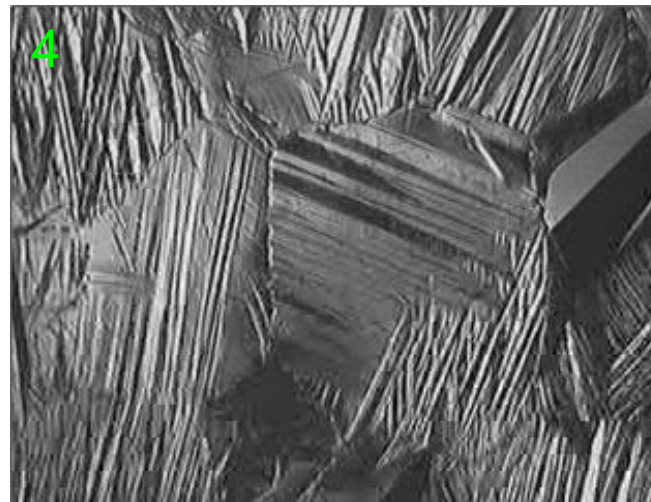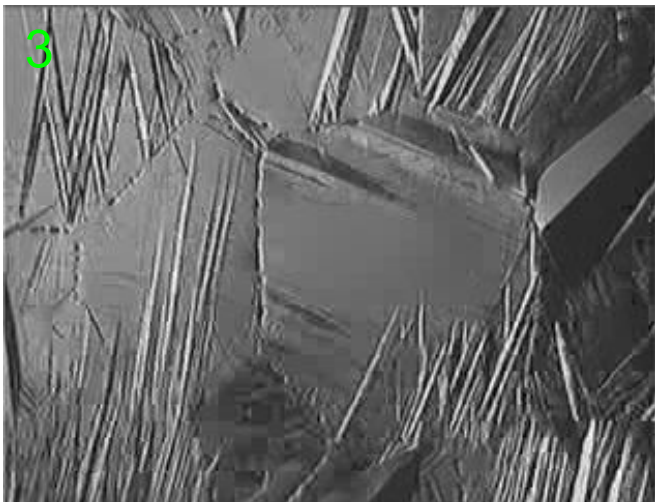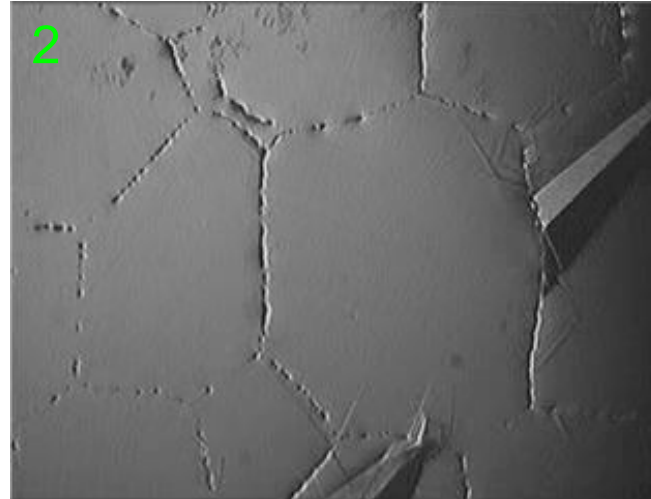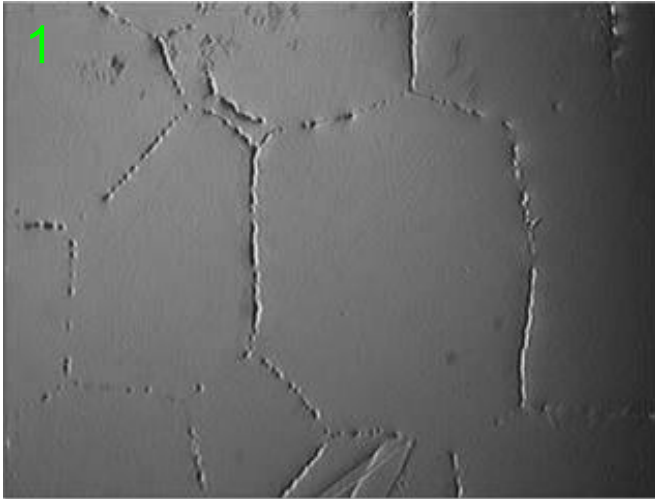
Phase transition taking place in tensioned SMA wire by macroscopic front propagation

Forward and reverse phase transition watched under optical microscope magnification

Kinetics of martensitic phase transition constitutes *additional information* to that contained in *Gibbs function*. Revealing the law of phase transition kinetics rules require separate, comprehensive research efforts.

Problem formulation – Micromechanical experimental motivation

Microscopic experimental observations deliver information that upon thermomechanical loading of SMA materials complex, multiscale microstructures of *thermoelastic martensite* appear.

Multiscale organization of martensitic phase in polycrystalline CuAl alloy:
(a) macroscopic sample in martensitic state;
(b) polycrystalline structure of martensitic phase with martensitic objects - plates, confined by grain boundaries;
(c) spear-like martensitic compound composed of two *habit plane martensitic variants* (HPV) - indicated by arrow;

(d) a configuration of parallel habit plane martensitic variants (HPV's) with visible striations revealing their lower-level internal structure composed of two *martensitic lattice correspondence variants* (CV's).

Photographs after Warlimont and Delaey (1974).
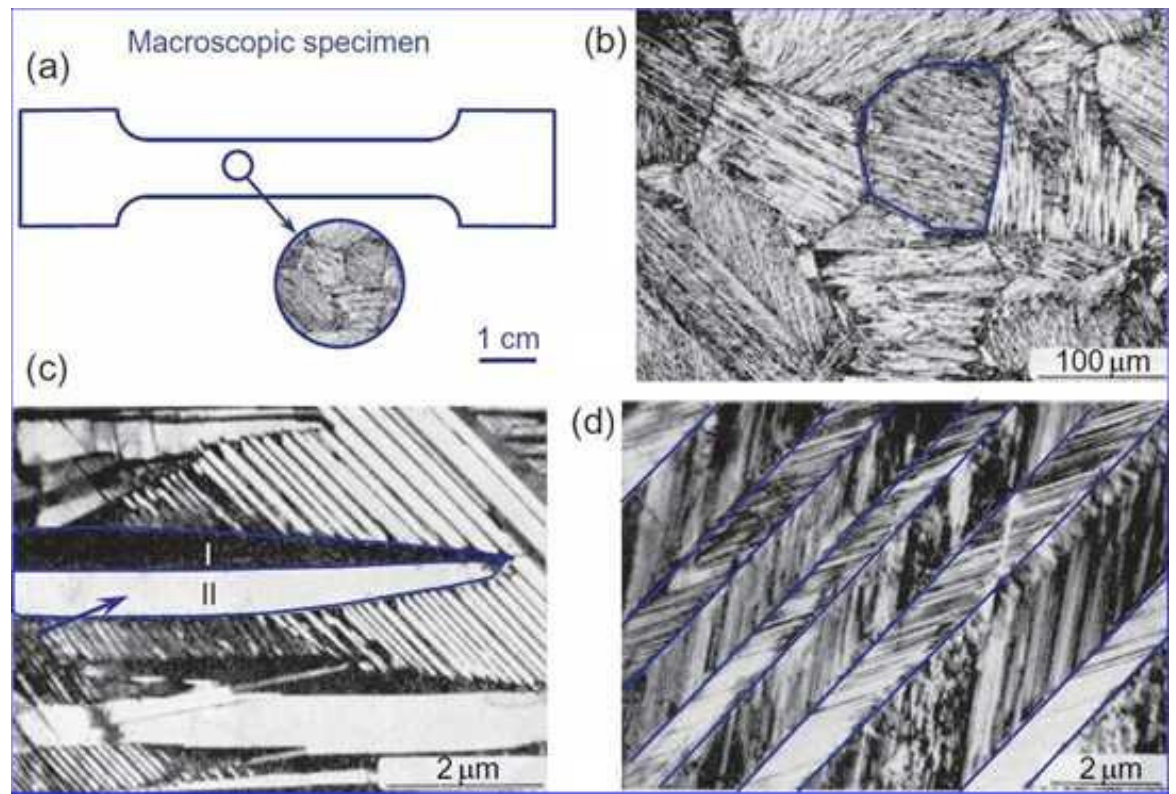
Problem formulation – Micromechanical motivation originating form microscopic observations

When phase transformation is temperature induced at zero assisting macroscopic stress then so called *self-accommodating martensitic meso-structures* exhibiting *zero macroscopic phase transformation strain* are formed. Such condition exists e.g. during DSC calorimetric tests. Wide variety of self-accommodating morphologies of thermoelastic martensite were already identified.

Fukuda et. al. (1992) identified in R-phase of $Ti_{48.2}Ni_{1.5at\%}Fe$ alloy V-shaped morphology composed of two HPV's and rhombic morphology composed of four HPV's. Photo and schematic drawing showing of *groups of HPV's* arranging itself in higher order structure so *self-accommodating martensite.*
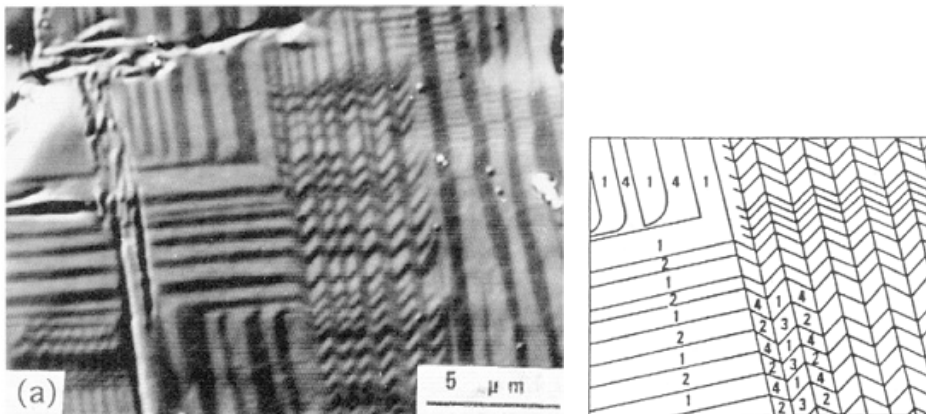
Four classes of self-accommodating morphologies in NiTi alloy were identfiied by Nishida et al. (2012)

Triangular morphology composed of three HPV's

Rhombic morphology composed of four HPV's,

Nishida M. et al. (2012), Self-accommodation of B19′ martensite in Ti–Ni shape memory alloys – Part I. Morphological and crystallographic studies of the variant selection rule, Philos. Mag.
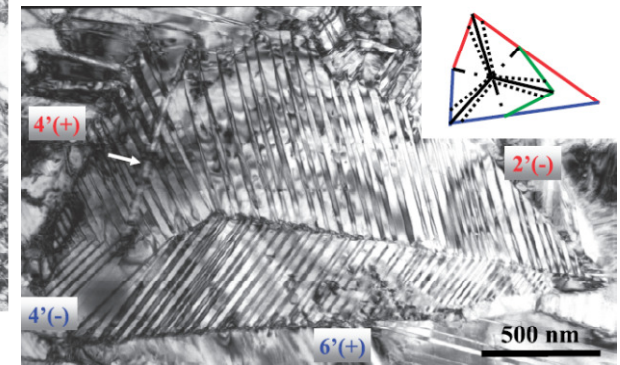
Problem formulation – Thermodynamic and micromechanical settings

Basic assumptions of micromechanical problem of thermoelasticity

Schematic illustration of *micromechanical model* of *SMA macroelement* (RVE) composed of *n-linear thermoelastic phases with eigenstrains*.
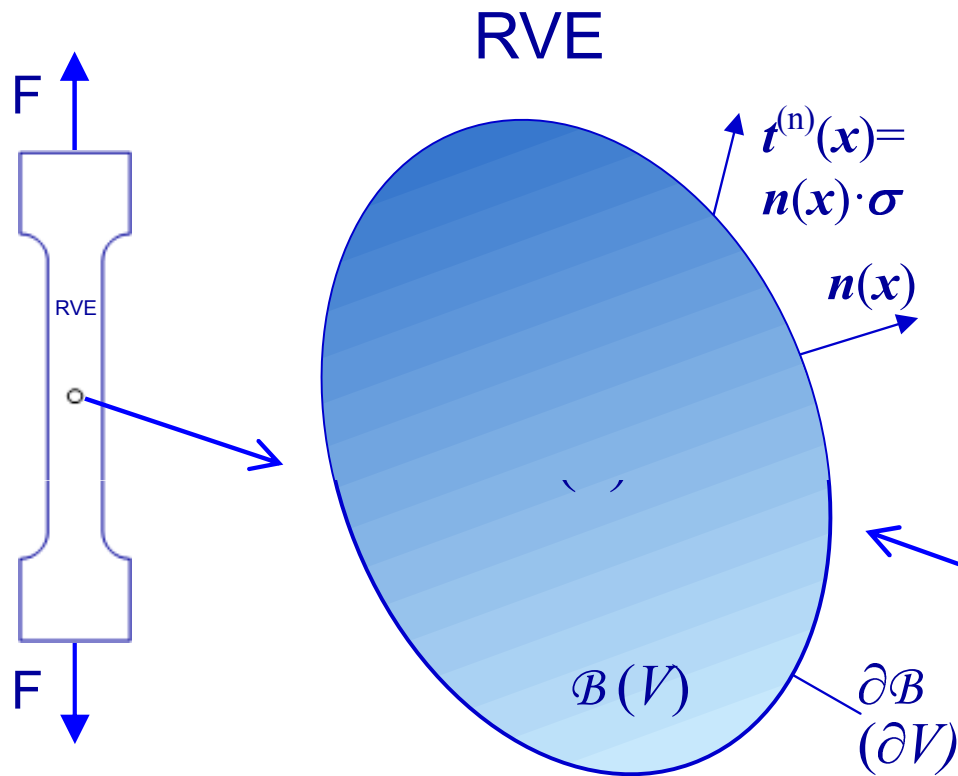
Evolution of CuAlBe microstructure under increasing tensile stress – austenite martensite phase transition microstructure in polycrystalline alloy.

RVE

$t^{(n)}(x) = n(x) \cdot \sigma$

$n(x)$

$\mathcal{B}(V)$

$\partial\mathcal{B}(\partial V)$

Photos courtesy Andre Eberhardt, originally published in Chemisky et al.(2011).

Ziółkowski A. (2017) On consistent micromechanical estimation of macroscopic elastic energy, coherence energy, ….

So, studied below micro structural configurations of RVE we will regard as microstructures constituting certain "frozen" configurations, which actually appear in macroelement during advancement of phase transformations at various levels of external thermomechanical loadings – values of stress and temperature (σ, T).
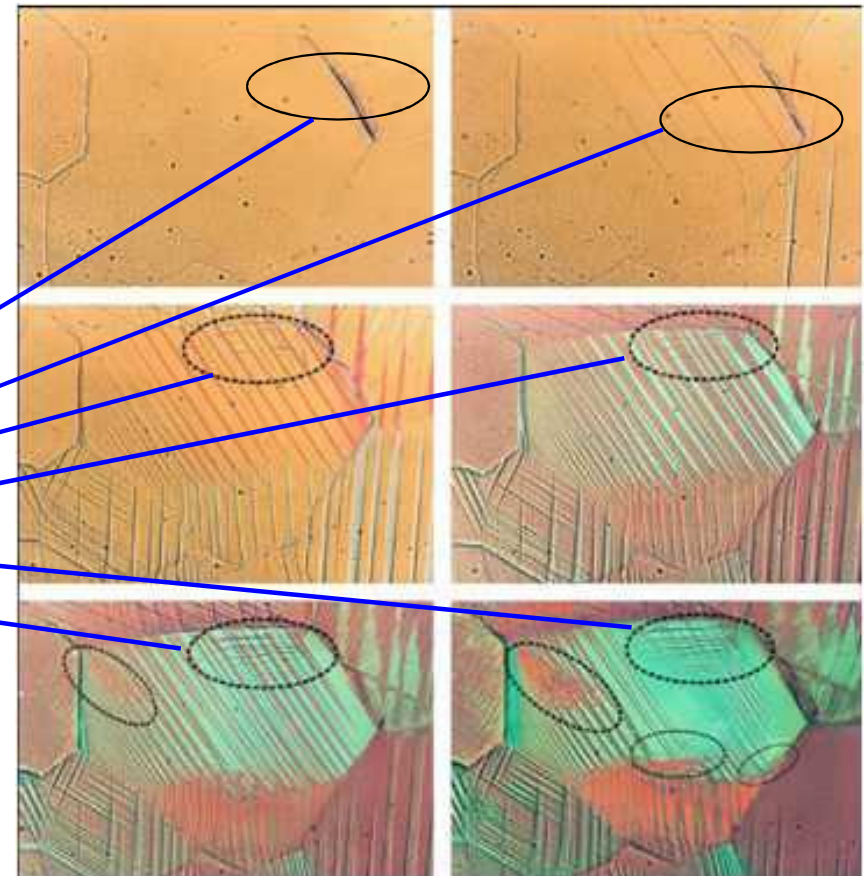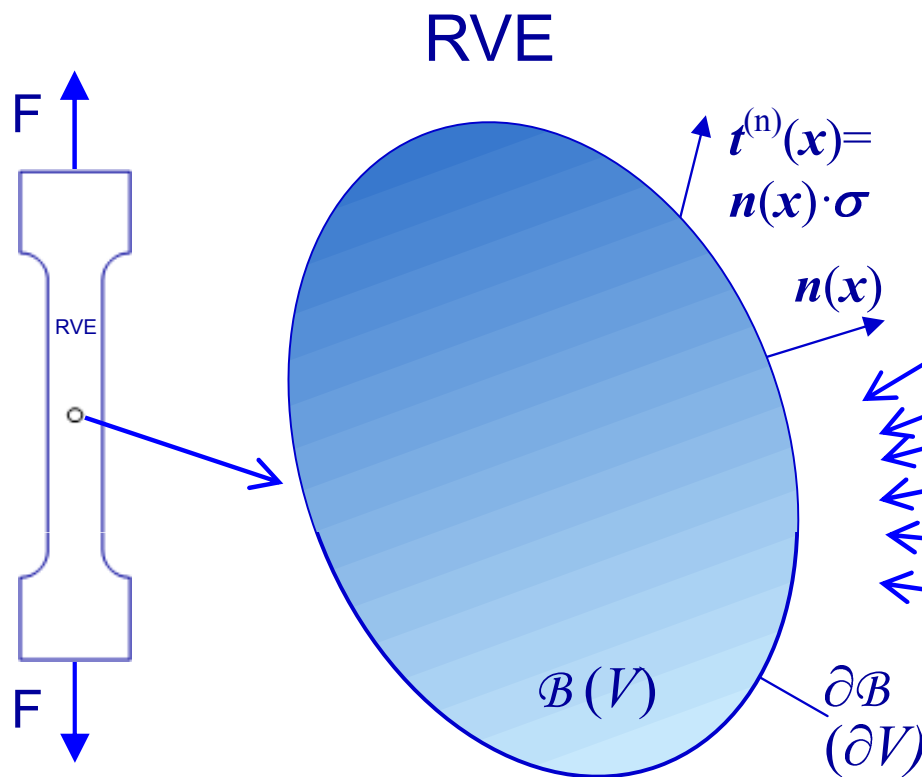
Photos courtesy Andre Eberhardt, originally published in Chemisky et al.(2011).

