

# Equation of State and Constitutive Properties

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## 1. Introduction:

The scientific underpinning of our confidence in ensuring the performance, safety and reliability of the nuclear weapons stockpile lies in our ability to predict — on the basis of experimentally validated physics-based models — the dynamic response of materials under a wide range of stress, temperature, strain, and strain rates. Under the current moratorium on nuclear testing, there is a premium value on the development of a fundamental understanding of the dynamic response of, and interactions among, materials — particularly as they change over time due to aging and/or re-manufacturing. The development of a comprehensive set of experimentally validated predictive capabilities to assess the effects of materials properties on stockpile margins and uncertainties is at the heart of the stockpile stewardship program and forms the basis of a scientific strategy to mitigate these uncertainties.

The dynamic response of materials can be approximately categorized into two classes of properties: *thermodynamic properties* and *engineering constitutive properties or models*. Generally, *thermodynamic properties* are fundamentally well defined at the quantum and atomic scales, and include equation of state (EOS), re-solidification (meta-stable trapping or frustration), phase boundaries and transitions across them such as melting and solid-solid polymorphism, thermodynamically derived transport and mechanical properties, and so on. On the other hand, *engineering scale constitutive response* typically is governed by phenomena occurring across length scales — from the quantum-level scale to the continuum — and is dominated by the collective behavior of defects and the evolution of material microstructure. As such, practical constitutive models are usually phenomenological due to unsolved technical challenges in incorporating all relevant sub-grid-scale physics. (Fracture, failure, and damage more generally, which are typically distinct from continuum-level [phenomenological] constitutive models, are examples of this.) Notable exceptions, in which constitutive response can sometimes be connected directly to fundamental material properties, include plastic deformation and yield strength. *Accurate physics-based constitutive models and fundamental properties are absolutely essential to development of a truly predictive scientific simulation capability.*

In its first decade, the ASC Academic Alliances program succeeded in demonstrating that very large-scale science and engineering simulations are feasible on scaleable high-performance computing platforms, and it demonstrated several significant applications of end-to-end simulation of

systems performance. These achievements position the computational science and engineering community to now focus intently on making progress on the perennial issues that limit the ultimate accuracy and predictive power of these simulations: predictive, robust, and efficient materials response properties and process models. The emerging challenge is to go beyond treatments of single-physics response of homogeneous regions to describing, with quantified accuracy, the coupled, multi-physics behavior of strongly heterogeneous media. The central goal of enabling *predictive* simulations creates the need for quantifiable accuracy and precision, which, in turn, demands performing a thorough verification and validation process, and, very likely, developing physically well founded and numerically effective multiple length- and time-scale (“multi-scale”) simulation capabilities.

## 2. Thermodynamic properties of materials:

- *Phase transformations, melt and solidification:*

Phase transformations have profound effects on materials response. They occur in a wide variety and under a broad range of conditions. These two aspects of phase transformations make developing accurate, robust, and efficient treatments of them a prerequisite to achieving predictive simulation capabilities. Following are selected illustrations where improved descriptions of phase transformations are needed.

The long-standing problem in this area is simply stated: greater knowledge is needed of real phase diagrams for pure elements, alloys, and compounds; and likewise for the mechanisms and kinetics of transformations across a phase boundary. Due to the influence of the phase transformations on microstructure development and evolution, understanding them can contribute greatly to efforts in predicting material properties. In addition to processes for single-component materials, the physics of phase transitions at interfaces between un-like materials is an area of significant interest. Both atomistic- and continuum-scale descriptions are of interest, for example, free energy-based phase field. Significant challenges exist in the latter case for phase transitions involving polyatomic molecular materials, due in part to the large number of order parameters that would be required in order to capture lattice symmetry, site symmetry, and molecular point group in these structurally and chemically complex materials.

High energy density physics (HEDP) experiments demonstrate that the appearance of the vapor phase can dramatically change the transport properties of warm, dense matter. Hence, accurately simulating the low temperature range of warm, dense matter depends on the fidelity of modeling liquid-vapor phase transitions, including treatment of the phase transformation kinetics, in hydrodynamic codes.

