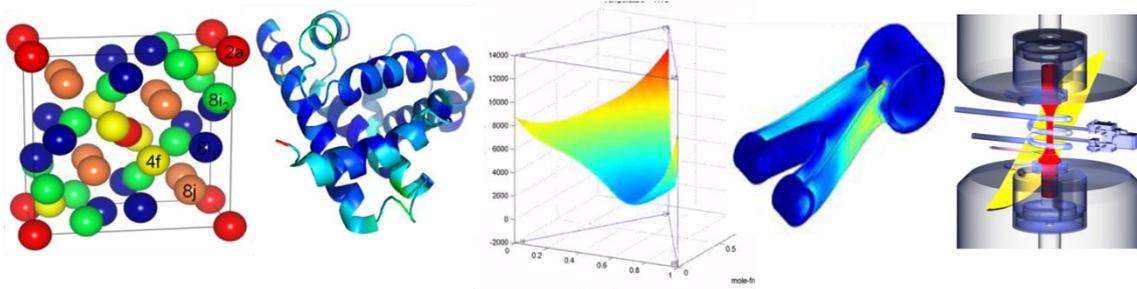


Kurzfassung zum Schwerpunktprogramm SPP1713



Strong coupling of thermo-chemical and thermo-mechanical states in applied materials

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Maerz 2013

Summary

Many applied materials like metals and solid-state polymers consist of multiple phases. Their properties depend crucially on the internal phase-structure¹, i.e. the fraction and local distribution of the phases, their composition and their molecular configuration. Chemical aspects influence the mechanical properties as well as mechanical load couples back to chemistry. This strong interrelation is expressed in the thermodynamic functional of the material which is composed of a thermo-chemical or thermo-solutal part on the one hand and a temperature-dependent mechanical part on the other hand. The mutual interaction between chemistry and mechanics in applied materials is the central goal of the proposed priority program.

Human hair, as a common example for a shape memory polymer, changes its shape by the intake of water, or it keeps its curly state after drying. Also metals, commonly viewed as dead bodies, show strong mechanical response on changes of their constitution. They expand or contract by the formation of new crystallographic phases, or show a macroscopic response by the sheering of crystal lattices. In return, external load or external fields can prevent or enhance phase separation both in metals and polymers. Most applied materials are stabilized far out of equilibrium by an internal balance of chemical and mechanical forces.

The separate focus on either the chemical aspect or the mechanical aspect respectively in different scientific communities, of course, results originally from good scientific practice: theoretical models are developed for cases in which individual phenomena can well be separated. In these cases a clear identification of cause and effect is possible which can be unambiguously formulated in constitutive equations including a consistent parameterization. Dependent on the tradition in the different scientific communities (here we address the communities of 'computational thermodynamics', 'continuum mechanics' and 'theory of materials', as well as 'polymer sciences' and 'metallurgy', in a broader sense the community of 'computational materials science') the individual focus on individual phenomena led to the development of different classes of theoretical descriptions specialized on individual features that are dominating in the applications under consideration. In this priority program we aim to combine these approaches for materials with strong thermo-chemo-mechanical coupling.

Examples of such materials are high strength steels, where the supersaturated crystal lattice locks plastic relaxation, Ni-base superalloys in which a two phase structure is stabilized by mechanical interaction. Immiscible polymer blends show enhanced stiffness and toughness due to a phase-separation between the components. In filled elastomers and fibre-reinforced polymers the mechanical properties depend on the chemical state of an interfacial layer which changes under external mechanical load. All these materials cannot be understood neglecting the interplay between phase-structure and mechanics.

Combining methods of computational thermodynamics and mechanics, developed for metals, with methods for history dependent phase-structures and their mechanical behavior, developed for polymers, on a general theoretical basis will evolve the full power of predictive materials modeling. It will enable scientists to describe structure and property of materials dependent on the process history and external chemo-mechanical load in a comprehensive way. In order to support the development and the validation of new comprehensive models and methods, also experimental investigations and the support from atomistic simulations are needed. This is the starting situation of the priority program:

- It is aimed to demonstrate the superiority and technological potential of coupled thermo-chemical and thermo-mechanical modeling for key metal and polymer materials.
- It is aimed to develop physically based material models with full coupling between chemistry and mechanics, taking into account the process history.
- It is aimed to develop comprehensive computational tools by joining the competence of different communities: materials, thermodynamics, mechanics, metals and polymers.
- It is aimed to integrate experimentalists and developers of simulation software to combine best data with best models and best numerical techniques.
- It is aimed at bringing together the scientific communities from computational thermodynamics, continuum mechanics and materials sciences.