Micromechanical problem of one component, multiphase thermoelastic system

It is reasonable to conjecture that at microscale, locally SMA material behaves like non-homogeneous *linear thermoelastic material with eigenstrains*

$$\breve{\sigma}(\boldsymbol{x}) = \breve{L}(\boldsymbol{x})[\breve{\varepsilon}(\boldsymbol{x}) - \breve{\Gamma}(\boldsymbol{x}) - \alpha(T - T_0)] \quad \Rightarrow$$

$$\breve{\varepsilon}(\boldsymbol{x}) = \breve{M}(\boldsymbol{x})\breve{\sigma}(\boldsymbol{x}) + \breve{\Gamma}(\boldsymbol{x}) + \alpha(T - T_0), \quad \breve{M}(\boldsymbol{x}) = \breve{L}^{-1}(\boldsymbol{x})$$

At any time there must be satisfied equations of thermomechanical static equilibrium

$$div\,\breve{\sigma}(\boldsymbol{x}) = 0,\, \boldsymbol{x} \in V, \quad \boldsymbol{t}^{(n)}(\boldsymbol{x}) = \breve{\sigma}(\boldsymbol{x})\boldsymbol{n}(\boldsymbol{x}) \quad \boldsymbol{x} \in \partial V$$

Upon solving a number of problems of micromechanics with relevant boundary conditions upon averaging resulting local fields there can be determined values of effective elastic properties of SMA RVE.

$$\sigma(t) = \frac{1}{2V}\int_{\partial V}(\breve{\boldsymbol{t}}^{(n)}(\boldsymbol{x},t) \otimes \boldsymbol{x} + \boldsymbol{x} \otimes \breve{\boldsymbol{t}}^{(n)}(\boldsymbol{x},t))dS = \frac{1}{V}\int_V \breve{\sigma}(\boldsymbol{x},t)dx = <\breve{\sigma}(\boldsymbol{x},t)>_V$$

$$\breve{\boldsymbol{t}}^{(n)}(\boldsymbol{x},t) = \sigma(t)\boldsymbol{n}(\boldsymbol{x},t) + \breve{\boldsymbol{t}}^{(f)}(\boldsymbol{x},t), \quad \boldsymbol{x} \in \partial V$$

$$\boldsymbol{t}^{(n)}(\boldsymbol{x}) = \boldsymbol{n}(\boldsymbol{x})\cdot\sigma$$

$$\boldsymbol{n}(\boldsymbol{x})$$

$$\Gamma(\boldsymbol{x})$$

$$\mathcal{B}(V) \qquad \partial\mathcal{B} \,(\partial V)$$
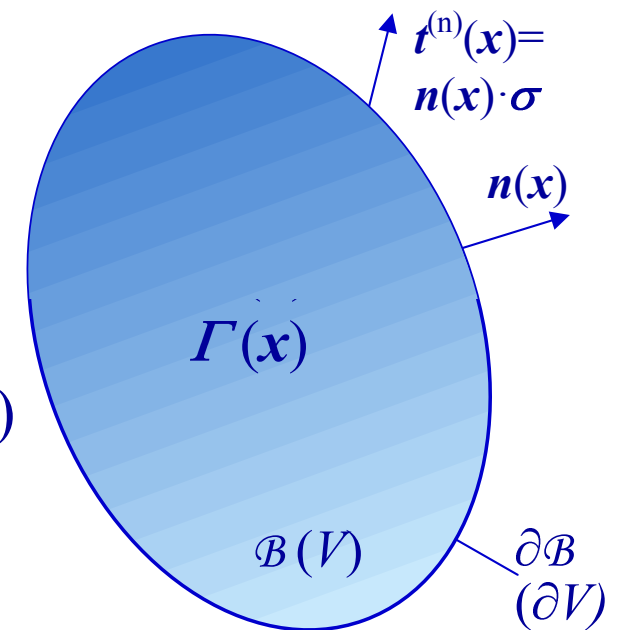
$$\breve{\sigma}(\boldsymbol{x}), \breve{\varepsilon}(\boldsymbol{x}), \breve{u}(\boldsymbol{x})$$

Macroscopic quantities calculated from relevant microscopic fields

$$\boldsymbol{B} = <\breve{\boldsymbol{B}}(\boldsymbol{x})>_V \equiv \frac{1}{V}\int_V \breve{\boldsymbol{B}}(\boldsymbol{x})dx$$

See also Saad M. (2005) Elasticity Theory, Applications, and Numerics, Elsevier.

Micromechanical problem of one component, multiphase thermoelastic system

The *boundary value problem of linear thermoelasticity* can be divided into two auxiliary problems

$$\breve{\sigma}(x) = \breve{\sigma}^{(ex)}(x) + \breve{\sigma}^{(in)}(x), \quad \breve{\varepsilon}(x) = \breve{\varepsilon}^{(ex)}(x) + \breve{\varepsilon}^{(in)}(x) + \alpha\,\Delta T$$

$$t^{(n)}(x) = n(x)\cdot\sigma$$

$$n(x)$$

$$\Gamma(x)$$

Problem I – external loading contribution

$$\breve{\varepsilon}^{(ex)}(x) = \breve{M}(x)\breve{\sigma}^{(ex)}(x) + \alpha\,\Delta T, \quad div\,\breve{\sigma}^{(ex)} = 0 \quad x \in V,$$

$$t^{(n)}(x) = \breve{\sigma}^{(ex)}(x)n(x) \quad x \in \partial V; \quad (here\ \breve{\sigma}^{(ex)} = \sigma = const)$$

$$\mathcal{B}(V)$$

$$\partial\mathcal{B} \\ (\partial V)$$

Problem II – phase eigenstrains field contribution

$$\breve{\varepsilon}^{(in)}(x) = \breve{M}(x)\breve{\sigma}^{(in)}(x) + \breve{\Gamma}(x), \quad div\,\breve{\sigma}^{(in)} = 0, \quad x \in V,$$

$$t^{(n)(in)}(x) = \breve{\sigma}^{(in)}(x)n = 0,\ x \in \partial V \implies \langle \breve{\sigma}^{(in)}(x)\cdot\breve{\varepsilon}^{(in)}(x)\rangle_V = 0$$

$$\breve{\sigma}(x), \breve{\varepsilon}(x), \breve{u}(x)$$

Macroscopic quantity calculated from relevant microscopic fields

It is assumed that external fields satisfy *Hill's postulate*

$$< \breve{\sigma}^{(ex)}\cdot\breve{\varepsilon}^{(ex)} >_V = < \breve{\sigma}^{(ex)} >_V \cdot < \breve{\varepsilon}^{(ex)} >_V = \sigma\cdot\varepsilon^E$$

$$B = < \breve{B}(x) >_V \equiv \frac{1}{V}\int_V \breve{B}(x)dx$$

Effective/macroscopic state variables and effective material properties

The averaging procedure of local stress and/or strain fields leads to the following connections between macroscopic measures of: elastic energy, coherence energy and transformation strain and microscopic fields

$$\rho\, g^{el} = 0.5 < \breve{\sigma}^{(ex)} \cdot \breve{M}\, \breve{\sigma}^{(ex)} >_V = 0.5\, \sigma \cdot M\sigma; \quad M = \rho\, \partial^2 g^{el} / \partial\sigma\, \partial\sigma, \ \sigma = \langle \breve{\sigma}(x) \rangle_V$$

$$\rho\, u^{coh} \equiv \frac{1}{2V} \int_V \breve{\Gamma}(x) \cdot [-\breve{\sigma}^{(in)}(x)]\, dx = \frac{1}{2V} \int_V \breve{\sigma}^{(in)}(x) \cdot \breve{M}(x)\, \breve{\sigma}^{(in)}(x)\, dx; \ \phi^{coh} \equiv u^{coh} + T \cdot s^{coh}$$

$$\varepsilon^{pt} = < \breve{\varepsilon}^{(in)}(x) >_V = \frac{1}{V} \int_V [\breve{\Gamma}(x) + \breve{M}(x)\breve{\sigma}^{(in)}(x)]\, dx$$

g^{el} macroscopic elastic complementary energy

M denotes effective/macroscopic modulus of elastic compliance

σ denotes macroscopic stress

ϕ^{coh} macroscopic free coherence energy ($\phi^{coh} = u^{coh} - T \cdot s^{coh}$)

ε^{pt} is macroscopic phase transformation strain

Micromechanical problem of one component, multiphase thermoelastic system composed of *n* phases

Motivated by microscopic observations of micro-morphologies of thermoelastic martensites, further study will be restricted to micro-structures composed of *n* (α=1,..,n) classes of linear thermoelastic phases. We shall also conjecture that these phases are homogeneous and thus obey the following constitutive relations.

Schematic illustration of *micro-mechanical model* of *SMA macroelement* composed of *n* generic phases each behaving like *linear thermoelastic material with eigenstrains*.

$$\breve{\sigma}_\alpha(x) = \breve{\sigma}_\alpha^{(ex)}(x) + \breve{\sigma}_\alpha^{(in)}(x), \quad \breve{\varepsilon}_\alpha(x) = \breve{\varepsilon}_\alpha^{(ex)}(x) + \breve{\varepsilon}_\alpha^{(in)}(x) + \alpha\,\Delta T$$

$$\breve{\varepsilon}_\alpha^{(ex)}(x) = M_\alpha \breve{\sigma}_\alpha^{(ex)}(x), \quad \breve{\varepsilon}_\alpha^{(in)}(x) = M_\alpha \breve{\sigma}_\alpha^{(in)}(x) + \Gamma_\alpha, \quad x \in V_\alpha$$

Piece wise uniform elastic properties and phase eigenstrains

$$\breve{M}_\alpha(x) = \boxed{M_\alpha,} \quad \breve{\Gamma}_\alpha(x) = \Gamma_\alpha + \cancel{\breve{\Gamma}_\alpha^f(x)}, \quad x \in V_\alpha, \quad \alpha = 1,..,n,$$

$$\breve{\Gamma}_1(x) \equiv 0, \quad x \in V_1, \qquad \Gamma_\alpha = <\breve{\Gamma}_\alpha(x)>_{V_\alpha}.$$

no fluctuating part of phase eigenstrains

Macroscopic total and partial (phase) stresses and strains

$$\sigma = \langle \breve{\sigma}(x) \rangle_V = \langle \breve{\sigma}(x)^{ex} \rangle_V, \quad \varepsilon = \langle \breve{\varepsilon}(x) \rangle_V = \langle \breve{\varepsilon}(x)^{ex} \rangle_V,$$

$$\sigma_\alpha = \langle \breve{\sigma}(x) \rangle_{V_\alpha}, \quad \varepsilon_\alpha = \langle \breve{\varepsilon}(x) \rangle_{V_\alpha}$$
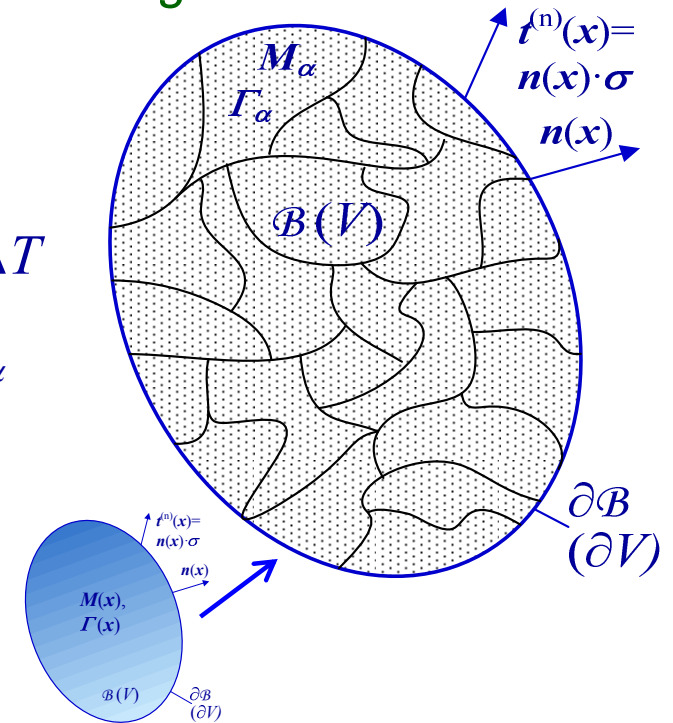
$$B_\alpha = < \breve{B}_\alpha(x) >_{V_\alpha} \equiv (1/V_\alpha)\int_{V_\alpha} \breve{B}(x)dx,$$

$$\breve{B}_\alpha^f(x) \equiv \breve{B}_\alpha(\underline{x}) - B_\alpha; \quad < \breve{B}_\alpha^f(x) >_{V_\alpha} = 0$$

Micromechanical problem of one component, multiphase thermoelastic system composed of n phases

The domain of SMA material RVE divided into n eigenphases still delivers a versatile and comprehensive general scheme.

It is very well suited for studying/analyzing multiscale structures appearing as a result of formation of martensitic phase.

Depending on the starting scale on which basic conjectures are made the *objects* to be distinguished as *generic phase* can be single *crystallographic variants* of martensitic phase (CV), *habit plane variants* (HPV's) or, e.g., still higher order structures like self-accommodating martensitic compounds, in the scale of observation where they can be meaningfully distinguished—cf., e.g., (Nishida et al., 2012).

Precise assessments of thermo-mechanical properties for various microstructures usually will require rather involved numerical–experimental studies to reach useful results.

Expected results of the present research work

Upon execution of the present study we expect three main results:

1. *Validation* of the posed heuristically explicit form of *Gibbs free energy function* for SMA materials (hints for its possible modification/ augmentation).

2. *Effective (macroscopic) properties and "effective" variables* characterizing state of SMA material. Principally we are interested in macroscopic stiffness tensor *E (4th order tensor in 3 dimensional space)*, phase transformation strain $\varepsilon^{\circ ph}$ (second order tensor in 3 dimensional space), coherency energy ϕ *(scalar)*.

3. A *new efficient, homogenization method* to attain mentioned above targets.

All that started with announcement by *Robert Hooke* of his law of elastic materials behavior

$$ceiiinossssttuv$$

relating force with deformation or (stress with strain).

Robert Hooke decoded his anagram two years later (1678)

$$ut\ tensio\ sic\ vis$$

or in the form that we know it today, it is

$$\sigma = L\,\varepsilon$$

J. Rychlewski (1983) *"CEIIINOSSSTTUV". Mathematical structure of elastic bodies [in Russian]*, Technical Report 217, Inst. Mech. Probl. USSR Acad. Sci., Moskva.
Isaac Asimov, Asimov's Biographical Encyclopedia of Science and Technology, The lives and Achievements of 1510 Great Scientists from Ancient Times to the Present Chronologically Arranged, 2-nd Rev. Ed., Doubleday, Toronto, 1982. 49

Spectral decomposition of elastic stiffness/compliance tensor

A motivating question arises *execution of how many and what kind of experimental tests* is necessary and effective to uniquely determine elastic properties of the most general elastic, anisotropic material, or speaking otherwise all components of elastic stiffness (compliance) tensor?

Enlightening to the above question are the results delivered by Rychlewski in his paper from 1984, where he proved that any symmetric fourth order tensor can be *spectrally decomposed* into 6 mutually orthogonal subspaces. Each subspace is characterized by *stiffness (Kelvin) modulus* λ_K – scalar, and *elastic eigenstate* ω_K - symmetric second order tensor ($K=1,..,6$). Each elastic eigenstate is characterized by 2 so called *stiffness distributors* $\aleph_\alpha$ ($\alpha=1,..,12$).

System

$$M_{ef}?, \quad E_{ef}=(M_{ef})^{-1}$$

+ Loading

Rychlewski (1984) J. *Elastic energy decompositions and limit criteria* [in Russian], Uspekhi Mekh., 7, 3.
Rychlewski J. (1985) Unconventional approach to linear elasticity, Arch. Mech.
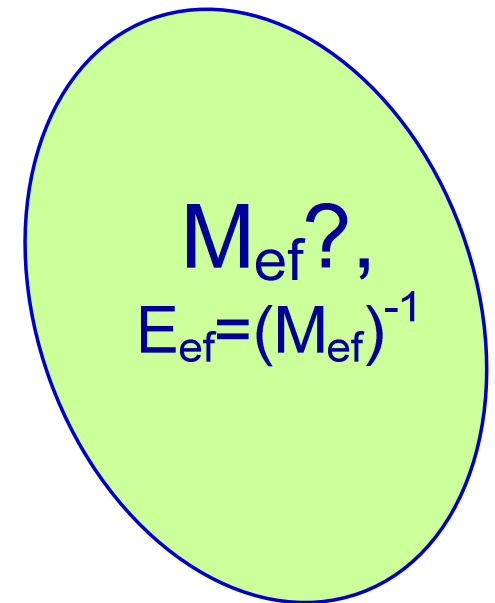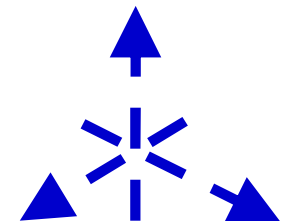
Spectral decomposition of elastic stiffness tensor

In summary set of 21 components/parameters determining any symmetric stiffness tensor can be divided into 3 classes

$$6 + 12 + 3 = 21$$

1. The first group consists of *6 Kelvin moduli* $\lambda_I, .., \lambda_{VI}$

2. The second group consists of *12 stiffness distributors* $\aleph_{1, ..., } \aleph_{12}$, generators of 6 *elastic eigenstates* $\omega_I, .., \omega_{VI}$

3. The third group consists of *3 Euler angles* ϕ_1, ϕ_2, ϕ_3

The *18 parameters* from the first and the second group are *invariants* of elastic stiffness tensor.

Pytanie: When 21 components of elastic stiffness tensor determined in an experimental testing program, with fixed reference frame, for two otherwise unknown specimen shows to have the same values.
Does that mean the specimen were made of the same material?

See also Kowalczyk–Gajewska K., Ostrowska –Maciejewska J. (2009) Review on spectral decomposition of Hooke's tensor for all symmetry groups of linear elastic material, Arch. Mech.

System

$$M_{ef}, \quad E_{ef} = (M_{ef})^{-1}$$
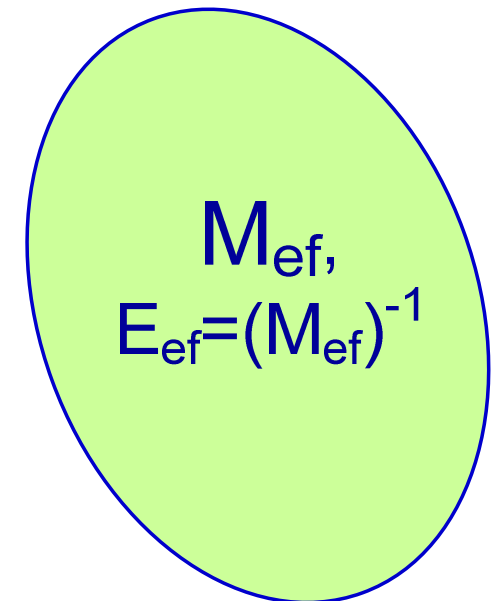
+ Loading
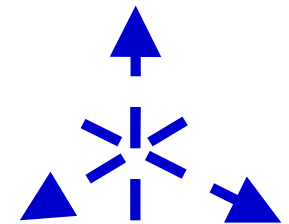
Representation of elastic stiffness tensor

It is worth noting that the tensor of elastic properties *fourth order* in three dimensional space can be, in strict mathematical sense, equivalently treated/represented as *second order* tensor in *six dimensional* Euclidean space

$$L = L_{ijkl}\, e_i \otimes e_j \otimes e_k \otimes e_l = L_{KL} a_K \otimes a_L; \quad i,j,k,l = 1,\ldots,3,\ K,L = 1,\ldots,6$$

$$11 \to 1;\ \ 22 \to 2;\ \ 33 \to 3;\ \ 2,3,3,2 \to 4;\ \ 1,3,3,1 \to 5;\ \ 1,2,2,1 \to 6$$

We feel intuitively what is the *direction* of a vector - first order tensor.
But how to "understand" the *direction* of higher order tensors?

<div style="display:flex;justify-content:space-between;">

Voigt notation

$$L_{ijkl} = \begin{bmatrix} L_{1111} & L_{1122} & L_{1133} & L_{1123} & L_{1113} & L_{1112} \\ L_{2211} & L_{2222} & L_{2233} & L_{2223} & L_{2213} & L_{2212} \\ L_{3311} & L_{3322} & L_{3333} & L_{3323} & L_{3313} & L_{3312} \\ L_{2311} & L_{2322} & L_{2333} & L_{2323} & L_{2313} & L_{2312} \\ L_{1311} & L_{1322} & L_{1333} & L_{1323} & L_{1313} & L_{1312} \\ L_{1211} & L_{1222} & L_{1233} & L_{1223} & L_{1213} & L_{1212} \end{bmatrix}$$

$$\sum_{i,j,k,l} L_{KL}^2 \neq \sum_{i,j,k,l} L_{ijkl}^2$$

Kelvin notation

$$L_{KL} = \begin{bmatrix} L_{11} & L_{12} & L_{13} & \sqrt{2}L_{14} & \sqrt{2}L_{15} & \sqrt{2}L_{16} \\ L_{21} & L_{22} & L_{23} & \sqrt{2}L_{24} & \sqrt{2}L_{25} & \sqrt{2}L_{26} \\ L_{31} & L_{32} & L_{33} & \sqrt{2}L_{34} & \sqrt{2}L_{35} & \sqrt{2}L_{36} \\ L_{41} & L_{42} & L_{43} & 2L_{44} & 2L_{45} & 2L_{46} \\ L_{51} & L_{52} & L_{53} & 2L_{54} & 2L_{55} & 2L_{56} \\ L_{61} & L_{62} & L_{63} & 2L_{64} & 2L_{65} & 2L_{66} \end{bmatrix}$$

$$\sum_{i,j,k,l} L_{KL}^2 = \sum_{i,j,k,l} L_{ijkl}^2$$

</div>

Effective properties – Bounding estimates

Bounding estimates of thermoelastic properties: *Voigt iso-strain* (1889), *Reuss iso-stress* (1929), *Voigt-Reuss-Hill* (VRH), VRH=½[Vo+Re]