- **Relevant research needs:** A method is needed for characterizing the appearance of two different phases of material, having potentially very large differences in specific volumes, as a fluid element enters the vapor dome. Currently codes treat only the mean properties within the vapor dome.

Phase transformations can significantly perturb material strength behavior. Conversely, deviatoric stress can alter the stress and temperature at which a phase transformation occurs. In addition, strain rate and plastic deformation effects can result in persistence of metastable phases that also change strength behavior.

- **Relevant research needs:** Breakthroughs in understanding and modeling all of these aspects of the interplay between phase transformations and strength are needed for achieving predictive simulations.

Solid-liquid transformations, melting, and solidification pose many problems in material modeling that require improved understanding and better numerical treatments. A topic of central importance is the prediction of the kinetic processes and ensuing microstructure evolution when a material undergoes stress and/or temperature-driven melt or solidification. That is, under a prescribed temperature/stress history, competition between kinetics and thermodynamics often leads to frustrated, or metastable, structures. This applies equally to metals and organics. Understanding this area is relevant to process modeling and manufacturing. Solidification determines microstructure, which, in turn, strongly influences material properties. A central aspect of solidification phenomena that is of interest is how it progresses under dynamic application of stress.

- **Relevant research needs:** Understanding and modeling efforts are needed to characterize the kinetics and metastability behaviors occurring under rapid, stress-induced solidification.

Very large-scale classical molecular dynamics (MD) simulations are now being used routinely within the scientific community. Electronic interactions are built into the classical interatomic potentials. However, when the electronic contribution to the entropy difference between two phases is large, for example solid and liquid, these methods are generally not expected to give accurate characterizations of melting. In contrast, quantum MD (QMD) simulations — usually implemented within the local density approximation (LDA) to density functional theory (DFT) — provide much more accurate treatments of electronic interactions, but are severely limited in the number of atoms that can be simulated.

- **Relevant research needs:** Development of a method to bridge between the desirable aspects of classical and quantum MD would be a valuable breakthrough of great significance to the field of materials simulations. The bridge could be an efficient coupling of the two methods or a well-founded approach for adding the effect of changes in electronic character to classical potentials, guided by the results of QMD calculations.

In the case of non-covalent organic solids, there is a need for improved electronic structure treatments that more accurately account for weak intermolecular (dispersion) forces that typically dominate molecular crystal

structures and properties under mild conditions of stress and temperature. Also, regardless of whether empirical or “quantum-based” forces are used, non-equilibrium MD simulations of organic materials suffer from deficiencies associated with classical (versus quantum) statistical mechanical treatments of the vibrations. Even given a “perfect” ground electronic state force field, this can lead to large errors, for example, in predicted temperatures/stresses behind a shockwave, with accompanying errors in chemical reaction rates and mechanisms.

- ***Equation of state (EOS):***

The physically-derived determination, prediction and thermodynamically-consistent tabulation of the thermal properties of materials are critical in the simulation of almost any complex system. Of particular importance, the EOS establishes fundamental relationships among thermodynamic variables (stress, density, temperature, etc.) and provides closure of the hydrodynamic equations that explicitly ensure conservation of mass, energy, and momentum. Hydrodynamic simulations require thermodynamic input data in every (numerical) zone and for every time step. Consequently, comprehensive and in-depth knowledge of materials EOS is absolutely essential to all simulations of this class. Other examples of critical thermodynamic properties of materials include melt temperatures required to establish the domain of materials strength. The absence of reliable EOS information over all relevant regions of thermodynamic state space renders impossible the development of a truly predictive capability for complex physical systems.

Of particular interest to the NNSA scientific programs, are materials EOS that cover a wide range of conditions of stress, temperature, and density. Such a wide range of EOS regimes typically requires multiple models, each covering a specific phenomenon that dominates the response over an interval of conditions. While this is often an effective modeling strategy, it requires intricate “phase matching” and interpolation between regions of the EOS that are represented with different models.