The collaborative research within the new SPP shall establish a new paradigm of physically bases material modeling integrating the influence of process history and external chemo-mechanical load to be applicable to optimize production, properties and life time of applied materials for a sustainable economy.

¹ The nomenclature of "microstructure", "constitution" and "composition" is not consistent within metals and polymers community. Therefore the umbrella term „phase-structure“ shall be used throughout the document to describe those aspects of microstructures which are related to the amount, distribution and shape of phases in metals and polymers.

Scientific goals

Metals and solid-state polymers are usually considered as bodies with a frozen internal structure of constituents and phases. Applied materials, however, are by no means static in their structure and their behavior. They exhibit a rich internal phase-structure which is in many applications far from equilibrium and stabilized only by a delicate balance of internal chemo-mechanical forces on the one hand. On the other hand this phase-structure reacts sensitively on external environmental changes and mechanical loads as well as external fields (electrical, magnetic or light). It dramatically changes during production, either by self-organized processes or by reaction on imposed loads. During the life-time of materials and service we have to accept inevitable degradation. Never the less, 'defects' determine the properties of applied materials which need to be designed such that their structure remains stable during their whole life time: we cannot accept failure and failure in most cases results from a combination of chemical and mechanical loads. Therefore the goals of the proposed SPP are:

- Identification of the coupling mechanisms between thermo-chemistry and thermo-mechanics.
- Physically based understanding of phase-structures in materials by the interplay of thermo-chemistry and thermo-mechanics, their generation and degradation.
- Development of materials models, numerical models and tools to cope with these phenomena.
- Establishing datasets predictive modeling capabilities by experiment and first principles simulations.
- Provide thermo-mechanical coupling coefficients from ab-initio simulation or experiment to complete theoretical models.
- Provide experimental benchmarks of materials states which show a strong chemo-mechanical coupling for verification of theoretical models.

It is well established that during industrial production, in particular during thermo-mechanical treatment of metals, extrusion, drawing and stretching of polymers, mechanical loads dictate the evolution of the internal structure and the external shape of the materials. It is less well established how internal mechanical and thermodynamic states interrelate with these external loads. Internal processes may counter-act the applied load by phase-separation or stress shielding. They may amplify external loads if activation barriers are overcome and accelerate the process significantly. A well-known example of such a mechanism is the shape memory effect where thermodynamic and mechanical transformations go hand in hand. It is observed in both metals and polymers. In the context of this priority program, however, purely massive deformation, which dominates the shape memory effect in metals, is not of interest. The shape memory effect in polymers, if it is triggered by chemical changes or external fields, falls within the scope of the program.

During service all materials exhibit the tendency to evolve towards equilibrium on the one hand. Advanced materials possess a complex internal phase-structure which is designed for the material property, but far from equilibrium where different internal structures compete in dominating the material properties on the macroscopic scale. This structure shall be static or frozen during the materials life time and the evolution toward equilibrium not only be kinetically hindered, but blocked, e.g. by internal stresses. On the other hand impacts like mechanical, thermal and chemical loads or radiation influence the balance in the internal phase-structure and may drive the material even further from equilibrium. In order to predict the life-time of materials it is necessary to quantify these effects of degradation in dependence on the balancing of thermo-chemical and thermo-mechanical forces.

The designers of materials need to understand the internal competition of structures to utilize it for a better performance, for an improved lifetime and for reduced degradation and corrosion of materials. They must understand how internal mechanical loads (micro stresses) influence the thermodynamic stability of materials and how changes in the thermodynamic state of the material influence the long term degradation of the mechanical properties. Only a coupled understanding of this interaction between mechanics and thermodynamics can lead to a consistent understanding of materials. This improved understanding, its transfer and establishment into the daily scientific practice are the central goals of this priority program

We aim for investigating 'complex' and 'applied' materials. 'Complex' in this context means that the material consists of several constituents (phases) with clearly distinct properties. 'Applied' in this context means that the material under investigation shall be multi-component to mimic materials for a special application, but not with full technical intricacy. This reduction shall allow detailed studies of individual phenomena for a basic understanding as addressed in this program.