Macroelement effective properties

$$M^{Re} = \sum f_i \cdot M_i$$

$$M^{Max} = M^{Re} \geq M_{ef} \geq M^V = M^{Min}$$

$$E^V = \sum f_i \cdot E_i; \quad L_i = (M_i)^{-1}$$

$$E^{Min} = E^{Re} \leq E^{ef} \leq E^V = E^{Max}$$

Reuss

P

$\sigma_1 = \sigma$ ε_1

$\sigma_2 = \sigma$ ε_2

$\sigma_3 = \sigma$ ε_3

M^{Max}, E^{Min} P

$M_{ef}, E_{ef} = (M_{ef})^{-1}$

$$\sigma = E_{ef}\, \varepsilon$$

Voigt

σ_1 $\varepsilon_1 = \varepsilon$

P σ_2 $\varepsilon_2 = \varepsilon$ P

E^{Max}
M^{Min} σ_3 $\varepsilon_3 = \varepsilon$
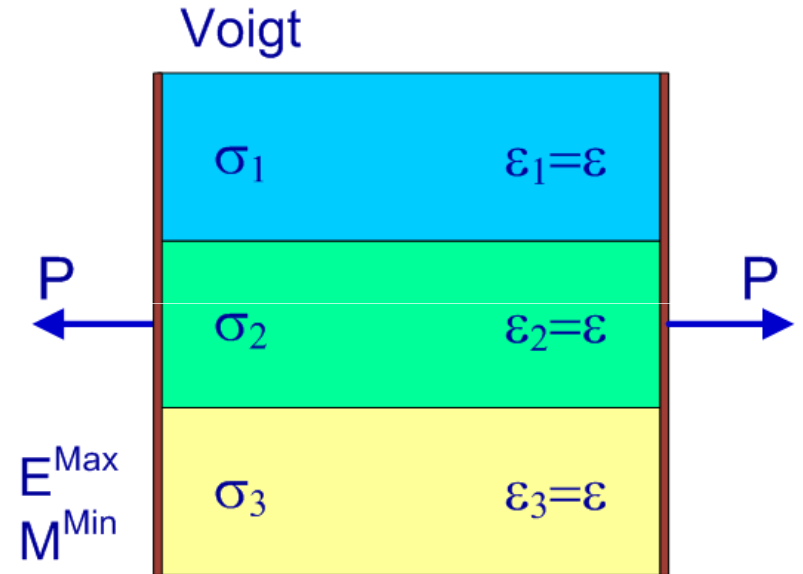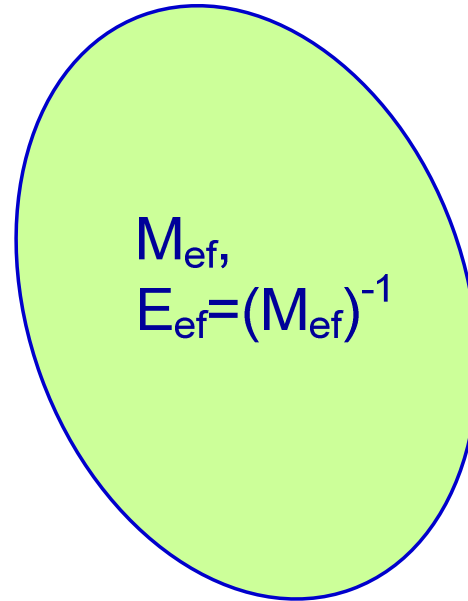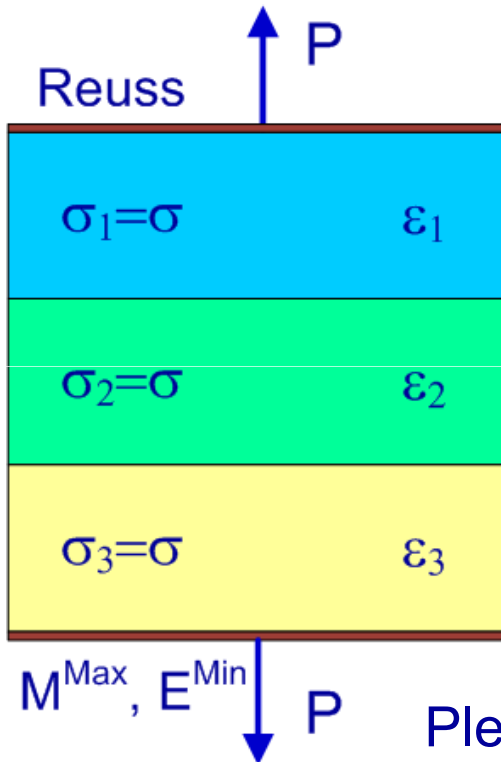
Please note that actually *the same (single) material* can exhibit Reuss or Voigt properties, depending *on loading orientation*.

Self-equilibrated Eigenstrains Influence Moduli (SEIM) method

Considerable number of *homogenization methods/schemes* have been already elaborated e.g. Mori-Tanaka or self-consistent. Excellent survey of these methods can be found in Dvorak book (2013) or older book by Nemat-Nasser and Hori (1993).

Here a new homogenization method is proposed based on so called *self-equilibrated eigenstrains influence moduli* (SEIM).

The advantage of this method is that it is well suited for interactive use in conjunction with experimental and/or numerical tests.

Let us return to our main boundary value problem

$$div\, \breve{\boldsymbol{\sigma}}(\boldsymbol{x}) = 0,\, \boldsymbol{x} \in V, \quad \boldsymbol{t}^{(n)}(\boldsymbol{x}) = \breve{\boldsymbol{\sigma}}(\boldsymbol{x})\boldsymbol{n}(\boldsymbol{x}) \quad \boldsymbol{x} \in \partial V$$

$$\breve{\boldsymbol{\sigma}}_\alpha(\boldsymbol{x}) = \breve{\boldsymbol{\sigma}}_\alpha^{(ex)}(\boldsymbol{x}) + \breve{\boldsymbol{\sigma}}_\alpha^{(in)}(\boldsymbol{x}),\ \breve{\boldsymbol{\varepsilon}}_\alpha(\boldsymbol{x}) = \breve{\boldsymbol{\varepsilon}}_\alpha^{(ex)}(\boldsymbol{x}) + \breve{\boldsymbol{\varepsilon}}_\alpha^{(in)}(\boldsymbol{x}) + \boldsymbol{\alpha}\,\Delta T$$

$$\breve{\boldsymbol{\varepsilon}}_\alpha^{(ex)}(\boldsymbol{x}) = \boldsymbol{M}_\alpha \breve{\boldsymbol{\sigma}}_\alpha^{(ex)}(\boldsymbol{x}),\ \breve{\boldsymbol{\varepsilon}}_\alpha^{(in)}(\boldsymbol{x}) = \boldsymbol{M}_\alpha \breve{\boldsymbol{\sigma}}_\alpha^{(in)}(\boldsymbol{x}) + \boldsymbol{\Gamma}_\alpha, \quad \boldsymbol{x} \in V_\alpha$$

Ziółkowski A. (2016) On consistent micromechanical estimation of macroscopic elastic energy ….
Nemat, N.S., Hori, M. (1993) Micromechanics: Overall Properties of Heterogeneous Materials, North Holland, London.
Dvorak, G.J. (2013) Micromechanics of Composite Materials. Springer, New York (2013)

Self-equilibrated Eigenstrains Influence Moduli (SEIM) method

Solution of linear elasticity problem of mechanical equilibrium with *piecewise uniform fields of elastic properties and eigenstrains* can be expressed with the aid of *self-equilibrated eigenstrains influence moduli* (SEIM). The formal solution of boundary value problems I, II can be expressed with the aid of SEIM tensor fields in the following form

$$\breve{\sigma}_{\alpha}^{(in)}(\boldsymbol{x}) = \sum_{\beta=1}^{n} \breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x}) \Gamma_{\beta}; \quad (\breve{\Gamma}_{\alpha}^{f}(\boldsymbol{x}) \equiv 0), \quad \breve{\sigma}_{\alpha}^{(ex)}(\boldsymbol{x}) = \sigma + \sum_{\beta=1}^{n} \breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x}) \cdot (\boldsymbol{M}_{\beta} \sigma)$$

The phase volume averages of respective local fields can be expressed with *self-equilibrated eigenstrains influence moduli*

$$\mathfrak{I}_{\alpha\beta}^{*} = < \breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x}) >_{V_{\alpha}} = \frac{1}{V_{\alpha}} \int_{V_{\alpha}} \breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x}) dx$$

$$\sigma_{\alpha}^{(in)} = < \breve{\sigma}_{\alpha}^{(in)}(\boldsymbol{x}) >_{V_{\alpha}} = \sum_{\beta=1}^{n} \mathfrak{I}_{\alpha\beta}^{*} \Gamma_{\beta}, \quad \sigma_{\alpha}^{(ex)} = < \breve{\sigma}_{\alpha}^{(ex)}(\boldsymbol{x}) >_{V_{\alpha}} = \sigma + \mathfrak{I}_{\alpha\beta}^{*} \cdot (\boldsymbol{M}_{\beta} \sigma)$$

Note: While the above formulas resemble Hooke's law, actually *self-equilibrated eigenstrains influence moduli* are *tensors valued functions/functionals* of various arguments e.g. phase's volume fractions z_{α} (scalars), phase's elastic moduli E_{α} (4th order tensors) but also set of variables of geometrical character describing actual RVE microstructure $\{h\}$, but not Γ_{α}.

Structure and properties
of Self-equilibrated Eigenstrains Influence Moduli

Self-equilibrated eigenstrains influence moduli $\mathfrak{I}^*_{\alpha\beta}$, in general, are *diagonally non-symmetric* fourth-order tensors.

The *non-symmetry of* $\mathfrak{I}^*_{\alpha\beta}$ finds its roots in possible *non-symmetry of microstructural patterns*.

For example, when $\Gamma_\beta = \Gamma = const$

By taking into account that:

a) $\mathfrak{I}^*_{\alpha\beta}$ must vanish when all Γ_β are compatible $(\breve{\sigma}^{(\text{in})}_\alpha(\boldsymbol{x}) = \sum_{\beta=1}^{n} \breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x})\Gamma_\beta = 0)$

b) by invoking *Betti's theorem* it can be shown
   that $\mathfrak{I}^*_{\alpha\beta}$ must fulfill the following relations $(\alpha\beta=1,2,...,n)$,

$$\sum_{\beta=1}^{n} \mathfrak{I}^*_{\alpha\beta} = 0, \qquad z_\alpha \mathfrak{I}^*_{\alpha\beta} = z_\beta \overset{\text{T}}{\mathfrak{I}^*_{\beta\alpha}}, \ (!\alpha,!\beta) \qquad \Rightarrow \qquad \sum_{\beta=1}^{n} \overset{\text{T}}{\mathfrak{I}^*_{\alpha\beta}} = 0$$

The $\mathfrak{I}^*_{\alpha\beta}$ moduli *are not independent* of each other.

As diagonal moduli $\mathfrak{I}^*_{\alpha\alpha}$ must obey relations $\mathfrak{I}^*_{\alpha\alpha}=(\mathfrak{I}^*_{\alpha\alpha})^\text{T}$ $(!\alpha)$, they must be *diagonally symmetric, positive semi-definite,* fourth-order tensors $(\mathfrak{I}_{\alpha\alpha})_{\text{ijmn}}=(\mathfrak{I}_{\alpha\alpha})_{\text{mnij}}$

Betti reciprocity theorem for (linear) elastic materials with eigenstrains

Let us investigate *two mechanical equilibrium states* denoted with subscripts "I" and "II" that are generated in linear elastic body, by two different sets of *all-round mechanical traction loadings* applied at the surface of the body and two known *eigenstrain fields* existing in the volume of body.

$$\breve{t}^{(I)}(x), \breve{t}^{(II)}(x), \ x \in \partial V, \quad \breve{\Gamma}^{(I)}(x), \breve{\Gamma}^{(II)}(x), \ x \in V$$

Sets of fields of *stresses, strains and displacements* constituting solution of mechanical equilibrium problem of linear elasticity for two sets of prescribed boundary tractions and eigenstrains fields are denoted by

$$\{\breve{\sigma}^{(I)}(x), \breve{\varepsilon}^{(I)}(x), \breve{u}^{(I)}(x)\}, \quad \{\breve{\sigma}^{(II)}(x), \breve{\varepsilon}^{(II)}(x), \breve{u}^{(II)}(x)\}$$

The stresses fields must satisfy *mechanical equilibrium equations* and respective *constitutive relations of linear elasticity* in all points of the volume and on the surface of body and they must fulfill boundary conditions

$$\breve{\sigma}^{(I)}(x)_{ij,j} = 0, \quad \breve{\sigma}^{(II)}(x)_{ij,j} = 0, \ x \in V$$

$$\breve{t}^{(I)}(x) = n(x) \cdot \breve{\sigma}^{(I)}(x), \ \breve{t}^{(II)}(x) = n(x) \cdot \breve{\sigma}^{(II)}(x), \ x \in \partial V$$

$$\breve{\varepsilon}^{(I)}(x) = \breve{M}(x) \breve{\sigma}^{(I)}(x) + \breve{\Gamma}^{(I)}(x), \quad \breve{\varepsilon}^{(II)}(x) = \breve{M}(x) \breve{\sigma}^{(II)}(x) + \breve{\Gamma}^{(II)}(x)$$

Betti reciprocity theorem
for (linear) elastic materials with eigenstrains

Taking advantage of the diagonal symmetry of elastic properties tensor it can be obtained

$$\check{\sigma}^{(I)}(\boldsymbol{x}) \cdot [\check{\varepsilon}^{(II)}(\boldsymbol{x}) - \check{\Gamma}^{(II)}(\boldsymbol{x})] = \check{\sigma}^{(II)}(\boldsymbol{x}) \cdot [\check{\varepsilon}^{(I)}(\boldsymbol{x}) - \check{\Gamma}^{(I)}(\boldsymbol{x})];$$

$$\check{\sigma}^{(I)}\check{\mathbf{M}}(\boldsymbol{x})\check{\sigma}^{(II)} = \check{\sigma}^{(II)}\check{\mathbf{M}}(\boldsymbol{x})\check{\sigma}^{(I)}$$

The *Betti's reciprocal theorem relation with eigenstrains* is obtained upon integrating above relation over the whole volume of the body, using Green-Gauss theorem and static admissibility of stress fields

$$\oint_{\partial V}(\check{\boldsymbol{t}}^{(I)} \cdot \check{\boldsymbol{u}}^{(II)})ds - \oint_{V}(\check{\sigma}^{(I)} \cdot \check{\Gamma}^{(II)})dV = \oint_{\partial V}(\check{\boldsymbol{t}}^{(II)} \cdot \check{\boldsymbol{u}}^{(I)})ds - \oint_{V}(\check{\sigma}^{(II)} \cdot \check{\Gamma}^{(I)})dV$$

Classical formulations of Betti theorem are easily recovered upon substituting

$$\check{\Gamma}^{(II)}(\boldsymbol{x}) = \check{\Gamma}^{(I)}(\boldsymbol{x}) = 0 \ \ and \ / \ or \ \ \check{\boldsymbol{t}}^{(I)} = \check{\boldsymbol{t}}^{(II)} = 0$$

$$\oint_{\partial V}(\check{\boldsymbol{t}}^{(I)} \cdot \check{\boldsymbol{u}}^{(II)})ds = \oint_{\partial V}(\check{\boldsymbol{t}}^{(II)} \cdot \check{\boldsymbol{u}}^{(I)})ds$$

Betti reciprocity theorem
for (linear) elastic materials with eigenstrains

Betti theorem allows to reveal important property of *self-equilibrated eigenstrains influence moduli.* Let us consider pairs of micro-eigenstrains fields (α and β are fixed):

$$\breve{\Gamma}^{I}(\boldsymbol{x}) = \begin{cases} \Gamma_{\alpha}^{I} & \boldsymbol{x} \in V_{\alpha} \\ 0 & \boldsymbol{x} \notin V_{\alpha} \end{cases}, \qquad \breve{\Gamma}^{II}(\boldsymbol{x}) = \begin{cases} \Gamma_{\beta}^{II} & \boldsymbol{x} \in V_{\beta} \\ 0 & \boldsymbol{x} \notin V_{\beta} \end{cases}$$

Micro-eigenstrain fields *I* and *II* induces pair of self-equilibrated in the investigated body (RVE) stress fields $\boldsymbol{t}^{I} = 0, \boldsymbol{t}^{II} = 0$:

$$\begin{aligned} \breve{\sigma}_{\gamma}^{(in)\,I}(\boldsymbol{x}) &= \breve{\mathfrak{I}}_{\gamma\alpha}(\boldsymbol{x})\Gamma_{\alpha}^{I} & \boldsymbol{x} \in V_{\gamma} \;\; (\gamma = 1\ldots n) \\ \breve{\sigma}_{\eta}^{(in)\,II}(\boldsymbol{x}) &= \breve{\mathfrak{I}}_{\eta\beta}(\boldsymbol{x})\Gamma_{\beta}^{II} & \boldsymbol{x} \in V_{\eta} \;\; (\eta = 1\ldots n) \end{aligned} \;;\;\; \boldsymbol{t}_{\gamma}^{I} = 0, \;\; \boldsymbol{t}_{\eta}^{II} = 0$$

Upon substituting the above and $\boldsymbol{t}^{I} = 0, \boldsymbol{t}^{II} = 0$ into Betti reciprocity theorem and averaging of phases domains one obtains the following properties of SEIM modules

$$V_{\alpha}\Gamma_{\alpha}^{I} \cdot \mathfrak{I}_{\alpha\beta}^{*}\Gamma_{\beta}^{II} = V_{\beta}\Gamma_{\beta}^{II} \cdot \mathfrak{I}_{\beta\alpha}^{*}\Gamma_{\alpha}^{I} \;\Rightarrow\; \Gamma_{\alpha}^{I} \cdot [z_{\alpha}\mathfrak{I}_{\alpha\beta}^{*} - z_{\beta}\overset{T}{\mathfrak{I}}{}_{\beta\alpha}^{*}]\Gamma_{\beta}^{II} = 0 \;\Rightarrow$$

$$\Rightarrow \boxed{z_{\alpha}\mathfrak{I}_{\alpha\beta}^{*} = z_{\beta}\overset{T}{\mathfrak{I}}{}_{\beta\alpha}^{*}} \qquad \left(\mathfrak{I}_{\alpha\beta}^{*} = <\breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x})>_{V_{\alpha}} = \frac{1}{V_{\alpha}}\int_{V_{\alpha}}\breve{\mathfrak{I}}_{\alpha\beta}(\boldsymbol{x})dx\right)$$

The $\mathfrak{I}^{*}_{\alpha\beta}$ moduli must satisfy *Betti's relations* $z_{\alpha}\mathfrak{I}^{*}_{\alpha\beta} = z_{\beta}(\mathfrak{I}^{*}_{\beta\alpha})^{\mathsf{T}}$, and must become zero ($\mathfrak{I}^{*}_{\alpha\beta}=0$) for $z_{\beta}=0$ and $z_{\alpha}\neq0$ ($\alpha\neq\beta$).

In order to identically fulfill these constraints, the considerations are restricted to a class of microstructure geometries for which the following relations hold

$$\mathfrak{I}_{\alpha\beta} = \mathfrak{I}^{(S)}_{\alpha\beta} + \mathfrak{I}^{(A)}_{\alpha\beta}, \quad \mathfrak{I}^{*}_{\alpha\beta} = z_{\beta}\mathfrak{I}_{\alpha\beta} \ (!\beta) \quad \Rightarrow \quad \mathfrak{I}_{\alpha\beta} = \overset{T}{\mathfrak{I}}_{\beta\alpha}$$

Thus, the SEIM moduli matrix is adopted to be the simple sum of symmetric and anti-symmetric matrix, where

$$\mathfrak{I}^{(S)}_{\alpha\beta} \equiv \tfrac{1}{2}(\mathfrak{I}_{\alpha\beta} + \mathfrak{I}_{\beta\alpha}) = \mathfrak{I}^{(S)}_{\beta\alpha}, \quad \mathfrak{I}^{(A)}_{\alpha\beta} \equiv \tfrac{1}{2}(\mathfrak{I}_{\alpha\beta} - \mathfrak{I}_{\beta\alpha}) = -\mathfrak{I}^{(A)}_{\beta\alpha}$$

It may readily be shown that *all elements* $\mathfrak{I}^{(S)}_{\alpha\beta}$ of symmetric matrix are *diagonally symmetric fourth-order tensors* $(\mathfrak{I}^{(S)}_{\alpha\beta})_{ijmn}= (\mathfrak{I}^{(S)}_{\alpha\beta})_{mnij}$, whereas *all elements* $\mathfrak{I}^{(A)}_{\alpha\beta}$ of antisymmetric matrix are *diagonally skew-symmetric tensors* $(\mathfrak{I}^{(A)}_{\alpha\beta})_{ijmn}= -(\mathfrak{I}^{(A)}_{\alpha\beta})_{mnij}$

$$\mathfrak{I}^{(S)}_{\alpha\beta} = \overset{\mathsf{T}}{\mathfrak{I}}^{(S)}_{\alpha\beta}, \ \mathfrak{I}^{(A)}_{\alpha\beta} = -\overset{\mathsf{T}}{\mathfrak{I}}^{(A)}_{\alpha\beta}, \quad for \ \alpha \neq \beta$$

The SEIM moduli matrix have the shown graphically structure

$$\mathfrak{I}^*_{\alpha\beta} = \begin{bmatrix} z_1\mathfrak{I}^{(S)}_{11} & ... & ... & ... & z_n\mathfrak{I}^{(S)}_{1n} \\ ... & ... & ... & ... & ... \\ ... & ... & ... & z_\beta\mathfrak{I}^{(S)}_{\alpha\beta} & ... \\ ... & .... & z_\beta\mathfrak{I}^{(S)}_{\alpha\beta} & ... & ... \\ z_n\mathfrak{I}^{(S)}_{1n} & ... & ... & ... & z_n\mathfrak{I}^{(S)}_{nn} \end{bmatrix} + \begin{bmatrix} 0 & ... & ... & ... & z_n\mathfrak{I}^{(A)}_{1n} \\ ... & ... & ... & ... & ... \\ ... & ... & 0 & z_\beta\mathfrak{I}^{(A)}_{\alpha\beta} & ... \\ ... & ... & z_\beta(-\mathfrak{I}^{(A)}_{\alpha\beta}) & 0 & ... \\ z_n(-\mathfrak{I}^{(A)}_{1n}) & ... & ... & ... & 0 \end{bmatrix}$$

There exists *(2·n-1)* independent relations connecting *n·n* moduli $\mathfrak{I}^*_{\alpha\beta}$,

$$\mathfrak{I}^*_{\alpha\alpha} = -\sum_{\beta=1,\beta\neq\alpha}^{n} z_\beta\mathfrak{I}^{(S)}_{\alpha\beta}, \qquad 0 = \sum_{\beta=1,\beta\neq\alpha}^{n} z_\beta\mathfrak{I}^{(A)}_{\alpha\beta} = -\sum_{\beta=1,\beta\neq\alpha}^{n} z_\beta\mathfrak{I}^{(A)}_{\beta\alpha}, \quad (!\,\alpha=1,2..,n)$$

Thus in the most general case, mathematically precise description of a *state of macroelement* (RVE) consisting of *n* phases requires *explicit knowledge of n·n* moduli $\mathfrak{I}^*_{\alpha\beta}$ expressed in terms of *n(n-1)/2* symmetric tensors $\mathfrak{I}^{(S)}_{\alpha\beta}$ and *(n-2)(n-1)/2* skew-symmetric tensors $\mathfrak{I}^{(A)}_{\alpha\beta}$ of the fourth order.

The general connection between $\mathfrak{I}^*_{\alpha\beta}$ and pair of tensors $\{\mathfrak{I}^{(S)}_{\alpha\beta}, \mathfrak{I}^{(A)}_{\alpha\beta}\}$ in compact mathematical form can be written as follows

$$\mathfrak{I}^*_{\alpha\beta} = (1 - \delta_{\alpha\beta}) z_\beta (\mathfrak{I}^{(S)}_{\alpha\beta} + \mathfrak{I}^{(A)}_{\alpha\beta}) - \delta_{\alpha\beta} \sum_{\gamma=1}^{n} (1 - \delta_{\gamma\alpha}) z_\gamma \mathfrak{I}^{(S)}_{\alpha\gamma}$$

The tensors $\mathfrak{I}^{(S)}_{\alpha\beta}$, $\mathfrak{I}^{(A)}_{\alpha\beta}$ will be collectively referred to as the *ingredients* of *self-equilibrated eigenstrains influence moduli*.

In general, $\mathfrak{I}^{(S)}_{\alpha\beta}$ *do depend* on phase composition z_α, elastic moduli of individual phases M_α and on a number of descriptors of the microstructure geometry $\{h\}$, but they are *not influenced by Γ_β*.

Note:
It is interesting to note that two phase material requires knowledge of only one diagonally symmetric tensor $\mathfrak{I}^{(S)}_{12}$ to determine four moduli $\mathfrak{I}^*_{\alpha\beta}$.
The three phase (n=3) material requires knowledge of three diagonally symmetric tensor $\mathfrak{I}^{(S)}_{12}$, $\mathfrak{I}^{(S)}_{13}$, $\mathfrak{I}^{(S)}_{23}$ and *one* diagonally skew-symmetric tensor $\mathfrak{I}^{(A)}_{12}$ to determine nine moduli $\mathfrak{I}^*_{\alpha\beta}$.

Two families of useful functions based on SEIM moduli

It will be prove convenient to introduce the following family of scalar valued functions $f_{\alpha\beta}(X, Y)$, $(\alpha \neq \beta)$ of two tensorial arguments, second-order symmetric tensors X, Y, is defined as follows

$$f_{\alpha\beta}(X,Y) \equiv 0.5\,[(X-Y)\cdot \mathfrak{I}^{(S)}_{\alpha\beta}(X-Y) - (X\cdot \mathfrak{I}^{(A)}_{\alpha\beta}Y - Y\cdot \mathfrak{I}^{(A)}_{\alpha\beta}X)],$$

$$f_{\alpha\beta}(X,Y) = f_{\beta\alpha}(Y,X), \quad f_{\alpha\beta}(X,X)=0.$$

It will also be useful to introduce an array of second-order tensor valued functions $\mathfrak{R}_{\alpha}(\chi_{\gamma})$ of n second-order symmetric tensors χ_{γ} will $(\alpha,\gamma=1,2,\dots,n)$

$$\mathfrak{R}_{\alpha}(\chi_{\gamma}) \equiv \sum_{\beta=1}^{n} \mathfrak{I}^{*}_{\alpha\beta}\chi_{\beta}, \quad \mathfrak{R}_{\alpha}(\chi_{\gamma}) = \sum_{\beta=1,\beta\neq\alpha}^{n} z_{\beta}[\mathfrak{I}^{(S)}_{\alpha\beta}(\chi_{\beta}-\chi_{\alpha}) + \mathfrak{I}^{(A)}_{\alpha\beta}\chi_{\beta}], \quad (\sum_{\alpha=1}^{n} z_{\alpha}\mathfrak{R}_{\alpha}=0)$$

In general case, both $\mathfrak{R}_{\alpha}$ and $f_{\alpha\beta}$ besides dependence on phase composition z_{γ} $(\gamma=1,2,\dots,n)$ will depend parametrically on variables $\{h\}$ characterizing the microstructure of SMA macroelement.
The following properties were used to obtain convenient mathematically form of functions $\mathfrak{R}_{\alpha}$

$$\sum_{\alpha,\beta=1,\,\alpha\neq\beta}^{n} z_{\alpha}z_{\beta}\mathfrak{I}^{(S)}_{\alpha\beta}(\chi_{\beta}-\chi_{\alpha})=0, \quad \sum_{\alpha,\beta=1,\,\alpha\neq\beta}^{n} z_{\alpha}z_{\beta}\mathfrak{I}^{(A)}_{\alpha\beta}\chi_{\beta} = 0.5 \sum_{\alpha,\beta=1,\,\alpha\neq\beta}^{n} z_{\alpha}z_{\beta}\mathfrak{I}^{(A)}_{\alpha\beta}(\chi_{\beta}-\chi_{\alpha}) = 0$$

Macroscopic state variables and properties given in terms of SEIM moduli

When the set of tensors $\{\mathfrak{I}^{(S)}_{\alpha\beta}, \mathfrak{I}^{(A)}_{\alpha\beta}\}$ ($\alpha,\beta = 1,...,n$) is known, has been determined by execution of some procedure theoretical, numerical or experimental, then the effective properties and/or state variables of RVE can be determined with the aid of the following formulas,

$$\sigma^{(ex)}_\alpha = \sigma + \mathfrak{R}_\alpha(M_\gamma\sigma), \quad \sigma^{(in)}_\alpha = \mathfrak{R}_\alpha(\Gamma_\gamma), \qquad \sigma_\alpha = \sigma + \mathfrak{R}_\alpha(M_\gamma\sigma + \Gamma_\gamma)$$

$$\varepsilon^{(ex)}_\alpha = M_\alpha\sigma^{(ex)}_\alpha, \qquad \varepsilon^{(in)}_\alpha = M_\alpha\sigma^{(in)}_\alpha + \Gamma_\alpha, \quad \varepsilon_\alpha = M_\alpha\sigma_\alpha + \alpha\Delta T + \Gamma_\alpha \quad (!\alpha)$$

The effective elastic compliance M, macroscopic (effective) elastic strain ε, macroscopic phase transition strain ε^{pt} can be expressed as follows,

$$M = M^{Re} - \sum_{\alpha,\beta=1, \beta\neq\alpha}^{n} z_\alpha z_\beta M_{\alpha\beta}; \quad M^{Re} \equiv \sum_{\alpha=1}^{n} z_\alpha M_\alpha \rightarrow M^{Re} = (M^{Re})^T, \quad \Delta M_{\alpha\beta} \equiv M_\alpha - M_\beta,$$

$$\boxed{M_{\alpha\beta} = 0.5[\Delta M_{\alpha\beta}\mathfrak{I}^{(S)}_{\alpha\beta}\Delta M_{\alpha\beta} - (M_\alpha\mathfrak{I}^{(A)}_{\alpha\beta}M_\beta - M_\beta\mathfrak{I}^{(A)}_{\alpha\beta}M_\alpha)] = M_{\beta\alpha},} \; (!\alpha,!\beta), \; M_{\alpha\beta} = M^T_{\alpha\beta}$$

$$\varepsilon^{(ex)} = M^{Re}\sigma + \sum_{\alpha=1}^{n} z_\alpha M_\alpha\mathfrak{R}_\alpha(M_\gamma\sigma) = M\sigma, \quad \varepsilon^{pt} = \Gamma + \sum_{\alpha=1}^{n} z_\alpha M_\alpha\mathfrak{R}_\alpha(\Gamma_\gamma), \; \Gamma = \sum_{\alpha=1}^{n} z_\alpha\Gamma_\alpha$$

M^{Re} denotes Reuss upper bound of effective elastic compliance, σ denotes macroscopic stress, σ_α denote macroscopic phase stresses.

Macroscopic state variables and properties given in terms of SEIM moduli

The macroscopic *complementary elastic energy* g^{el} of the solid phase conglomerate can be expressed in the form

$$g^{el} = \sum_{\alpha=1}^{n} z_\alpha g_\alpha^{(0)el} - 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta g_{\alpha\beta}^{el},$$

$$\rho g_\alpha^{(0)el} \equiv 0.5\,\boldsymbol{\sigma} \cdot \boldsymbol{M}_\alpha \boldsymbol{\sigma}, \quad \boxed{\rho g_{\alpha\beta}^{el} \equiv \boldsymbol{\sigma} \cdot \boldsymbol{M}_{\alpha\beta} \boldsymbol{\sigma} = f_{\alpha\beta}(\boldsymbol{M}_\alpha \boldsymbol{\sigma}, \boldsymbol{M}_\beta \boldsymbol{\sigma})}$$

The macroscopic *coherence internal energy* u^{coh} can be expressed in the form

$$\rho u^{coh} = -0.5 \sum_{\alpha,\beta=1}^{n} z_\alpha \boldsymbol{\Gamma}_\alpha \cdot \mathfrak{I}_{\alpha\beta}^{*} \boldsymbol{\Gamma}_\beta \geq 0 \quad (\rho u^{coh} = 0.5 \sum_{\alpha=1}^{n} z_\alpha (-\boldsymbol{\sigma}_\alpha^{(in)}) \cdot \boldsymbol{\Gamma}_\alpha \geq 0)$$

$$\rho u^{coh} = 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta \, \rho u_{\alpha\beta}^{(0)coh}, \quad \boxed{\rho u_{\alpha\beta}^{(0)coh} = f_{\alpha\beta}(\boldsymbol{\Gamma}_\alpha, \boldsymbol{\Gamma}_\beta)}$$

The above formulas are valid for *piecewise uniform* phase transformation eigenstrains Γ_α

$$(\breve{\Gamma}_\alpha(\boldsymbol{x}) = \boldsymbol{\Gamma}_\alpha + \underset{=0}{\cancel{\breve{\Gamma}_\alpha^{f}(\boldsymbol{x})}}, \quad \boldsymbol{x} \in V_\alpha, \quad \boldsymbol{\Gamma}_\alpha = <\breve{\Gamma}_\alpha(\boldsymbol{x})>_{V_\alpha}; \quad \alpha = 1,..,n)$$

Heuristic conjecture on coherence entropy

The studies presented here are focused *coherence internal energy* u^{coh}.
They *do not and cannot* deliver information on *coherence entropy* s^{coh}.

Experimental data exists (not to be discussed here) that influence of coherence entropy cannot be neglected in modeling SMA materials behavior.

A reasonable *heuristic conjecture* is to accept a general explicit expression for *coherence entropy* in the form analogous to expression for *coherence internal energy*, i.e.

$$\rho\, s^{coh} = \sum_{\alpha=1}^{n} z_\alpha\, \rho\, s_\alpha^{coh} \; + \; 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta\, \rho\, s_{\alpha\beta}^{coh}$$

In the sequel, we shall adopt conjecture that *coherence entropy* can be expressed with still more simple formula $(s_{\alpha\beta}{}^{coh}=0)$

$$\rho s^{coh} = \sum_{\alpha=1}^{n} z_\alpha\, \rho s_\alpha^{coh}$$

By definition the *free coherence energy* is equal to $\rho\,\phi^{coh} \equiv \rho\, u^{coh} - T\,\rho s^{coh}$

Special cases
of SEIM method consistent estimations
of SMA materials thermostatic properties
and state variables

Case of anisotropic elastic components (phases) forming anisotropic two-phase aggregate ($n=2$)

In the case of two phase materials (n=2) all the SEIM tensors $\mathfrak{I}^*_{\alpha\beta}$ can be expressed with single symmetric tensor $\mathfrak{I}^{(S)}_{12}$ as in such case $\mathfrak{I}^{(A)}_{12}$ must be equal to zero

$$\mathfrak{I}^*_{11} = -\mathfrak{I}^*_{12} = -z\,\mathfrak{I}^{(S)}_{12}, \quad \mathfrak{I}^*_{22} = -\mathfrak{I}^*_{21} = -(1-z)\,\mathfrak{I}^{(S)}_{12}$$

The internal and external phase stresses reduce to

$$\sigma_1^{(ex)} = [\mathbf{I} + z\,\mathfrak{I}^{(S)}_{12}(M_2 - M_1)]\,\sigma, \quad \sigma_2^{(ex)} = [\mathbf{I} - (1-z)\mathfrak{I}^{(S)}_{12}(M_2 - M_1)]\,\sigma,$$

$$\sigma_1^{(in)} = z\,\mathfrak{I}^{(S)}_{12}(\Gamma_2 - \Gamma_1), \qquad \sigma_2^{(in)} = -(1-z)\mathfrak{I}^{(S)}_{12}(\Gamma_2 - \Gamma_1)$$

The effective elastic compliances and macroscopic phase strain become

$$M = M^{Re} - (1-z)z(M_1 - M_2)\mathfrak{I}^{(S)}_{12}(M_1 - M_2), \quad M^{Re} = (1-z)M_1 + zM_2$$

$$\varepsilon^{pt} = (1-z)\Gamma_1 + z\Gamma_2 - (1-z)z(M_1 - M_2)\mathfrak{I}^{(S)}_{12}(\Gamma_1 - \Gamma_2)$$

The nonzero coefficients of elastic complementary energy and coherence internal energy take the form

$$g^{el}_{12} = g^{el}_{21} = \tfrac{1}{2}\sigma \cdot (M_1 - M_2)\mathfrak{I}^{(S)}_{12}(M_1 - M_2)\sigma / \rho, \quad (\rho g^{el} = \tfrac{1}{2}\sigma \cdot M\sigma)$$

$$u^{(0)coh}_{12} = u^{(0)coh}_{21} = \tfrac{1}{2}(\Gamma_1 - \Gamma_2) \cdot \mathfrak{I}^{(S)}_{12}(\Gamma_1 - \Gamma_2) / \rho, \qquad (\rho u^{coh} = \Delta\Gamma_{12} \cdot \mathfrak{I}^{(S)}_{12}\Delta\Gamma_{12})$$

Note: The formulas devoted to two-phase SMA material were earlier presented by (Bernardini, 2001); ($\mathbf{R} = -z_1 z_2 \mathfrak{I}^{(S)}_{12}$).

Case of anisotropic elastic components (phases) forming anisotropic two-phase aggregate ($n=2$)

The formula linking effective elastic moduli $\boldsymbol{M}$ with ingredient of SEIM moduli $\mathfrak{I}^{(S)}{}_{12}$ delivers very interesting *CLUE* for the *SEIM method* practical *engineering exploitation in a semi-experimental procedure*. A viable option might be experimental determination of components of effective elastic compliance, what can subsequently serve for estimation of the other material properties. Simple transformations lead to the relation

$$z_1 z_2 \mathfrak{I}^{(S)}_{12} = (\boldsymbol{M}_1 - \boldsymbol{M}_2)^{-1}(\boldsymbol{M}^{Re} - \boldsymbol{M})(\boldsymbol{M}_1 - \boldsymbol{M}_2)^{-1}, \quad \boldsymbol{M}_2 \neq \boldsymbol{M}_1$$

$$(\mathfrak{I}^{(S)}_{12} = \boldsymbol{L} \quad \text{when} \quad \boldsymbol{M}_2 = \boldsymbol{M}_1)$$

In order to facilitate establishing link between the present developments and classical analytical and/or computational mechanics-oriented studies of heterogeneous media presented e.g. in (Hill, 1963), (Dvorak&Benveniste, 1992), (Nemat-Nasser&Hori, 1993) or recently (Dvorak, 2013) it is worth to specify explicitly relations between *SEIM moduli* $\mathfrak{I}^{*}_{\alpha\beta}$ and classical, *in general case*, diagonally non-symmetric, dimensionless, fourth-order tensors $\mathcal{B}_{\alpha}$ ($\sigma_{\alpha} = \mathcal{B}_{\alpha}\sigma$) called *stress concentration tensors*, cf. e.g. (Hill, 1963). They are

$$\mathcal{B}_{\alpha} = \boldsymbol{I} + \sum_{\beta=1}^{n} \mathfrak{I}^{*}_{\alpha\beta} \boldsymbol{M}_{\beta}, \quad \mathcal{B}_{\alpha} = \boldsymbol{I} + \sum_{\beta=1, \beta \neq \alpha}^{n} z_{\beta}[\mathfrak{I}^{(S)}_{\alpha\beta} \Delta \boldsymbol{M}_{\beta\alpha} + \mathfrak{I}^{(A)}_{\alpha\beta} \boldsymbol{M}_{\beta}]$$

Reuss-type consistent bounding relationships

The *Reuss estimate* of RVE effective properties and state parameters for *anisotropic aggregate* consisting of *n anisotropic phases* requires setting all the SEIM moduli to zero value ($\mathfrak{I}^*_{\alpha\beta}=0$). This implies

$$\mathfrak{I}^{*\,\mathrm{Re}}_{\alpha\beta} = 0 \implies \mathfrak{R}^{\mathrm{Re}}_{\alpha} = 0,\; f^{\mathrm{Re}}_{\alpha\beta} = 0,\; M^{\mathrm{Re}}_{\alpha\beta} = 0,\; g^{el}_{\alpha\beta} = 0 \implies$$

$$M = M^{\mathrm{Re}}\,(M^{Re} \equiv \sum_{\alpha=1,..,n} z_\alpha M_\alpha),\; \boxed{\sigma^{(\mathrm{ex})}_\alpha = \sigma_\alpha = \sigma,}\; \sigma^{(\mathrm{in})}_\alpha = 0,\;\; \varepsilon^{(\mathrm{in})}_\alpha = \Gamma_\alpha,$$

$$g^{el} = \tfrac{1}{2}\sigma \cdot M^{\mathrm{Re}}\,\sigma,\;\; u^{coh} = 0,\;\; \phi^{coh} = -T\cdot s^{coh},\;\; \varepsilon^{pt} = \sum_{\alpha=1}^{n} z_\alpha \Gamma_\alpha$$

The M^{Re} make an *upper bound of compliance moduli* M.

The Reuss estimate of Gibbs free energy takes the form

$$\rho g^{(\mathrm{Re})} = \sum_{\alpha=1}^{n} z_\alpha\, \rho[u^0_\alpha - T(s^0_\alpha + s^{coh}_\alpha)] + c_p[\Delta T - T\ln(T/T_0)] - \Delta T \sigma \cdot \alpha - 0.5\sigma \cdot M^{\mathrm{Re}}\sigma - \sigma \cdot \varepsilon^{pt}$$

The *Reuss values* of properties/state variables would actually result from the rigorous solutions of UT – uniform traction, boundary-value problems for a class of special microstrain fields $M_\alpha\sigma$ and Γ_α ($x \in V_\alpha$, $\alpha=1,\ldots,n$), *compatible at all interfaces* and for special microstructural geometries, the ones leading to *uniform stresses* all over domain of RVE.