Structural and thermodynamic states must be closely coupled i.e.

- The phase-structure of the material which determines its properties, deviates considerably from the equilibrium state of the individual phases. This deviation is completely stabilized, or its rate of change is significantly reduced by internal mechanical forces.
- The phase-structure changes under external chemo-mechanical loads and external fields.

Examples are:

- Coupled thermo-chemical effects in the thermo-mechanics of multiphase steels like press hardening, where mechanical deformation triggers phase separation.
- Thermoplastic semi-crystalline polymers where the process-induced microstructure determines the local and global mechanical behavior
- Nickel-based superalloys where soft γ -channels separate and protect hard and brittle γ' -precipitates
- Polymer blends and their specific morphology of different (polymer) phases
- Diffusion processes, intermetallic phases, and Kirkendal effect in special systems like Au-Al wire-bonding .
- Thermoplastic elastomers and block-copolymers with local phases
- Precipitation hardened Aluminum alloys which attain their properties by 'aging'
- Strain-induced crystallization of natural rubber
- Degradation of polymers under environmental loads
- Degradation of joints between metals under thermo-mechanical and environmental loads
- Functional polymers with field-controllable shape and mechanical properties

There will also be a strong synergetic cooperation between the different communities. While the metals community is mainly focused on elasto-plastic or elasto-visco-plastic materials, visco-plastic or visco-elastic materials are predominant in the area of polymers. Diffusion, creep and flow dominate materials transport in different regimes of both materials. Metal scientists shall learn from polymer scientists about the effect of oriented phase-structures on plastic flow behavior. Polymer scientists shall learn from metallurgists about models of phase transformations, crystallization and melting dependent on the materials chemistry. Both communities shall meet at the common focus on materials where the local materials chemistry and the response to mechanical loads are intrinsically coupled.

Work program

The work program addresses tasks which are needed for a consistent description of materials where thermodynamic, thermo-chemical and thermo-mechanical aspects are strongly coupled. This comprises model development, data acquisition, numerical implementation, simulation studies and experimental verification. Individual tasks are detailed corresponding to the different aspects of this SPP:

Thermodynamic and thermo-mechanic theories, constitutive equations and transport equations.

Many mechanism-based models in mechanics of metals and polymers are still formulated in a purely mechanical setting. Thermodynamical approaches often neglect the influence of mechanical quantities on the equilibrium state. Both simplifications imply that the transfer between mechanical, internal and chemical energies is massively oversimplified in most models applied in materials science and engineering. An extension of the models requires additional theoretical analyses of the constitutive equations, more elaborated experiment-based identification techniques and, finally, significantly more advanced numerical solution techniques. Therefore, the focus will be on:

- Model approaches where the balances of linear momentum and internal energy are taken into account on the continuum scale by means of chemo-mechanically strongly coupled and thermodynamically consistent material models.
- Numerical implementation of these models within finite element, finite volume and finite difference schemes.
- Identification of coupling parameters by means of experiments or atomistic simulations.

In addition to phenomenological approaches, special attention is given to scale bridging techniques in order to take into account microstructural information in the thermodynamical modeling.

Atomistic models and coarse graining strategies

While first studies show the great potential of atomistic methods in describing thermo-mechanical coupling for a link to the meso- and macroscale simulations or to experiment a number of challenges have to be addressed.

First, the atomistic approaches do not distinguish between thermo-mechanical and thermo-chemical contributions since both aspects are intrinsically and inseparably included. We have therefore the paradox situation that at the larger scale we have to connect these two contributions whereas at the atomistic level we have to separate them to provide consistent input to the large scale simulations and to help them with identifying the correct coupling relations. Concepts to do this are still in their infancy and require careful considerations e.g. to avoid double counting of energy contributions that involve both thermodynamic and mechanical ones. To achieve this experts from both scales have to work closely together.