Voigt-type consistent bounding relationships

The following mathematical relation exists between *Reuss* moduli M^{Re} (*upper bound of effective compliance* M) and *Voigt* moduli L^V (*upper bound* of effective *stiffness* L ($L = M^{-1}$)).

$$M^{Re} - \overset{-1}{L}{}^V = \sum_{\alpha,\beta=1,\, \beta\neq\alpha}^{n} z_\alpha z_\beta M_{\alpha\beta}^V, \quad M_{\alpha\beta}^V \equiv -0.5 \Delta M_{\alpha\beta} \Delta L_{\alpha\beta} \overset{-1}{L}{}^V, \qquad \begin{aligned} \Delta M_{\alpha\beta} &\equiv M_\alpha - M_\beta \\ \Delta L_{\alpha\beta} &\equiv L_\alpha - L_\beta \end{aligned}$$

$$\{ L^V = (L^V)^T, \ M^{Re} = (M^{Re})^T \} \Rightarrow \{ \overset{-1}{L}{}^V \Delta L_{\alpha\beta} \Delta M_{\alpha\beta} = \Delta M_{\alpha\beta} \Delta L_{\alpha\beta} \overset{-1}{L}{}^V \}$$

$$\Rightarrow \quad \{ M_{\alpha\beta}^V = (-\tfrac{1}{4})(\overset{-1}{L}{}^V \Delta L_{\alpha\beta} \Delta M_{\alpha\beta} + \Delta M_{\alpha\beta} \Delta L_{\alpha\beta} \overset{-1}{L}{}^V) = (M_{\alpha\beta}^V)^T \}$$

The tensors $M_{\alpha\beta}{}^V$ can also be expressed in the following form

$$\boxed{M_{\alpha\beta}^V(M_\alpha, L_\alpha) = 0.5(\Delta M_{\alpha\beta}\, L_{\alpha\beta}^{(S)}\, \Delta M_{\alpha\beta} - M_\alpha\, L_{\alpha\beta}^{(A)}\, M_\beta + M_\beta\, L_{\alpha\beta}^{(A)}\, M_\alpha), \quad (!\alpha, \beta)}$$

where

$$L^V \equiv \sum_{\alpha=1}^{n} z_\alpha L_\alpha \ (L_\alpha = M_\alpha^{-1}), \ L_\alpha = z_\alpha L_{\alpha\alpha}^{(S)} + \sum_{\alpha,\beta=1;\ \alpha\neq\beta}^{n} z_\beta L_{\alpha\beta}^{(S)},$$

$$\boxed{L_{\alpha\beta} \equiv L_\alpha \overset{-1}{L}{}^V L_\beta,}\ L_{\alpha\beta}^{(S)} \equiv \tfrac{1}{2}(L_{\alpha\beta} + L_{\beta\alpha}), \ L_{\alpha\beta}^{(A)} \equiv \tfrac{1}{2}(L_{\alpha\beta} - L_{\beta\alpha}); \quad L_{\alpha\beta}^{(S)} = \overset{T}{L}{}_{\alpha\beta}^{(S)}, \ \overset{T}{L}{}_{\alpha\beta}^{(A)} = -L_{\alpha\beta}^{(A)}$$

Voigt-type consistent bounding relationships

It can be shown that the effective moduli of the anisotropic aggregate RVE will take the values of *Voigt estimate* $M=(L^V)^{-1}$ provided that the *ingredients of stress concentration moduli* take the form

$$\mathfrak{I}_{\alpha\beta}^{V(S)} = L_{\alpha\beta}^{(S)} = \tfrac{1}{2}(L_\alpha \overset{-1}{L}^V L_\beta + L_\beta \overset{-1}{L}^V L_\alpha), \quad \mathfrak{I}_{\alpha\beta}^{V(A)} = L_{\alpha\beta}^{(A)} = 0$$

or equivalently

$$\mathfrak{I}_{\alpha\beta}^{V(S)} = -0.5\,[(\Delta M_{\alpha\beta})^{-1}\overset{-1}{L}^V \Delta L_{\alpha\beta} + \Delta L_{\alpha\beta} \overset{-1}{L}^V (\Delta M_{\alpha\beta})^{-1}] \quad (!\,\alpha,\beta), \quad \mathfrak{I}_{\alpha\beta}^{V(A)} = 0$$

when $z_\beta \to 1$ then $\mathfrak{I}^{V(S)}{}_{\alpha\beta} \to L_\alpha \to \sigma_\alpha^{(in)}\big|_{z_\beta=1} = -L_\alpha \Gamma_\alpha$ provided $\Gamma_\beta = 0$

Voigt-type estimation of families of functions $f_{\alpha\beta}$ and $\mathfrak{R}_\alpha$ consistent with the Betti reciprocity theorem take the following form

$$f_{\alpha\beta}(X,Y) = 0.5(X-Y)\cdot L_{\alpha\beta}^{(S)}(X-Y)$$

$$\mathfrak{R}_\alpha^V(z_\gamma,\Gamma_\gamma) = L_\alpha[\varepsilon_0^P - \Gamma_\alpha], \quad \Leftarrow \quad \mathfrak{R}_\alpha^V(z_\gamma,\Gamma_\gamma) = \sum_{\beta=1,\,\beta\neq\alpha}^n z_\beta[L_{\alpha\beta}^{(S)}(\Gamma_\beta - \Gamma_\alpha) + \underbrace{L_{\alpha\beta}^{(A)}}_{=0}\Gamma_\beta]$$

$$\varepsilon_0^P(z_\gamma,\Gamma_\gamma) \equiv \sum_{\beta=1}^n z_\beta \overset{-1}{L}^V L_\beta \Gamma_\beta$$

Voigt-type consistent bounding relationships

The *Voigt* estimate of *anisotropic aggregate* RVE effective properties and values of state parameters can be expressed as follows

$$M = \overset{-1}{L}{}^{V}, \quad \sigma_{\alpha}^{(\mathrm{ex})} = L_{\alpha}\varepsilon_{\alpha}^{(\mathrm{ex})}, \qquad\qquad \varepsilon_{\alpha}^{(\mathrm{ex})} = \overset{-1}{L}{}^{V}\sigma,$$

$$\sigma_{\alpha}^{(\mathrm{in})}(z_{\gamma},\Gamma_{\gamma}) = L_{\alpha}[\varepsilon_{0}^{P} - \Gamma_{\alpha}], \quad \varepsilon_{\alpha}^{(\mathrm{in})} = \varepsilon^{pt} = \varepsilon_{0}^{P} = \sum_{\beta=1}^{n} z_{\beta}\overset{-1}{L}{}^{V}L_{\beta}\Gamma_{\beta}$$

The Voigt estimate moduli L^{V} make an *upper bound of stiffness moduli L.*

It displays uniform distribution of strain $\quad\boxed{\varepsilon_{\alpha} = (L^{V})^{-1}\sigma + \varepsilon_{0}^{P} + \alpha\,\Delta T}$

The Voigt-type estimation of Gibbs free energy takes the form

$$\rho g^{(V)} = \left(\sum_{\alpha=1}^{n} z_{\alpha}\rho g_{\alpha}^{0}\right) - \underbrace{0.5\,\sigma\cdot\overset{-1}{L}{}^{V}\sigma}_{\rho g^{el}(z_{\gamma},\sigma)} - \sigma\cdot\varepsilon_{0}^{P} + \underbrace{0.5\sum_{\alpha=1}^{n} z_{\alpha}(\Gamma_{\alpha} - \varepsilon_{0}^{P})\cdot L_{\alpha}(\Gamma_{\alpha} - \varepsilon_{0}^{P})}_{=\rho u^{coh}(z_{\gamma},\Gamma_{\gamma})\geq 0},$$

$$g_{\alpha}^{0} = u_{\alpha}^{0} - T(s_{\alpha}^{0} + s_{\alpha}^{coh}) + c_{p}[\Delta T - T\ln(T/T_{0})] - \Delta T\sigma\cdot\alpha/\rho$$

Voigt-type consistent bounding relationships

It will prove convenient to introduce the concept of *partial ultimate phase eigenstrains* κ_α as follows

$$\kappa_\alpha(z_\gamma, \Gamma_\gamma) = \overset{-1}{L}{}^V L_\alpha \Gamma_\alpha + (I - \overset{-1}{L}{}^V L_\alpha) \varepsilon_0^P(z_\gamma, \Gamma_\gamma)$$

then macroscopic phase transition strain can be expressed as

$$\varepsilon^{pt} = \sum_{\alpha=1}^n z_\alpha \kappa_\alpha = \varepsilon_0^P$$

The *Voigt* values of properties, state variables would actually result from the rigorous solutions of UT boundary-value problems for a class of specific microstrain fields $M_\alpha \sigma$ and Γ_α ($x \in V_\alpha, \alpha=1,\ldots,n$), and special micro-structural geometries leading to *uniform strains* all over RVE.

In obtaining the relations between Reuss and Voigt moduli there were used the following identities

$$(L_\alpha - L_\beta)^{-1} L_\alpha = -M_\beta (M_\alpha - M_\beta)^{-1}, \quad M_\alpha L_\beta + M_\beta L_\alpha = 2I - \Delta M_{\alpha\beta} \Delta L_{\alpha\beta},$$

$$\Delta M_{\alpha\beta} \equiv M_\alpha - M_\beta, \quad \Delta L_{\alpha\beta} \equiv L_\alpha - L_\beta, \quad \sum_{\alpha=1}^n z_\alpha^2 = 1 - \sum_{\alpha,\beta=1,\alpha\neq\beta}^n z_\alpha z_\beta$$

Experiment-oriented, parametric ($A_{\alpha\beta}$) class of SEIM estimation

Introducing *parametric objects* in *modeling description* to conveniently and efficiently take into account influence of inhomogeneous elastic properties, inhomogeneous or incompatible eigenstrains, and/or evolution of microstructure, e.g. resulting from active phase transitions, on *effective thermoelastic properties* of RVE still poses an *open scientific problem.*

The specific form of formulas expressing Voigt estimations of effective parameters deliver interesting *CLUE* for introducing *parametric objects* into *SEIM moduli* homogenization method.

Experiment-oriented, parametric ($A_{\alpha\beta}$) class of SEIM estimation

Let us accept conjecture that for *non-isotropic phases* generating *non-isotropic aggregate* RVE the ingredients of eigenstrains influence moduli $\mathfrak{I}^{*}_{\alpha\beta}$ have the following form ($\alpha \neq \beta$) ($\alpha!$),

$$\mathfrak{I}^{V+A_{\alpha\beta}(S)}_{\alpha\beta} = -0.5\,[\Delta L_{\alpha\beta}\, \overset{-1}{L}^{V+A_{\alpha\beta}}_{\alpha\beta}\, \Delta M_{\alpha\beta}^{-1} + \Delta M_{\alpha\beta}^{-1}\, \overset{-1}{L}^{V+A_{\alpha\beta}}_{\alpha\beta}\, \Delta L_{\alpha\beta}],\quad \mathfrak{I}^{V+A_{\alpha\beta}(A)}_{\alpha\beta} = 0,$$

$$L^{V+A_{\alpha\beta}}_{\alpha\beta} \equiv L^{V} + A_{\alpha\beta},\quad A_{\alpha\alpha} = 0\ (!\alpha);\quad A_{\alpha\beta} = A_{\beta\alpha},\ A_{\alpha\beta} = A^{T}_{\alpha\beta},$$

Tensors $A_{\alpha\beta}$ make an array of $n(n-1)/2$ independent positive semi-definite, diagonally symmetric fourth-order tensors. The tensors may, in general, depend on phase composition and parameters characterizing the current geometry of RVE microstructure.

The *conjecture* $\mathfrak{I}^{V+A_{\alpha\beta}(A)}_{\alpha\beta} = 0$ *is purely pragmatic*, and it is made not to introduce unnecessary complications without relevant knowledge supporting some other more adequate conjecture. Validation of correctness of this assumption for specific material microstructures requires experimental studies.

Experiment-oriented, parametric ($A_{\alpha\beta}$) class of SEIM estimation

The homogenization based on ingredients $\mathfrak{I}_{\alpha\beta}^{V+A_{\alpha\beta}}$ posses the feature that all effective properties become *Voigt*-type or *Reuss*-type estimations when $A_{\alpha\beta}=0$ and $A_{\alpha\beta}\rightarrow\infty$, respectively. Provided that some of M_{α} are different.

Relations for $\mathfrak{I}_{\alpha\beta}^{V+A_{\alpha\beta}}$ make a very convenient theoretical tool for obtaining precise assessments of thermomechanical properties/state variables for various microstructures. However, in general this will require rather involved numerical–experimental studies, e.g. finite element method (FEM) based, to reach useful results.

The very comprehensive scheme taking advantage of the matrix of tensors $A_{\alpha\beta}$, very well suited for fundamental research will be now left for future studies.

In the sequel further simplifications will be adopted of the three kinds:
a) the *matrix of tensors* $A_{\alpha\beta}$ will be reduced to *one tensor* A,
b) attention will be focused on *isotropic aggregate* of n *isotropic phases*
c) *number of distinguished phases* will be limited to *two (n=2)*.

Ad a) Let us assume that it is possible to relevantly describe material properties with single tensor A, i.e. it can be accepted that

$$L_{\alpha\beta}^{V+A_{\alpha\beta}} = L^{V+A} \equiv L^V + A$$

The attraction of such an approach relies on the fact that upon this conjecture *all the effective properties* may be consistently expressed *in terms of elastic compliance moduli* (M).
It can be shown upon simple transformations that

$$M^{\mathrm{Re}} - M = 0.5[(M^{\mathrm{Re}}L^V - I)\overset{-1}{L}^{V+A} + \overset{-1}{L}^{V+A}(L^V M^{\mathrm{Re}} - I)], \quad L^{V+A} \equiv L^V + A, \quad A^T = A$$

The above connection may be regarded as the algebraic equation enabling to find unknown components of tensor $(L^{V+A})^{-1}$ in terms of M_α, L_α and M.

SEIM method with one parametric tensor A for anisotropic RVE containing n anisotropic phases

The nonzero ingredients of eigenstrains influence moduli $\mathfrak{I}_{\alpha\beta}^{V+A}$ can be expressed in terms of M_α, L_α oraz $(L^{V+A})^{-1}$, i.e. M *treated as known* as follows

$$\mathfrak{I}_{\alpha\beta}^{V+A(S)} = -0.5[\Delta L_{\alpha\beta} \overset{-1}{L}^{V+A}(\Delta M_{\alpha\beta})^{-1} + (\Delta M_{\alpha\beta})^{-1} \overset{-1}{L}^{V+A} \Delta L_{\alpha\beta}], \quad \mathfrak{I}_{\alpha\beta}^{(A)} = 0,$$

$$\mathfrak{R}_{\alpha}^{V+A}(\Gamma_\gamma) = \sum_{\beta=1, \beta \neq \alpha}^{n} z_\beta \mathfrak{I}_{\alpha\beta}^{V+A(S)}(\Gamma_\beta - \Gamma_\alpha)$$

$$f_{\alpha\beta}^{V+A}(X,Y) = 0.5(X-Y) \cdot \mathfrak{I}_{\alpha\beta}^{V+A(S)}(X-Y) \quad (!\,\alpha, \beta = 1,2...n)$$

Obtaining estimations of the values of thermostatic properties, state variables, remaining in consistency with the Betti reciprocity theorem, requires substitution of $\mathfrak{I}_{\alpha\beta}^{V+A}$ into relations for $\sigma_\alpha^{(ex)}, \sigma_\alpha^{(in)}, \varepsilon_\alpha^{(ex)}, \varepsilon_\alpha^{(in)}, M, \varepsilon^{pt}, g^{el}, u^{coh}, g.$

These formulas have the same explicit form as the formulas for Voigt-type estimates but in place of L^V there must be substituted L^{V+A} .

Two scalar parameters $(A^{(\mu)}, A^{(k)})$ SEIM method estimation for isotropic RVE of n isotropic phases $(A_{\alpha\beta}=A, n)$

Considerable simplifications are possible when it can be conjectured that modeled material macroelement (RVE) consisting of *n isotropic phases* always arranges into *isotropic resulting aggregate*. The Rychlewski theorem on spectral decomposition of 4th order, tensor of elastic stiffness states that in the case of *isotropic elastic* materials $\boldsymbol{L}$ ($\boldsymbol{M}$) tensor can be unambiguously decomposed into *spherical* and *distortional* parts, as follows

$$\boldsymbol{L}_\alpha = 3k_\alpha \mathbf{J} + 2\mu_\alpha \mathbf{K}, \quad \boldsymbol{M}_\alpha = (1/3k_\alpha)\mathbf{J} + (1/2\mu_\alpha)\mathbf{K}, \quad \mathbf{K} = \mathbf{I} - \mathbf{J}, \quad \mathbf{J} = \tfrac{1}{3}\boldsymbol{1} \otimes \boldsymbol{1},$$

$$\mathbf{J}^2 = \mathbf{J}, \quad \mathbf{K}^2 = \mathbf{K}, \quad \mathbf{K}\mathbf{J} = 0, \quad \boldsymbol{L}^V = 3k^V \mathbf{J} + 2\mu^V \mathbf{K}, \quad \overset{-1}{\boldsymbol{L}}{}^V = \frac{1}{3k^V}\mathbf{J} + \frac{1}{2\mu^V}\mathbf{K},$$

$$\boldsymbol{L}^{V+A} = 3(k^V + A^{(k)})\mathbf{J} + 2(\mu^V + A^{(\mu)})\mathbf{K}, \quad \boldsymbol{A} = 3A^{(k)}\mathbf{J} + 2A^{(\mu)}\mathbf{K}, (\mathbf{J}_{ijkl} = \tfrac{1}{3}\delta_{ij}\delta_{kl})$$

Walpole (1981) seems to be the first to use this type of decomposition. Bernardini (2001) also employed this decomposition. Then $\mathfrak{I}_{\alpha\beta}^{V+A_{\alpha\beta}}$ reduces to

$$\mathfrak{I}_{\alpha\beta}^{V+A(S)} = \frac{3k_\alpha k_\beta}{k^V + A^{(k)}}\mathbf{J} + \frac{2\mu_\alpha \mu_\beta}{\mu^V + A^{(\mu)}}\mathbf{K}, \qquad \mathfrak{I}_{\alpha\beta}^{(A)} = 0, \quad \alpha \neq \beta$$

$$k_\alpha = \frac{E_\alpha}{3(1 - 2\nu_\alpha)}, \quad \mu_\alpha = \frac{E_\alpha}{2(1 + \nu_\alpha)}, \quad k^V = \sum_{\alpha=1}^{n} z_\alpha k_\alpha, \quad \mu^V = \sum_{\alpha=1}^{n} z_\alpha \mu_\alpha$$

k_α and μ_α denote the average value of the bulk and shear moduli

Effective compliance tensor $\mathbf{M}$ takes the form

$$\mathbf{M} = (1/3k)\mathbf{J} + (1/2\mu)\mathbf{K}, \quad k = k^{\mathrm{Re}}\frac{k^{V} + A^{(k)}}{k^{\mathrm{Re}} + A^{(k)}}, \quad \mu = \mu^{\mathrm{Re}}\frac{\mu^{V} + A^{(\mu)}}{\mu^{\mathrm{Re}} + A^{(\mu)}}$$

$$\mathbf{M}^{\mathrm{Re}} = (1/3k^{\mathrm{Re}})\mathbf{J} + (1/2\mu^{\mathrm{Re}})\mathbf{K}, \quad 1/k^{\mathrm{Re}} = \sum_{\alpha=1}^{n}(z_{\alpha}/k_{\alpha}), \quad 1/\mu^{\mathrm{Re}} = \sum_{\alpha=1}^{n}(z_{\alpha}/\mu_{\alpha})$$

Complementary elastic energy $\rho\, g^{el}$ takes the form

$$\rho g^{el} = 0.5\,\boldsymbol{\sigma}\cdot\mathbf{M}^{\mathrm{Re}}\boldsymbol{\sigma} - 0.5\sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_{\alpha}z_{\beta}f_{\alpha\beta}(\mathbf{M}_{\alpha}\boldsymbol{\sigma},\mathbf{M}_{\beta}\boldsymbol{\sigma}), \quad \boldsymbol{\sigma}\cdot\mathbf{M}^{\mathrm{Re}}\boldsymbol{\sigma} = \frac{p^{2}}{k^{\mathrm{Re}}} + \frac{\boldsymbol{\sigma}'\cdot\boldsymbol{\sigma}'}{2\mu^{\mathrm{Re}}}$$

$$f_{\alpha\beta}(\mathbf{M}_{\alpha}\boldsymbol{\sigma},\mathbf{M}_{\beta}\boldsymbol{\sigma}) = \frac{(k_{\alpha}-k_{\beta})^{2}}{2k_{\alpha}k_{\beta}[k^{V}+A^{(k)}]}p^{2} + \frac{(\mu_{\alpha}-\mu_{\beta})^{2}}{4\mu_{\alpha}\mu_{\beta}[\mu^{V}+A^{(\mu)}]}\boldsymbol{\sigma}'\cdot\boldsymbol{\sigma}'$$

$$p\mathbf{1} = \tfrac{1}{3}(\mathbf{1}\otimes\mathbf{1})\boldsymbol{\sigma} = \mathbf{J}\boldsymbol{\sigma} = \tfrac{1}{3}tr(\boldsymbol{\sigma})\mathbf{1}, \quad \boldsymbol{\sigma}' = \mathrm{dev}\,\boldsymbol{\sigma} = \boldsymbol{\sigma} - \mathbf{J}\boldsymbol{\sigma} = \mathbf{K}\boldsymbol{\sigma}, \quad \mathrm{dev}\,\boldsymbol{\sigma} \equiv \boldsymbol{\sigma} - \tfrac{1}{3}tr\boldsymbol{\sigma}$$

Internal coherency energy $\rho\, u^{coh}$ takes the form

$$\rho u^{coh} = 0.5\sum_{\alpha,\beta=1,\beta\neq\alpha}^{n} z_{\alpha}z_{\beta}f_{\alpha\beta}(\Gamma_{\alpha},\Gamma_{\beta}), \quad f_{\alpha\beta}(\Gamma_{\alpha},\Gamma_{\beta}) = \frac{k_{\alpha}k_{\beta}}{2(k^{V}+A^{(k)})}(\gamma_{\alpha\beta}^{(v)})^{2} + \frac{\mu_{\alpha}\mu_{\beta}(\gamma_{\alpha\beta}')^{2}}{\mu^{V}+A^{(\mu)}}$$

The estimates of effective properties k, μ satisfy familiar inequalities

$$k^{V} \geq k \geq k^{\mathrm{Re}}, \quad \mu^{V} \geq \mu \geq \mu^{\mathrm{Re}}, \quad A^{(k)} \geq 0, \quad A^{(\mu)} \geq 0$$

Two scalar parameters ($A^{(\mu)}$, $A^{(k)}$) SEIM method estimation for isotropic RVE of n isotropic phases ($A_{\alpha\beta}=A$, n)

Estimates of macroscopic *phase transition strains* and *phase averages of self-equilibrated internal stresses* are

$$\mathrm{dev}\,\varepsilon^{pt} = \sum_{\alpha=1}^{n} z_\alpha dev\Gamma_\alpha + \sum_{\alpha,\beta=1,\,\alpha\neq\beta}^{n} z_\alpha z_\beta \frac{\mu_\beta}{\mu^V + A^{(\mu)}} dev(\Gamma_\beta - \Gamma_\alpha), \quad \mathrm{dev}\,\varepsilon^{pt} = \mathbf{K}\,\varepsilon^{pt}$$

$$tr\,\varepsilon^{pt} = \sum_{\alpha=1}^{n} z_\alpha tr(\Gamma_\alpha) + \sum_{\alpha,\beta=1,\,\alpha\neq\beta}^{n} z_\alpha z_\beta \frac{k_\beta}{k^V + A^{(k)}} \gamma_{\beta\alpha}^{(v)}, \qquad tr\,\varepsilon^{pt} = \mathbf{J}\,\varepsilon^{pt}$$

$$\mathrm{dev}\,\sigma_\alpha^{(\mathrm{in})} = \mathrm{dev}\,\mathfrak{R}_\alpha(\Gamma_\gamma) = 2\mu_\alpha \sum_{\beta=1}^{n} z_\beta \frac{\mu_\beta}{\mu^V + A^{(\mu)}} dev(\Gamma_\beta - \Gamma_\alpha)$$

$$tr\,\sigma_\alpha^{(\mathrm{in})} = tr\,\mathfrak{R}_\alpha(\Gamma_\gamma) = 3k_\alpha \sum_{\beta=1}^{n} z_\beta \frac{k_\beta}{k^V + A^{(k)}} \gamma_{\beta\alpha}^{(v)}$$

$$\gamma_{\alpha\beta}^{(v)} \equiv tr(\Gamma_\alpha - \Gamma_\beta), \quad (\gamma_{\alpha\beta}')^2 \equiv dev(\Gamma_\alpha - \Gamma_\beta)\cdot dev(\Gamma_\alpha - \Gamma_\beta)$$

Central result

The SEIM method estimation of *Gibbs free energy* $g^{(V+A)}$ of *isotropic agregate SMA macroelement* composed of n isotropic phases takes the form

$$\rho g^{(V+A)} = (\sum_{\alpha=1}^{n} z_\alpha \rho g_\alpha^0) - \rho g^{el} - \boldsymbol{\sigma} \cdot \boldsymbol{\varepsilon}^{pt} + \rho \phi^{coh}$$

$$g_\alpha^0 = u_\alpha^0 - Ts_\alpha^0 + c_p[\Delta T - T \ln(T/T_0)] - \Delta T \boldsymbol{\sigma} \cdot \boldsymbol{\alpha}/\rho$$

$$\rho g^{el} = 0.5[\frac{1}{k^{\text{Re}}} p^2 + \frac{\boldsymbol{\sigma}' \cdot \boldsymbol{\sigma}'}{2\mu^{\text{Re}}}] - 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta [\frac{(k_\alpha - k_\beta)^2 p^2}{2k_\alpha k_\beta [k^V + A^{(k)}]} + \frac{(\mu_\alpha - \mu_\beta)^2 \boldsymbol{\sigma}' \cdot \boldsymbol{\sigma}'}{4\mu_\alpha \mu_\beta [\mu^V + A^{(\mu)}]}]$$

$$\rho \phi^{coh} = \rho(u^{coh} - T \cdot s^{coh}) = 0 + 0.5 \sum_{\alpha,\beta=1,\beta\neq\alpha}^{n} z_\alpha z_\beta (\frac{k_\alpha k_\beta (\gamma_{\alpha\beta}^{(v)})^2}{2(k^V + A^{(k)})} + \frac{\mu_\alpha \mu_\beta (\gamma_{\alpha\beta}')^2}{\mu^V + A^{(\mu)}}) - T \sum_{\alpha=1}^{n} z_\alpha \rho s_\alpha^{coh}$$

$$\boldsymbol{\varepsilon}^{pt} = \tfrac{1}{3} tr(\boldsymbol{\varepsilon}^{pt})\boldsymbol{1} + dev(\boldsymbol{\varepsilon}^{pt}), \quad tr\boldsymbol{\varepsilon}^{pt} = \sum_{\alpha=1}^{n} z_\alpha tr(\boldsymbol{\Gamma}_\alpha) + \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta \frac{k_\beta}{k^V + A^{(k)}} \gamma_{\beta\alpha}^{(v)},$$

$$\text{dev}\,\boldsymbol{\varepsilon}^{pt} = \sum_{\alpha=1}^{n} z_\alpha dev\boldsymbol{\Gamma}_\alpha + \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta \frac{\mu_\beta}{\mu^V + A^{(\mu)}} dev(\boldsymbol{\Gamma}_\beta - \boldsymbol{\Gamma}_\alpha)$$

The above relations *explicitly reveal connections* between *microproperties microstructure* of SMA macroelement and the *objects/terms* present in macroscopic Gibbs function for isotropic SMA macroelement composed of isotropic phases.

Central result

Summary of SEIM method two parameter ($A^{(\mu)}$, $A^{(k)}$) estimation of effective properties (isotropic aggregate RVE composed of *n* isotropic phases).

Estimation	$A^{(k)}$	$A^{(\mu)}$	M	$\phi^{coh} = u^{coh} - T \cdot s^{coh}$
Voigt	0	0	M^V	
Hashin–Shtrikman lower bound (*n*=2)	$\dfrac{3k_1 k_2}{4\mu_1}$	$\dfrac{6\mu_1(k_2 + 2\mu_2)}{9k_2 + 8\mu_2}$	$M = \frac{1}{3k}\mathbf{J} + \frac{1}{2\mu}\mathbf{K}$	$0.5 \sum\limits_{\alpha,\beta=1,\beta\neq\alpha}^{n} z_\alpha z_\beta \cdot$
Semi-experimental SEIM method	$A^{(k)}_{\exp}$	$A^{(\mu)}_{\exp}$	$k = k^{Re}\dfrac{A^{(k)} + k^V}{A^{(k)} + k^{Re}}$	$[\dfrac{k_\alpha k_\beta (\gamma^{(v)}_{\alpha\beta})^2}{2(k^V + A^{(k)})} +$ $+\dfrac{\mu_\alpha \mu_\beta (\gamma'_{\alpha\beta})^2}{\mu^V + A^{(\mu)}}]$
Hashin–Shtrikman upper bound (*n*=2)	$\dfrac{3k_1 k_2}{4\mu_2}$	$\dfrac{6\mu_2(k_1 + 2\mu_1)}{9k_1 + 8\mu_1}$	$\mu = \mu^{Re}\dfrac{A^{(\mu)} + \mu^V}{A^{(\mu)} + \mu^{Re}}$	$-T\sum\limits_{\alpha=1}^{n} z_\alpha \rho s^{coh}_\alpha$
Reuss	∞	∞	M^{Re}	0

Note: Conjectures made to obtain estimates of *Hashin–Shtrikman* lead to *mutual coupling of distortional and spherical deformation modes*. This kind of coupling does not take place in the case of proposed here SEIM method of estimation.

Central result

Variation of effective bulk modulus of two phase RVE with volume fraction of second phase z_2 for several values of parameter $A^{(k)}$ according to SEIM method: $A^{(k)}=(0.5,2,10,,40,400)$, $k_2/k_1=(4, 200)$ $HS^-=2k_1$, $HS^+=2k_2$.
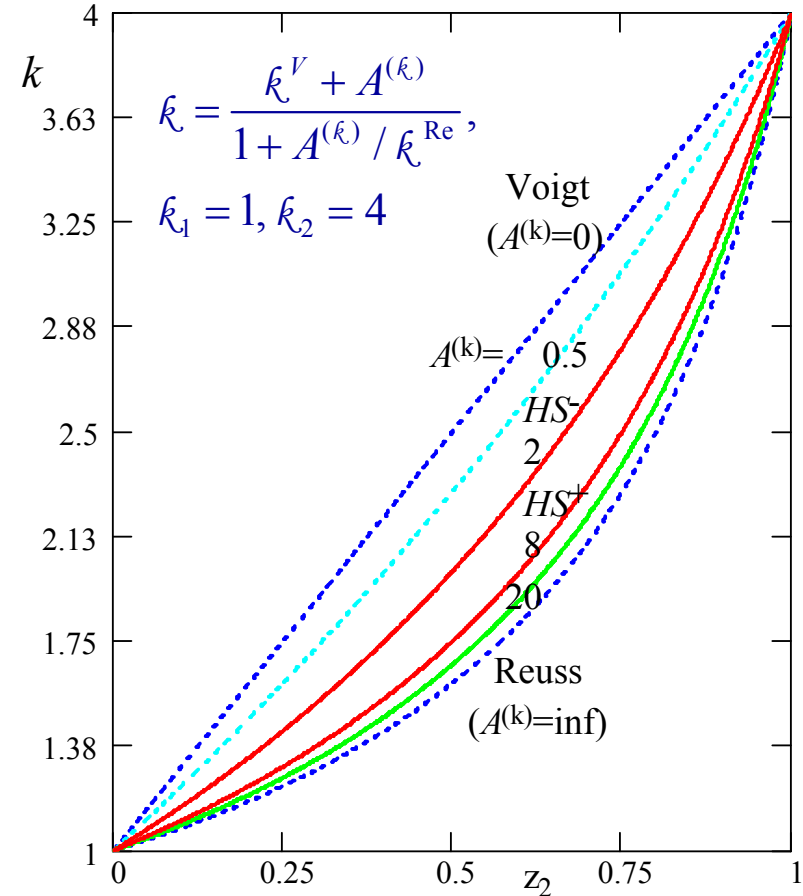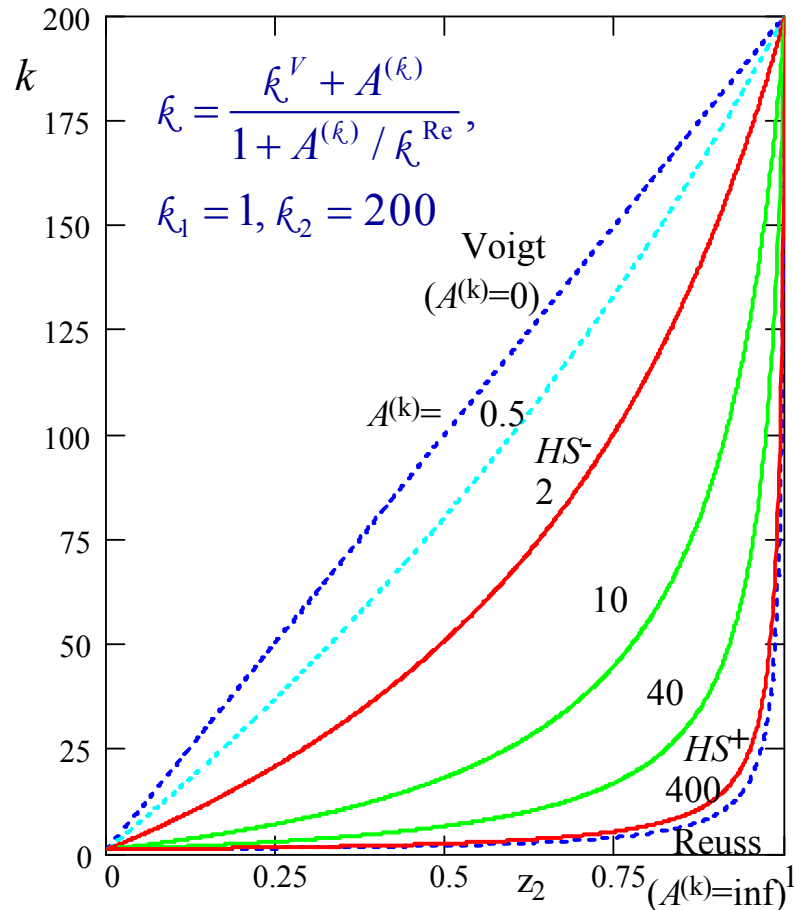
The parameter $A^{(k)}$ is taken here to be *constant*. However, more realistic conjecture is that in general $A^{(k)}$ is some kind of function depending on evolution of RVE microstructure, thus at minimum depending on volume fraction z_2. The explicit form of such dependence can/must be found experimentally.

Two scalar parameters ($A^{(\mu)}$, $A^{(k)}$) SEIM method estimation for isotropic RVE of n isotropic phases ($\boldsymbol{A}_{\alpha\beta}=\boldsymbol{A}$, n)

Experiment-oriented SEIM method of estimation, for isotropic RVE composed of *n* isotropic phases, with one parametric tensor $\boldsymbol{A}$.

Simple transformations allow to obtain formulas for values of parameters $A^{(\mu)}$, $A^{(k)}$ expressed in terms of values of *effective elastic moduli* k^V, μ^V

$$\frac{1}{k^V + A^{(k)}} = \frac{k - k^{\mathrm{Re}}}{k\,[k^V - k^{\mathrm{Re}}]}, \qquad \frac{1}{\mu^V + A^{(\mu)}} = \frac{\mu - \mu^{\mathrm{Re}}}{\mu\,[\mu^V - \mu^{\mathrm{Re}}]}$$

Thus, upon use of the above formulas *it is possible to determine estimates of effective coherency energy and/or phase transition strains*, for the isotropic RVE composed of *n* isotropic phases, *when there will be measured/ there are known values effective elastic moduli*.

Estimations for isotropic RVE consisting of *n* isotropic phases with no elastic heterogeneity ($M_\alpha = M$)

When all phases have the same values of elastic moduli ($\mu^V = \mu^{Re} = \mu_\alpha = \mu$, $k^V = k^{Re} = k_\alpha = k$, $g^{el}_{\alpha\beta} = 0$), i.e. SMA material RVE is elastically homogeneous then $\mathfrak{I}_{\alpha\beta} = L$, and estimates of respective quantities are as follows,

$$\rho g^{el} = 0.5[p^2 / k + \sigma' \cdot \sigma' / (2\mu)],$$

$$\rho \phi^{coh} = \rho \sum_{\alpha=1}^{n} z_\alpha (0 - Ts_\alpha^{coh}) + 0.5 \sum_{\alpha,\beta=1,\beta\neq\alpha}^{n} z_\alpha z_\beta \left(\frac{k (\gamma_{\alpha\beta}^{(v)})^2}{2[1 + A^{(k)} / k]} + \frac{\mu (\gamma'_{\alpha\beta})^2}{[1 + A^{(\mu)} / \mu]} \right) \geq 0,$$

$$\gamma_{\alpha\beta}^{(v)} \equiv tr(\Gamma_\alpha - \Gamma_\beta), \quad (\gamma'_{\alpha\beta})^2 \equiv dev(\Gamma_\alpha - \Gamma_\beta) \cdot dev(\Gamma_\alpha - \Gamma_\beta),$$

$$\varepsilon^{pt} = \langle \Gamma \rangle_V \equiv \sum_{\alpha=1}^{n} z_\alpha \Gamma_\alpha,$$

$$tr \sigma_\alpha^{(in)} = \frac{3k[\langle tr\Gamma \rangle_V - tr\Gamma_\alpha]}{1 + A^{(k)} / k}, \quad dev\sigma_\alpha^{(in)} = \frac{2\mu[\langle dev\Gamma \rangle_V - dev\Gamma_\alpha]}{1 + A^{(\mu)} / \mu}$$

In this case the coherency energy coefficients may depend on z_α only through possible dependence of $A^{(k)}$ and $A^{(\mu)}$ on phase composition.

Sensitivity analysis of *isotropic* RVE composed of *two isotropic* phases regarding *nonhomogeneity* of elastic properties

Let us return to commonly used at present assumption that SMA RVE is in general composed of austenitic and martensitic phase, i.e. (n=2).

The two-phase mixture is characterized by zero phase eigenstrains in austenite (Γ_1=0), and deviatoric only phase eigenstrains in martensite ($\mathrm{dev}\Gamma_2$=Γ, $\mathrm{tr}\Gamma_2$=0) – a typical modeling assumption for polycrystalline SMA materials. Thus, all volumetric effects are zero for studied here case $\gamma^{(v)}_{\alpha\beta} = 0$

Let us introduce convenient *normalized estimations* defined as follows

$$y \equiv \frac{\rho\, u^{coh}}{(\Gamma_{eq} \cdot \mu^G \Gamma_{eq})} = z_1 z_2 \frac{(3/2)\mu^G}{[z_1\mu_1 + z_2\mu_2 + A^{(\mu)}]}, \qquad \frac{\varepsilon^{pt}_{eq}}{\Gamma_{eq}} \equiv \frac{z_2(\mu_2 + A^{(\mu)})}{(1-z_2)\mu_1 + z_2\mu_2 + A^{(\mu)}}$$

The symbol μ^G denotes the geometric mean of shear moduli, ε^{pt}_{eq} is the equivalent macroscopic phase strain, and Γ_{eq} is the equivalent eigenstrain of martensitic phase.

$$\rho\, u^{coh} = z_1 z_2 (3/2)(\mu^G \Gamma_{eq})^2 / (\mu^V + A^{(\mu)}), \quad \varepsilon^{pt} = z_2\Gamma + z_1 z_2 \Gamma(\mu_2 - \mu_1)/(\mu^V + A^{(\mu)})$$

$$\mu^G \equiv \sqrt{\mu_1\mu_2}, \quad \mu_{12} \equiv \mu_1/\mu_2, \quad \varepsilon^{pt}_{eq} = \sqrt{\tfrac{2}{3}\varepsilon'^{pt} \cdot \varepsilon'^{pt}}, \quad \Gamma_{eq} \equiv \sqrt{\tfrac{2}{3}\mathrm{dev}\Gamma \cdot \mathrm{dev}\Gamma}$$

Sensitivity analysis of *isotropic* RVE composed of *two isotropic* phases regarding *non-homogeneity* of elastic properties

The dependence of normalized (dimensionless) *internal coherency energy* y on the martensite volume fraction z_2 for several values of parameters μ_{12} (0.5,1,2,4) and $A^{(\mu)}/\mu_G$ (0,10). $\rightarrow$

The maximum values of normalized coherency energy and coordinates of their location are

$$y_{max} \equiv \left.\frac{\rho u^{coh}}{\mu^G(\Gamma_{eq})^2}\right|_{z_2=z_{2\,max}} = \frac{3}{2}\mu^G\left[\frac{\sqrt{\mu_1+A^{(\mu)}}-\sqrt{\mu_2+A^{(\mu)}}}{\mu_1-\mu_2}\right]^2$$

$$z_{2\,max} - 0.5 = \frac{\sqrt{\mu_1+A^{(\mu)}}-\sqrt{\mu_2+A^{(\mu)}}}{2[\sqrt{\mu_1+A^{(\mu)}}+\sqrt{\mu_2+A^{(\mu)}}]}$$

The highest peak among the Voigt-type estimates maxima of the coherency energy arises when there is no microscopic heterogeneity of elastic properties, i.e. $\mu_1 = \mu_2$

$$y_{1\,max} \equiv \left.y_{max}\right|_{\mu_1=\mu_2=\mu^G} = \frac{3}{8}\frac{1}{(1+A^{(\mu)}/\mu^G)}$$
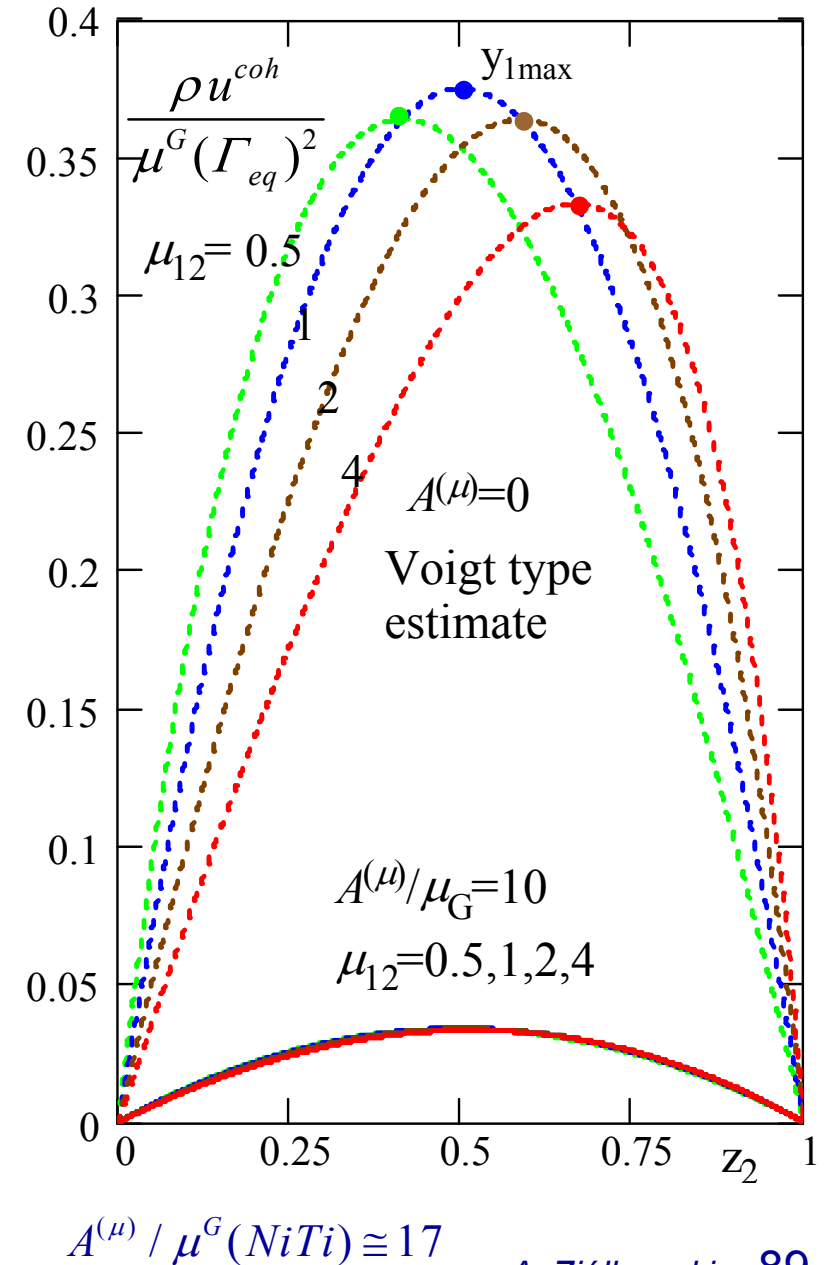
$A^{(\mu)}/\mu^G(NiTi) \cong 17$