Second, a major challenge is the accurate yet computational efficient computation of thermodynamic averages over a large number of structural and chemical configurations. Various strategies shall be investigated and explored such as mapping of the ab initio data on empirical potentials, coarse graining in configuration space, or cluster expansion. Third, since all practical ab initio schemes provide no error bars careful and systematic benchmarks against experiments are critical.

Numerical implementations and applications

In the case of multi-field problems like the addressed thermo-chemo-mechanical coupled problems, general strategies and algorithms are already available. Therefore, the focus in the SPP is on the implementation of the developed constitutive theories in numerical schemes like the finite element method for solving initial-boundary value problems. The mere development of new numerical techniques for established models is not the focus of the SPP. However, the implemented algorithms for solving the constitutive behavior should be as efficient and precise as required.

Thermodynamic databases and their extension to mechanical properties and polymers

As stated above, CALPHAD type databases are capable to consider pressure-volume work and its influence on phase stability. This has to be generalized to elastic energy and the treatment of Gibbs energy dependent on the deviation of the equilibrium shape of the phases. This will allow deriving the elastic coefficients of the different phases depending on its composition.

Other topics are the extension of thermodynamic models of materials with significant defects, point- and line defects. It is necessary to consider defects outside equilibrium as well as the dependence of the solubility of phases for individual constituents on the density of defects.

Storage of mechanical data like yield criteria, activation energies for glide consistent with the internal phase composition as a result of Gibbs energy minimization. The latter will allow to treat mechanical data dependent on the alloy concentration which is largely missing today.

A central task will be the development of concepts to handle thermo-chemical data of polymers, a consistent and transferable data format and rules to generate the data from experiment or first principle calculations. Kinetic data have to be an integral part of this concept.

Phase field models

Phase-field models shall be combined with micromechanical models both from the metals, as well as from the polymers community. This comprises

- Plastic relaxation of stress, large deformation and creep in multiphase systems
- Thermodynamically consistent treatment of defects in the thermodynamic functional
- Creation of defects under load and solute defect interaction
- Sub-grid models for micro-defects and their relation to thermodynamic functions
- Thermodynamic consistent models for phase mixtures and polymers
- Realistic models for internal energy dissipation in mixtures and defect structures.

New algorithms are needed to cope with respective constitutive laws. Also the consistent treatment of defects and phases must be advanced. The numerical models shall either be able to cope with advanced models of bulk phases with internal phase-structure or in a scale bridging approach with the explicit resolution of the phase-structure. Also coarse graining strategies from the atomic scale are needed. All models and simulations shall be verified with respective experimental investigations inside the SPP and with available literature.

Long term stability, aging and over-aging and degradation

In the SPP, both the detailed experimental investigation and the thermomechanical representation of the process-dependent material behavior of semicrystalline polymers on the one hand and of filled or thermoplastic elastomers on the other hand are needed. The pronounced time- and temperature-dependent mechanical material properties or ageing, degradation and long-term stability, for example of crystalline phases are central aspects in this research which must be taken into account. The stability of phases under different temperature conditions is also a key aspect in the area of metals. The constitutive models to be developed in the SPP in this context should be compatible with the fundamental laws of thermodynamics and experimentally validated.

Microstructure evolution during thermal and thermo-mechanical processes

Different kinds of thermo-chemo-mechanical microstructure evolution in metals during thermal and thermo-mechanical processes are well known in metallic materials. Some of them are actively used since several centuries for optimizing metal products; others cannot be effectively avoided during the processing of metals. Examples are:

- forming of precipitations by heat treatment in the sense of aging in order to utilize the effect of precipitation hardening
- solid-solution hardening by generating adequate distributions of solute atoms by heat treatment
- adjustment of special phases with adequate morphological textures in multiphase materials
- chemical inhomogeneity like segregations which are influenced by mass transport due to diffusion and mechanical loads; in general such chemical inhomogeneity can result in significant internal stresses
- diffusion-induced stress including stress accompanying the formation of intermetallic phases

In all these examples, the mechanisms of diffusion in metals like the substitutional diffusion processes by vacancies or grain boundary plays a vital role. In this context, it is well established that the speed of diffusion depend strongly on the diffusion mechanism and superimposed stress states can significantly influence the speed and also the direction of diffusion processes. There are certain examples in literature, where such thermo-chemo-mechanical coupling effects in metals have been observed and investigated:

- Stress-driven diffusion processes and stress-induced phase transformations in Ti-Al-Fe alloys
- Influence of the delta-phase on the grain size evolution during dynamic recrystallization and implications on the microstructure under deformation as well as the mechanical properties
- Formation of Ni_4Ti_3 precipitates in NiTi shape memory alloys under the application of stress
- Negative mechanical driving force due misfit strains around incoherent precipitates, which can strongly influence the growth of precipitates
- Kirkendall effect and Kirkendall voids as a result of different diffusion rates in the considered materials

In all, there is a strong thermo-chemo-mechanical coupling between movement of the atoms by diffusion process and under superimposed internal and external stresses as well as the formation of solid solution and intermetallic phases. In contrast to the phase formation by martensitic phase transitions, which have been intensively discussed in literature, the thermo-chemo-mechanical coupling effects in diffusion dominated processes are much more complex and less investigated.

The main focus of the SPP is on the representation of thermo-chemo-mechanical coupled processes, but also additional fields like electrical and magnetical fields must be incorporated if required. In the field of metals, the SPP will concentrate on thermo-chemo-mechanical processes in the bulk material on the basis of diffusion processes. As long as diffusion processes are not considered, the consideration of materials showing martensitic phase transitions are not a central topic of the SPP. Surface effects like corrosion will not be taken into account. This means that also the considered degradation effects takes place in the bulk material and not on the surface. Often, the thermo-chemo-mechanical reactions will change the microstructure in such a way that the hardening behavior is strongly influenced. Both the short time evolution of the microstructure as well as the long term stability under service conditions are of special interest. Moreover, carefully designed experimental setups are required to identify the material behavior and the material parameters of the developed constitutive theories. For the central aspect of the SPP, the representation of the chemical coupling in the sense of the kinetics of phase formation, it seems to be indispensable to enhance and couple methods for the calculation of phase diagrams and the kinetics of phase formation. Often, the representation of intermetallic phases will be a key challenge.

Field-controllable functional polymers

Instead of using state-of-the-art approaches which do not consider local interaction between the mechanical and the external fields, it is planned to explore approaches with a partial or a full coupling between these fields. Elaboration of such approaches is especially important in the case of strong external fields, when the micro-deformation may become very different from the macro-deformation, and thus the assumption of affine deformation fails. The full coupling can be implemented for example by solving simultaneously the mechanical displacement and the field potential at each node in the frame of finite element modeling. Due to complexity of the coupled-field problem a 2D modeling should be tried first, before switching to a full 3D formulation. This will help to investigate the role of non-affinity effects on the material behavior under strong electrical, magnetic or light field. Alternatively, one can introduce a partial coupling between the fields by introducing appropriate cross-terms into analytical expressions for the free energy. The coupling strength can be varied by adjusting a value of the coupling parameter. Comparison between the numerical and analytical approaches shall help to verify the region of validity of existing rescaling approaches and to elaborate a new formulation of the coupled-field problem. A possible extension will be consideration of thermal effects arising in the presence of strong (electro)magnetic fields. This will lead to a coupled multi-field formulation – thermo-photo/magneto-mechanical – similar as it is presently done in the field of intelligent hydrogels.

Experimental support, data acquisition, atomistic simulation and model verification

Experimental projects and atomistic studies must be closely coordinated with projects focused on theoretical model development before submission of the proposal. They can be either group projects, or stand alone projects which have a direct link to at least one modeling project. The measured properties shall provide a direct input for the simulation models, or provide a benchmark for simulations. Examples are:

- Elastic constants, Young's/shear modulus, Poisson's ratio
- Tensile/compression test, hardness, indentation test
- Digital image correlation
- Light microscopy, REM, TEM, EBSD (microstructure, grains size, volume fraction of phases, dislocation structure, stacking faults, stacking fault energy, twins)
- X-ray and synchrotron diffraction (volume fraction of phases, grain size effect, texture)
- Techniques for analyzing the chemical composition like EDX , etc
- Miniaturized mechanical testing
- Degradation/aging of microstructures under external environmental and mechanical load