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Sensitivity analysis of *isotropic* RVE composed of *two isotropic* phases regarding *non-homogeneity* of elastic properties

Let us introduce *dimensionless, sensitivity measures of elastic properties heterogeneity* Δy *and* Δe *as follows,*

$$|\varepsilon^{pt} - z_2\Gamma| = |\tfrac{2}{3}y\frac{(\mu_2-\mu_1)}{\mu^G}\Gamma| =$$

$$\Delta y \equiv (y_{1\max}/y_{\max})-1, \quad \Delta e \equiv \tfrac{2}{3}y_{\max}\left|\mu_2-\mu_1\right|/\mu^G$$

$$\tfrac{2}{3}y\frac{|\mu_2-\mu_1|}{\mu^G}\cdot\Gamma_{eq} \leq \Delta e \cdot \Gamma_{eq}$$

These measures enable evaluation what influence has SMA material elastic properties nonhomogeneity on estimates of internal coherency energy and phase transition strains.

$$A^{(\mu)}/\mu^G(NiTi) \cong 17$$

Figure (a) Variation of the relative error Δy in estimation of the coherency energy, with the value of ratio $A^{(\mu)}/\mu_G$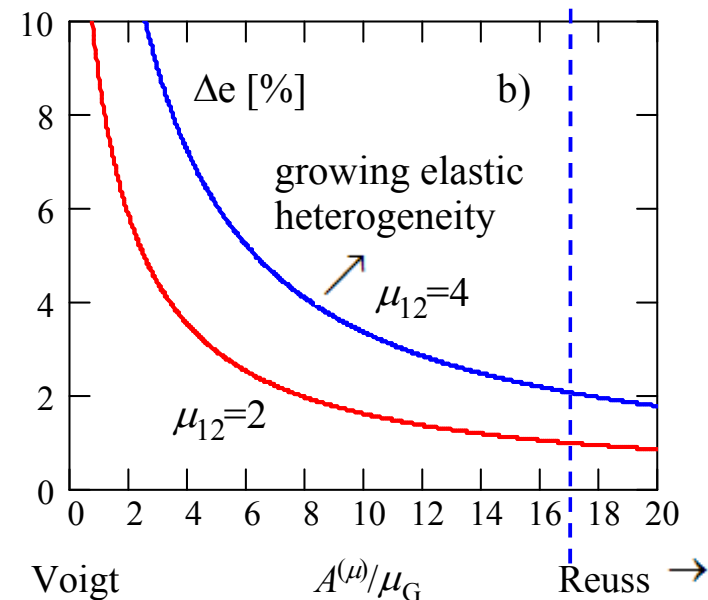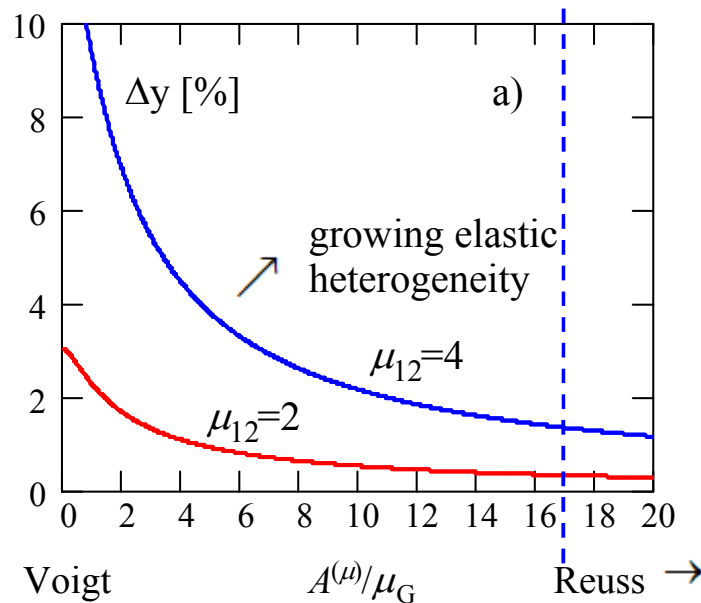, (b) Variation of the relative error Δe in estimation of the equivalent macroscopic phase strain ε^{pt}_{eq}, with the value of ratio $A^{(\mu)}/\mu_G$.

Sensitivity analysis of *isotropic* RVE composed of *two isotropic* phases regarding *nonhomogeneity* of elastic properties

What are the realistic values of ratio $A^{(\mu)}/\mu_G$, e,g, for NITi alloy?

In order to evaluate the values it will be used the *key presumption* underlying the R_L family models of SMA materials treated as *two-phase* stating that phase transitions (p.t.) are initiated in SMA materials, when they reach *unstable thermodynamically phase equilibria*.

This supposition means that *criteria for forward and reverse phase transitions are derivable directly from Gibbs function*. For example in the case of R_L models criteria for active phase transition initiation require that thermodynamic driving force of p.t. takes the zero value. These conditions, for pure phases, take the following mathematical form

$$\left.\begin{array}{l}\pi^{1-2}(\sigma_{ten}^{AM},T,z=0)=(\pi_0^f-\phi_2^{st})-\phi_{it}+\gamma_{ten}\cdot\sigma_{ten}^{AM}/\rho=0\\[2mm]\pi^{1-2}(\sigma_{ten}^{MA},T,z=1)=(\pi_0^f-\phi_2^{st})+\phi_{it}+\gamma_{ten}\cdot\sigma_{ten}^{MA}/\rho=0\end{array}\right\}\Rightarrow 2\rho\phi_{it}=(\sigma_{ten}^{AM}-\sigma_{ten}^{MA})\gamma_{ten}$$

$$\rho\phi_{it}\cong\rho\phi_{12}^{(0)coh}=\mu^G\tfrac{3}{2}(\gamma_{ten})^2/(1+A^{(\mu)}/\mu^G)$$

σ_{ten}^{AM} denotes the critical uniaxial stress at which the pseudoelastic flow starts for pure austenite, σ_{ten}^{MA} denotes the critical uniaxial stress at which the pure martensite starts to decompose reverse pseudoelastic flow starts, γ_{ten} is pseudoelastic flow amplitude at uniaxial tension.

Sensitivity analysis of *isotropic* RVE composed of *two isotropic* phases regarding *nonhomogeneity* of elastic properties

Stress strain chart for Ni51at%-Ti alloy.

Ni$_{51at\%}$Ti

Tension, T=315 K

$\rho\,\phi_{12}^{(0)coh}$

$\sigma_{ef}{}^{AM}$

$\sigma_{ef}{}^{MA}$

E = 64.8, ν= 0.43

σ_{ef}

ε_{eq}

Stress σ_1

σ^{AM}

σ^{MA}

$\rho\,\phi_{12}^{(0)coh}$

γ_{tn} Strain ε_1

$\sigma^{AM}{}_{ten}$ denotes the critical uniaxial stress at which the pseudoelastic flow starts for pure austenite, $\sigma^{MA}{}_{ten}$ denotes the critical uniaxial stress at which the pure martensite starts to decompose reverse pseudoelastic flow starts, γ_{ten} is pseudoelastic flow amplitude at uniaxial tension.

The term $2\rho\,\phi_{it}$ determines area of hysteresis loop in stress–strain coordinates.

Sensitivity analysis of *isotropic* RVE composed of *two isotropic* phases regarding *nonhomogeneity* of elastic properties

The *experimental data* for polycrystalline $Ni_{51at\%}$-Ti alloy obtained in isothermal experiments performed in the temperature range of pseudoelasticity suggest that, cf. (Raniecki et al., 2001) show

$$\mu_1 = \mu_2 = \mu^G \approx 20 \times 10^3 \,[\text{MPa}], \ \gamma_{ten} = 0.06, \ (\sigma_{ten}^{AM} - \sigma_{ten}^{MA}) \approx 200 \,[\text{MPa}]$$

$$\Rightarrow \rho\,\phi_{12}^{(0)coh} \approx 6\,[\text{MPa}] \quad \Rightarrow \quad A^{(\mu)}/\mu^G = \mu^G \tfrac{3}{2}(\gamma_{ten})^2 / \rho\,\phi_{12}^{(0)coh} - 1 \approx 17$$

$$\Rightarrow \rho\,\phi_{max}^{coh} \approx 1.25\,[\text{MPa}] = 0.19\,[\text{J}/\text{g}] = 11\,[\text{J}/\text{mol}] \quad (\rho\,\phi^{coh} = z_1 z_2\,\rho\,\phi_{12}^{(0)coh})$$

The estimate of maximum value of NiTi alloy *coherency energy per mol* to be $\phi^{coh}_{max} \approx 11\,[\text{J/mol}]$ (NiTi data μ_{NiTi}=56g/mol, ρ_{NiTi}=6500 kg/m^3) gives premises to evaluate that the forces assuring continuity of displacements field can neither be qualified as the typical *chemical forces* (e.g. of covalent bonds), nor as the typical forces of *physical interaction* (e.g. of melting, dissolution, adsorption).

The sensible *latent heat of phase transition* for NiTi alloys, connected with forces of phases microstructural reorganization remains in the range of Δu=10-30 [J/g], i.e. it is about two orders larger (~10^2) than coherency energy ϕ^{coh}_{max}.

Note: Experimental data indicate that for NiTi alloys, it is reasonable to accept that coherency entropy $s_{12} \cong 0$. Thus $\phi^{coh} \equiv u^{coh} + s_{12} \cdot T = u^{coh}$, cf. e.g. chapter 5 in Ziolkowski (2015) Pseudoelasticity of Shape memory Alloys.

Central result

The sensitivity analysis shows that *neglecting non-homogeneity of elastic properties of SMA material phases*, even when it is relatively high (e.g. modules of austenite are several times larger/smaller than modules of martensite), *does not lead to considerable errors* in evaluation the values of *coherency energy* and/or macroscopic *phase transition strains*.

For example when $\mu_1/\mu_2 \approx 4$ and $A^{(\mu)}/\mu_G \approx 17$ the error in evaluation of coherency energy and/or effective phase transition strains is lesser than 2.0%, cf. charts on slide 90.

Stored coherency energy and fluctuating part of microeigenstrain field $\breve{\Gamma}_\alpha^f(\mathbf{x}) \neq 0$

Let us release the early constraints and admit *nonzero fluctuating parts of microeigenstrain fields*, i.e. let us assume that local phase transformation fields have the following form

$$\breve{\Gamma}_\alpha(\mathbf{x}) = \Gamma_\alpha + \breve{\Gamma}_\alpha^f(\mathbf{x}), \ \mathbf{x} \in V_\alpha; \ \breve{\Gamma}_\alpha^f(\mathbf{x}) \neq 0, \ < \breve{\Gamma}_\alpha^f(\mathbf{x}) >_{V_\alpha} = 0, \ (\alpha = 1,..,n)$$

Since the distribution of elastic compliances is still presumed to be piecewise constant all general expressions derived earlier concerning averaged quantities of *external fields* and macroscopic complementary elastic energy *remain valid*. The expressions concerning *internal fields* including the macroscopic phase transformation strains *must be modified*.

In order to evaluate influence of phase fluctuations of eigenstrains on estimation of coherence energy *internal fields problem is additively divided* into the fields generated by *phase averages* and *phase fluctuations* of eigenstrains field.
The symbolic solution of auxiliary problems can be denoted as follows

$$\breve{\varepsilon}_\alpha^{(in)}(\mathbf{x}) = \breve{\varepsilon}_\alpha^{(a\text{-}in)}(\mathbf{x}) + \breve{\varepsilon}_\alpha^{(f\text{-}in)}(\mathbf{x}), \quad \breve{\sigma}_\alpha^{(in)}(\mathbf{x}) = \breve{\sigma}_\alpha^{(a\text{-}in)}(\mathbf{x}) + \breve{\sigma}_\alpha^{(f\text{-}in)}(\mathbf{x}), \quad \mathbf{x} \in V_\alpha,$$

The above fields are supposed to fulfill the following constitutive relations

$$\breve{\varepsilon}_\alpha^{(a\text{-}in)}(\mathbf{x}) = \mathbf{M}_\alpha \breve{\sigma}_\alpha^{(a\text{-}in)}(\mathbf{x}) + \Gamma_\alpha, \quad \breve{\varepsilon}_\alpha^{(f\text{-}in)}(\mathbf{x}) = \mathbf{M}_\alpha \breve{\sigma}_\alpha^{(f\text{-}in)}(\mathbf{x}) + \breve{\Gamma}_\alpha^f(\mathbf{x}), \quad (!\alpha)$$

The constitutive relations between phase averages of the local fields in each volume V_α are

$$\boldsymbol{\varepsilon}_\alpha^{(\text{a-in})} = \boldsymbol{M}_\alpha \boldsymbol{\sigma}_\alpha^{(\text{a-in})} + \boldsymbol{\Gamma}_\alpha, \quad \boldsymbol{\varepsilon}_\alpha^{(\text{f-in})} = \boldsymbol{M}_\alpha \boldsymbol{\sigma}_\alpha^{(\text{f-in})}, \quad \sum_{\alpha=1}^n z_\alpha \boldsymbol{\sigma}_\alpha^{(\text{a-in})} = 0, \quad \sum_{\alpha=1}^n z_\alpha \boldsymbol{\sigma}_\alpha^{(\text{f-in})} = 0$$

$$\boldsymbol{\varepsilon}_\alpha^{(\text{a-in})} = <\breve{\boldsymbol{\varepsilon}}^{(\text{a-in})}(\boldsymbol{x})>_{V_\alpha}, \quad \boldsymbol{\varepsilon}_\alpha^{(\text{f-in})} = <\breve{\boldsymbol{\varepsilon}}^{(\text{a-in})}(\boldsymbol{x})>_{V_\alpha}, \quad \boldsymbol{\sigma}_\alpha^{(\text{a-in})} = <\breve{\boldsymbol{\sigma}}^{(\text{a-in})}(\boldsymbol{x})>_{V_\alpha}, \quad \boldsymbol{\sigma}_\alpha^{(\text{f-in})} = <\breve{\boldsymbol{\sigma}}^{(\text{f-in})}(\boldsymbol{x})>_{V_\alpha}$$

The macroscopic transformation strains $\boldsymbol{\varepsilon}^{pt}$ are influenced by $\boldsymbol{\varepsilon}_\alpha^{(\text{f-in})}$ when some phases have different elastic compliances

$$\boldsymbol{\varepsilon}^{pt} = \sum_{\alpha=1}^n z_\alpha \boldsymbol{\varepsilon}_\alpha^{(\text{in})}, \qquad \text{when } \boldsymbol{M}_\alpha = \boldsymbol{M} \ (\alpha = 1, .., n) \text{ then } \boldsymbol{\varepsilon}^{pt} = \sum_{\alpha=1}^n z_\alpha \boldsymbol{\Gamma}_\alpha$$

$$\boldsymbol{\varepsilon}_\alpha^{(\text{in})} = \boldsymbol{\Gamma}_\alpha + \boldsymbol{M}_\alpha(\boldsymbol{\sigma}_\alpha^{(\text{a-in})} + \boldsymbol{\sigma}_\alpha^{(\text{f-in})}), \quad \boldsymbol{\varepsilon}_\alpha^{(\text{in})} = \boldsymbol{\Gamma}_\alpha + \sum_{\beta=1, \beta \neq \alpha}^n z_\beta \boldsymbol{M}_\alpha [\mathfrak{I}_{\alpha\beta}^{(S)}(\boldsymbol{\Gamma}_\beta - \boldsymbol{\Gamma}_\alpha) + \mathfrak{I}_{\alpha\beta}^{(A)} \boldsymbol{\Gamma}_\beta] + \boldsymbol{\varepsilon}_\alpha^{(\text{f-in})}$$

The macrscopic transformation strains $\boldsymbol{\varepsilon}^{pt}$ can be *alternatively decomposed* as follows

$$\boldsymbol{\varepsilon}^{pt} = z_1 \boldsymbol{\Gamma}_1 + \sum_{\alpha=2}^n z_\alpha \boldsymbol{\kappa}_\alpha, \quad \boldsymbol{\kappa}_\alpha \equiv \boldsymbol{\Gamma}_\alpha + (\boldsymbol{M}_\alpha - \boldsymbol{M}_1)\boldsymbol{L}_\alpha(\boldsymbol{\varepsilon}_\alpha^{(\text{a-in})} + \boldsymbol{\varepsilon}_\alpha^{(\text{f-in})} - \boldsymbol{\Gamma}_\alpha), \quad (!\alpha)$$

Tensors $\boldsymbol{\kappa}_\alpha$ ($\alpha = 2, ... n$) are called *macroscopic ultimate phase transition strains*

The general form for the internal energy of coherency, including influence of transformation strains fluctuations, takes the following form

$$u^{coh} = u^{(a)coh} + u^{(a-f)coh} + u^{(f)coh} \geq 0,$$

$$\boxed{\rho\, u_{\alpha\beta}^{(0)coh} = f_{\alpha\beta}(\Gamma_{\alpha}, \Gamma_{\beta})}$$

$$u^{(a)coh} = \frac{1}{2\rho} \sum_{\alpha=1}^{n} z_{\alpha} \Gamma_{\alpha} \cdot (-\boldsymbol{\sigma}^{(\text{a-in})}); \quad u^{(a)coh} \equiv 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_{\alpha} z_{\beta} \cdot u_{\alpha\beta}^{(0)coh},$$

$$u^{(a-f)coh} = \frac{1}{2} \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_{\alpha} z_{\beta} u_{\alpha\beta}^{(f)coh}; \quad u_{\alpha\beta}^{(f)coh} \equiv -\frac{1}{\rho}[(\Gamma_{\alpha} - \Gamma_{\beta}) \cdot \boldsymbol{\sigma}_{\alpha}^{(\text{f-in})} + (\Gamma_{\beta} - \Gamma_{\alpha}) \cdot \boldsymbol{\sigma}_{\beta}^{(\text{f-in})}],$$

$$u^{(f)coh} = \sum_{\alpha=1}^{n} z_{\alpha} u_{\alpha}^{coh}, \qquad u_{\alpha}^{coh} \equiv 0.5 \frac{1}{\rho} < \breve{\Gamma}^{f}(\boldsymbol{x}) \cdot (-\breve{\boldsymbol{\sigma}}^{(\text{f-in})}(\boldsymbol{x})) >_{V_{\alpha}} \geq 0$$

The above convenient form of expressions entering internal coherency energy was obtained upon use of the following relation resulting from reciprocal (Betti) theorem.

$$\sum_{\alpha=1}^{n} z_{\alpha} \Gamma_{\alpha} \cdot \boldsymbol{\sigma}_{\alpha}^{(\text{f-in})} = \sum_{\alpha=1}^{n} z_{\alpha} < \breve{\Gamma}^{f}(\boldsymbol{x}) \breve{\boldsymbol{\sigma}}^{(\text{a-in})}(\boldsymbol{x}) >_{V_{\alpha}}$$

Stored coherency energy
and fluctuating part of microeigenstrain field $\breve{\Gamma}^f_\alpha(\boldsymbol{x}) \neq 0$

Upon taking into account phase fluctuations of transformation eigenstrains field macroscopic internal coherence energy takes the following general form

$$\rho u^{coh} = \sum_{\alpha=2}^{n} z_\alpha \left(\rho u^{coh}_\alpha \right) + 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta \, \rho u^{coh}_{\alpha\beta}; \quad \rho u^{coh}_{\alpha\beta} \equiv \rho \left(u^{(0)coh}_{\alpha\beta} + u^{(f)coh}_{\alpha\beta} \right)$$

$$\rho \phi^{coh} = \rho (u^{coh} - T \cdot s^{coh})$$

terms induced by phase fluctuations of eigenstrains

the same structure has coherence energy posed heuristically for two phase ($n=2$) RVE in family of R_L models of SMA materials $\phi^{coh} = \phi_2^{st} z_2 + \phi_{it} z_1 z_2$

After completion of austenitic transformation into the single martensitic compound ($z_2=1$), the term $\phi^{(f)coh}$ *usually does not disappear*, it represents the energy stored in RVE due to the presence of residual self-equilibrated stresses.
In general case $\phi^{(f)coh} \big|_{z_\alpha=1} \neq 0, \; (\alpha=2,..,n)$

The *nonzero contribution* of the term $\phi^{(f)coh}$, *induced by transformation eigenstrains fluctuations*, to the coherency energy allows for explanation of some effects present in macroscopic behavior of NiTi alloys observed experimentally.

In 2007 Popov and Lagoudas reported about discovered by them experimentally new effect in behavior of NiTi SMA materials. For material not submitted to mechanical loading the austenite start temperature determined in standard DSC test A_s^0 considerably differed, by about ~25°C, from such austenite start temperature A_s^{2-1} determined for NiTi material submitted before DSC test to considerable mechanical loading when it was in martensitic state.

Popov and Lagoudas indicated (incorrectly) that this effect appears due to plastic deformation of martensitic phase.

Popov P., Lagoudas D.C. (2007) A 3-D constitutive model for shape memory alloys incorporating pseudoelasticity and detwinning of self-accommodated martensite, Int. J. Plastaticity

Stored coherency energy
and fluctuating part of microeigenstrain field $\breve{\Gamma}_\alpha^f(\boldsymbol{x}) \neq 0$

In order to control (exclude) the influence of plastic deformations on the characteristic temperatures. The NiTi specimen was submitted to thermomechanical treatment consisting in tensioning it one time to 500MPa at room temperature $T=22°C>A_s^0$.
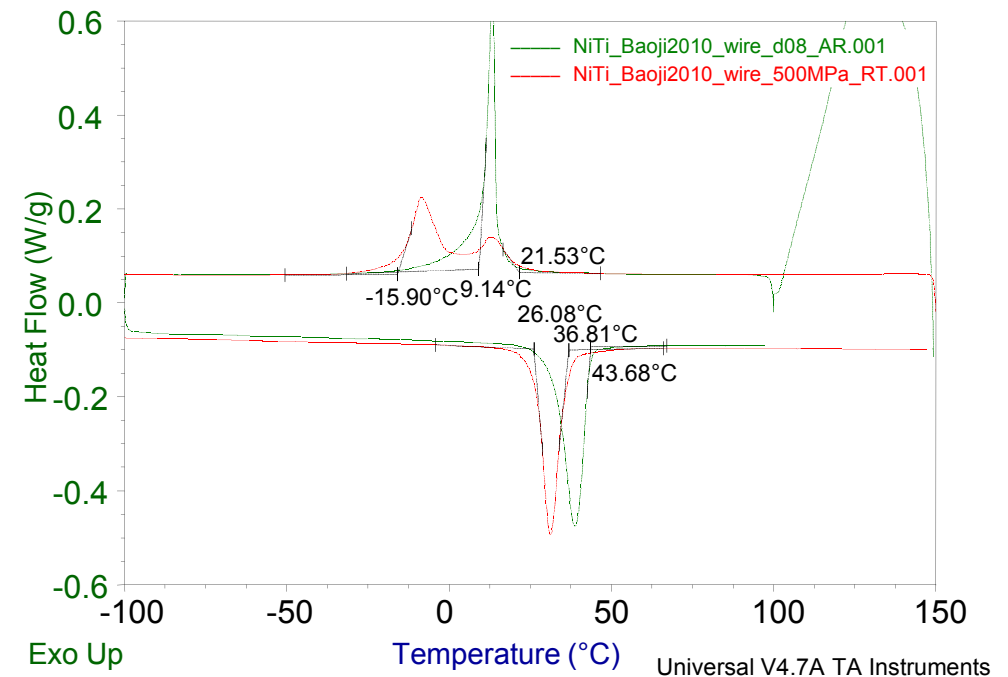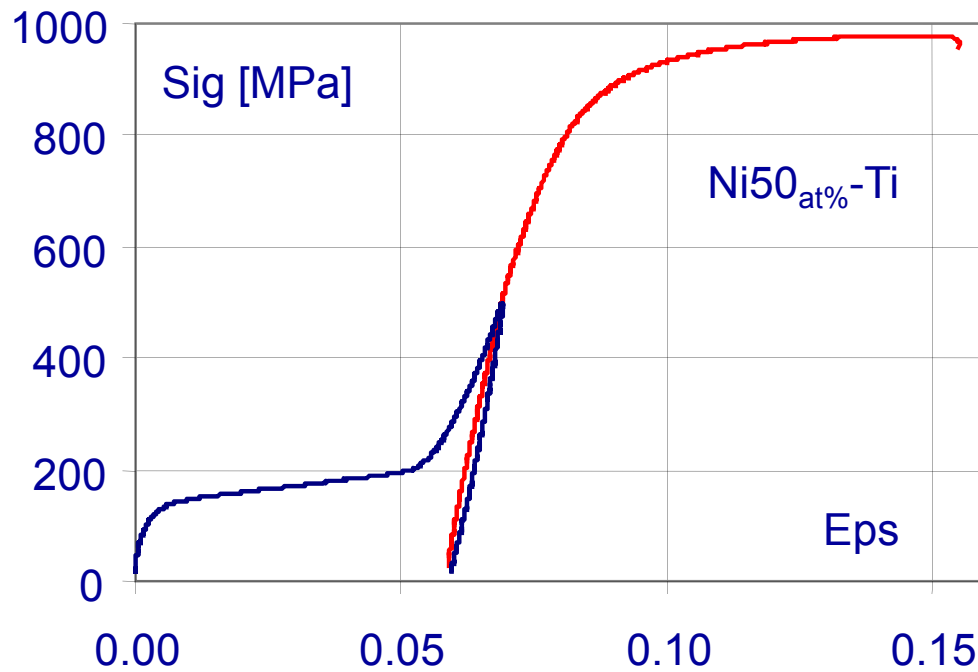
a) Nominal stress – uniaxial strain chart of $Ni_{50at\%}$-Ti wire specimen: loaded up to break (red), and the one loaded to 500 MPa and unloaded - TMT_{500x1} (blue) at room temperature 22°C; b) Comparison of DSC thermographs for specimen after delivery and after TMT_{500x1} treatment.

After loading-unloading the NiTi specimen in martensitic state to 450MPa (completely reorienting the martensitic phase) the austenite start temperature increased by $A_s^{2-1}-A_s^0=25°C$. It can be shown in modeling terms that *this effect can be explained* by different values of *coherence internal energy* u^{coh} and *coherence entropy* s^{coh} of thermally induced (self-accommodating) and mechanically induced (oriented) martensitic structures.
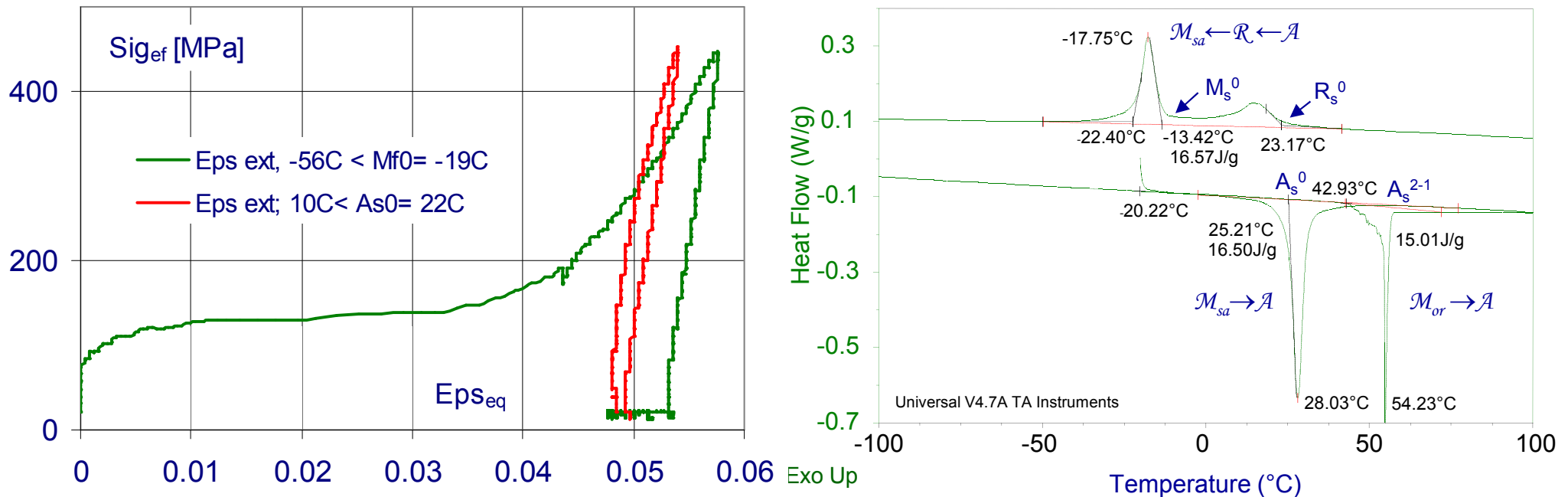
a) Isothermal stress-strain curves of polycrystalline $Ni_{50at\%}$-Ti wire samples in martensitic state submitted to tension at temperature -56°C and 10°C < A_s^0=26°C,
b) DSC thermograph of specimen initially in fully oriented martensite state (z_2=1)

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Central result

The present study allows for drawing conclusion that for *n* phases SMA macroelement (RVE), it is reasonable to adopt the *Gibbs potential* which is consistent with the following general form

$$g(\mathrm{Y}_h^{T\sigma}, z_\gamma) = \sum_{\alpha=1}^{n} z_\alpha (u_\alpha^0 - Ts_\alpha^0) + c_p[\Delta T - T\ln(T/T_0)] - \Delta T \boldsymbol{\sigma} \cdot \boldsymbol{\alpha}/\rho$$

$$-[\overbrace{\sum_{\alpha=1}^{n} z_\alpha g_\alpha^{(0)el} - 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta \ g_{\alpha\beta}^{el}}^{g^{el}=0.5\boldsymbol{\sigma}\cdot\boldsymbol{M}\boldsymbol{\sigma}/\rho}] + \overbrace{\sum_{\alpha=2}^{n} z_\alpha \phi_\alpha^{coh} + 0.5 \sum_{\alpha,\beta=1,\alpha\neq\beta}^{n} z_\alpha z_\beta \phi_{\alpha\beta}^{coh}}^{+\phi^{coh}} - \overbrace{\sum_{\alpha=2}^{n} z_\alpha \ g_\alpha^{ult}(Y_h^\sigma)}^{\boldsymbol{\sigma}\cdot\boldsymbol{\varepsilon}^{pt}/\rho}$$

where

$$\rho g_\alpha^{(0)el}(\boldsymbol{\sigma}) = 0.5\boldsymbol{\sigma}\cdot\boldsymbol{M}_\alpha\boldsymbol{\sigma}, \quad \rho g_{\alpha\beta}^{el}(Y_h^\sigma, z_\gamma) = f_{\alpha\beta}(\boldsymbol{M}_\alpha\boldsymbol{\sigma}, \boldsymbol{M}_\beta\boldsymbol{\sigma}) = \boldsymbol{\sigma}\cdot\boldsymbol{M}_{\alpha\beta}\boldsymbol{\sigma},$$

$$\rho g_\alpha^{ult}(\mathrm{Y}_h^\sigma) \equiv \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}_\alpha, \ \phi_\alpha^{coh}(\mathrm{Y}_h^T, z_\gamma) = u_\alpha^{coh} - Ts_\alpha^{coh} \geq 0; \ u_\alpha^{coh} \equiv 0.5 < \breve{\varGamma}_\alpha^f(\boldsymbol{x})(-\breve{\sigma}_\alpha^{(\text{f-in})}(\boldsymbol{x})) >_{V_\alpha}$$

$$\phi_{\alpha\beta}^{coh}(\mathrm{Y}_h^T, z_\gamma) = u_{\alpha\beta}^{(0)coh} + u_{\alpha\beta}^{(f)coh} - T\cdot 0, \quad \rho u_{\alpha\beta}^{(f)coh} \equiv -(\varGamma_\alpha - \varGamma_\beta)\cdot(\boldsymbol{\sigma}_\alpha^{(\text{f-in})} - \boldsymbol{\sigma}_\beta^{(\text{f-in})}),$$

$$\rho u_{\alpha\beta}^{(0)coh} \equiv f_{\alpha\beta}(\varGamma_\alpha, \varGamma_\beta), \quad \mathrm{Y}_h^{T\sigma} \equiv \{T, \boldsymbol{\sigma}, h\}, \ \mathrm{Y}_h^\sigma \equiv \{\boldsymbol{\sigma}, h\}, \ \mathrm{Y}_h^T \equiv \{T, h\}$$

When $u_\alpha^0 = u_{\mathcal{M}}^0, \ s_\alpha^0 = s_{\mathcal{M}}^0 \ (\alpha = 2,..,n)$ then $\sum_{\alpha=1}^{n} z_\alpha(u_\alpha^0 - Ts_\alpha^0) \Rightarrow u_{\mathcal{A}}^0 - Ts_{\mathcal{A}}^0 - (1-z_1)\pi_0^f(T)$

Central result

The *phase transformation strains* can be expressed as follows

$$\varepsilon^{pt} = z_1 \Gamma_1 + \sum_{\alpha=2}^{n} z_\alpha \boldsymbol{\kappa}_\alpha, \quad \boldsymbol{\kappa}_\alpha \equiv \Gamma_\alpha + (M_\alpha - M_1) L_\alpha (\varepsilon_\alpha^{(\text{a-in})} + \varepsilon_\alpha^{(\text{f-in})} - \Gamma_\alpha), \quad (!\alpha), (\alpha = 1,...\text{n})$$

Tensors $\boldsymbol{\kappa}_\alpha$ are called *ultimate phase transformation strains.*

In the literature devoted to SMA materials austenitic phase is frequently regarded as a matrix phase (α=1) with zero phase eignestrains

$$\breve{\Gamma}_1(\boldsymbol{x}) = 0, \, \boldsymbol{x} \in V_1 \quad \Rightarrow \quad \Gamma_1 \equiv 0, \, \phi_1^{coh} = 0 \quad \Rightarrow \quad \varepsilon^T = \sum_{\alpha=2}^{n} z_\alpha \boldsymbol{\kappa}_\alpha$$

The functions $g_\alpha^{ult}(\text{Y}_\text{h}\sigma)$ (α=2,...n) represent work of constant fixed macroscopic stress exerted upon the *ultimate transformation strains* $\boldsymbol{\kappa}_\alpha$. When their explicit form is known, for example from some experimental procedure, then they can be used as *potentials* for determination of *ultimate transformation strains*

$$\rho g_\alpha^{ult}(\text{Y}_\text{h}^\sigma) \equiv \boldsymbol{\sigma} \cdot \boldsymbol{\kappa}_\alpha \Rightarrow \boldsymbol{\kappa}_\alpha = \partial(\rho g_\alpha^{ult}) / \partial \boldsymbol{\sigma}$$

Conclusions and concluding remarks

The SEIM method allowed to derive explicit form of macroscopic Gibbs function (potential) for SMA materials treated as of n-phases conglomerate from experimentally supported assumptions on their behavior in microscale of observation.

Basing on the revealed explicit form of Gibbs potential for SMA materials:
- it was shown that *neglecting SMA material phases elastic properties non-homogeneity*, even when it is relatively high (of the order of several times), *does not lead to considerable errors* in evaluation the value of coherency energy and/or macroscopic phase strain.

- it was identified that some *coherency energy is stored in SMA material* even after full completion of martensitic transformation. It was revealed that the physical source of this stored energy is *fluctuating part of incompatible phase transformation strains*.

- it was shown that the *stored coherency energy* is responsible for considerable change in characteristic temperatures of reverse martensitic transformation $A_s^0 \rightarrow A_s^{21}$; ($A_s^{21} - A_s^0 \approx 25°C$ for NiTi).

Conclusions and concluding remarks

A number of difficult, *open scientific problems* still exists within the domain of modeling prediction of SMA materials behavior and/or their characterization.

Upon identification of realistic form of Gibbs potential for SMA materials treated as *n*-phases conglomerate, the desirable next steps can consist in:

- elaboration of *unified model of SMA materials behavior* capable for description of *pseudoelastcity* and *one way memory effect*. It is already known that this will necessarily require introduction of *more then two-phases RVE model*.
- elaboration of *criteria of forward/reverse phase transition* resulting from adopted specific form of Gibbs function and conjecture on *thermodynamic instability of phases* as the driving force for transformation,
- identification and derivation of explicit formulae for *thermodynamic driving forces of individual phases transformations*
- elaboration of *rules of phase transformation kinetics*
- development of *rules of evolution of ultimate eigenstrains tensors* (κ_α)

All the above targets require elaboration and execution of a broad experimental program.

Elements of experimental tests program
for development of SMA materials model

Schematic representation of desirable programs of SMA materials thermomechanical loadings in multiaxial stress states.
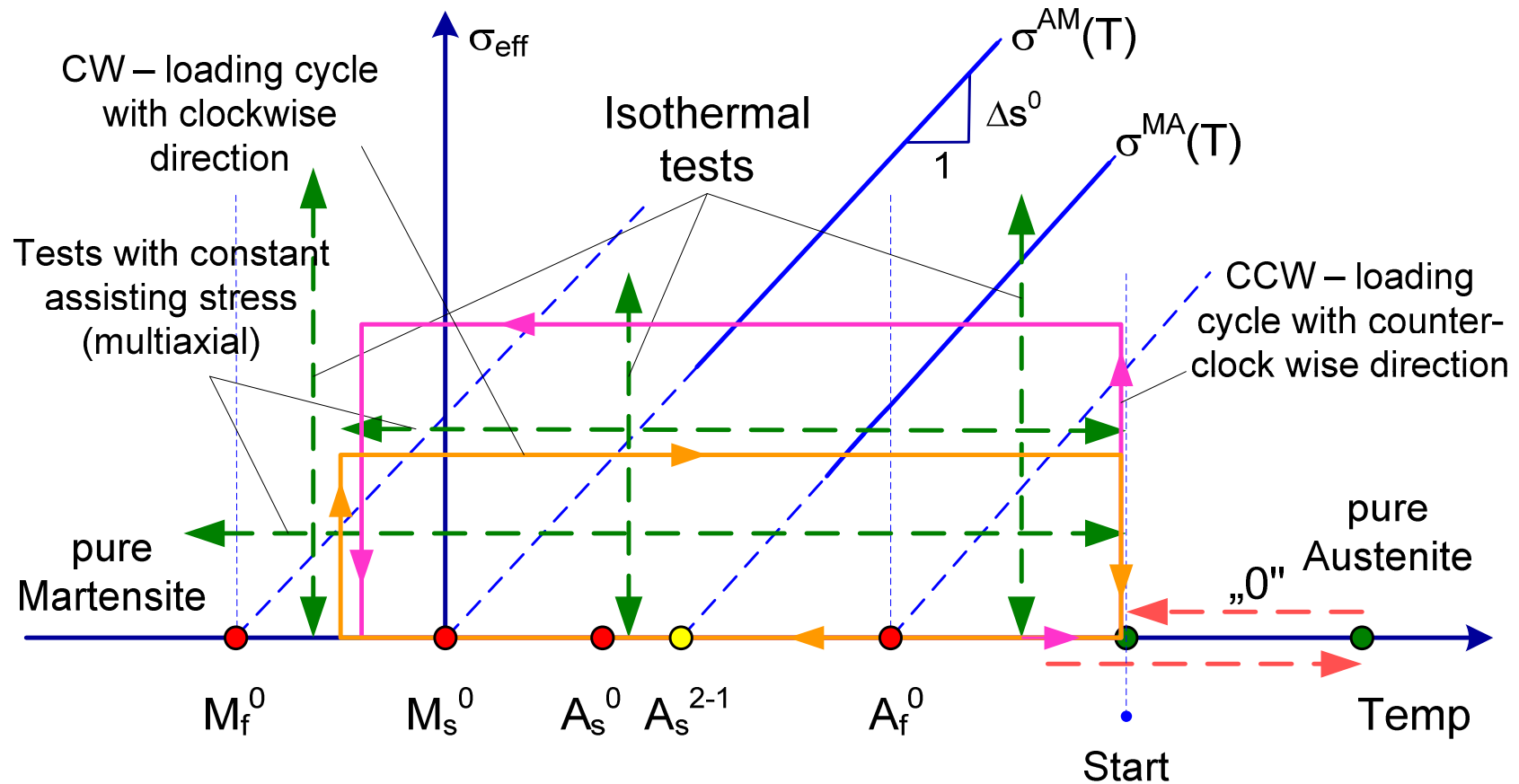
Conclusions and concluding remarks

The SEIM method, originally developed for the purposes of SMA materials modeling and characterization seems to have much broader application domain.

The SEIM method seems to be a convenient tool for evaluation of the influence of microstructure on macroscopic properties of many other modern materials e.g. sintered powders.

It looks to be well fitted for use in evaluation of he advancement/state of pathological processes in bones (porous and anisotropic structures).

It can be rather straightforwardly adapted to evaluate the advancement of damage processes, for example in wood or reinforced composites.

It offers handy tool for semi-experimental evaluation of the influence of different elements of manufacturing processes on overall resilience of the end product materials. For example how combined effect of foaming and extrusion influences the properties of Extruded Polystyrene Foams (XPS).

It seems that the *SEIM method* has the chance to gain independent existence as a method of *parametric characterization* of *advanced composite materials*.

Conclusions and concluding remarks

A number of difficult, *open scientific problems* still exists within the stream of tensor functions induced by their use i description of behavior and properties of advanced materials.

For example it is useful and required:
- to elaborate *quantitative measure* of the *degree of anisotropy* of a material
  Rychlewski has made first step in this direction
- to elaborate *quantitative measure* of *anisotropic material effort* and *limit criteria* for such effort.

Straightforward extension of Huber Mises criterion is not possible because in the case of anisotropic media, decomposition of the total elastic energy, stored in the material under loading, into the parts connected with the change of volume and the change of shape is impossible as indicated by Rychlewski, who proposed the notion of *"energy-orthogonal" states of stress* to overcome arising difficulties.

Notes