- **Relevant research needs:** The development of physically-based models that naturally make the needed phase matching and ensure thermodynamic consistency across the phases.

Though properties at standard temperature and stress (STP) conditions are usually quite accessible to measurement, it is important for EOS to accurately predict properties at STP for several reasons. The zero stress crystal volume is found to strongly influence EOS accuracy at high stress. Conversely, though an EOS may be accurate at high stress and temperature, unless the mathematical form used is physically correct *and* sufficient information is available to constrain its behavior under ambient conditions, it may not provide an acceptable description close to STP — but this, too, can be important for the overall accuracy of a simulation. An example where such details are important is prediction of the temperature behind a shock wave propagating through a high explosive. Here uncertainties in “simple” (temperature- and stress-dependent) properties such as bulk modulus, specific heat, and thermal expansion coefficients can lead

to large uncertainties in predicted temperatures; which, given nominally exponential dependencies of chemical reaction rate upon temperature, can lead to large errors in predictions of important processes such as detonation sensitivity and initiation behavior. In addition to being accurate over wide intervals of temperature and stress, EOS models that extend beyond simple elasticity need to be accurate over several decades of strain rate; viscoelastic response of polymers is one among several good examples where this is true.

Existing EOS theories often break down in certain structural phases exhibited by  $f$ -electron metals where it is known that strong electron-electron correlation is inadequately treated by standard mean-field electronic structure techniques — such as density functional theory (DFT). Of central importance to the ASC program is the development of rigorous theoretical and computational techniques that afford a predictive treatment of EOS in the regime where electron correlation dominates. These goals might be achieved by using a combination of effective Hamiltonian and quantum Monte Carlo (QMC) techniques developed specifically for strongly-correlated electron systems. In parallel with QMC treatment of effective Hamiltonians with reduced numbers of orbitals per site, more approximate solutions are being carried out both for these effective Hamiltonians as well as for the full all-orbitals-per-site case. This enables immediate calibration of QMC computational benchmarks to the physically relevant regime. Recently, advanced simulation methods such as dynamical mean field theory (DMFT) have been used to describe the properties of strongly correlated materials. In any case, significant questions still remain regarding the optimal path for upscaling EOS information for perfect materials at atomistic scales into descriptions that incorporate mesoscopic and larger scale defect structures.

- **Relevant research needs:** The development of advanced electronic structure methods that afford a predictive treatment of the EOS of materials in the regime where electron correlation dominates.

Modern theoretical frameworks have been extremely successful in predicting the properties of condensed matter systems at low temperature (typically below the melt temperature,  $T_m$ ) and plasmas at high temperature (typically above the Fermi temperature,  $T_F$ ). However, there exists an important regime within the density-temperature phase space where “warm” states of matter are inadequately described by either conventional condensed matter physics-based or plasma physics-based theories, and where the greatest uncertainties exist in our ability to predict the thermodynamic properties of matter. From a condensed matter physics perspective, warm dense matter refers to states of matter with solid-like densities and temperatures comparable to  $T_F$ . From a plasma physics perspective, warm dense matter refers to states of matter that are plasma-like, but that are too dense and/or too cold to be adequately treated by standard plasma physics approaches. Consequently, this warm dense matter regime — roughly spanning the energy range between  $T_m$  and  $T_F$  — defines states of matter between solids and plasmas. The simulation of warm dense

states of matter is particularly challenging because many competing processes are active while none dominate.

Scientifically, the warm dense matter region of density-temperature phase space is attracting considerable interest, both theoretically and experimentally. Within the experimental condensed matter physics community, interest has been stimulated by the emergence of new techniques for generating strong shock waves in materials, and new methods for confining and interrogating “warm” samples at high stress. Within the plasma physics community, the development of novel sources enabling experimental access to plasma-like states of matter at low temperature and high density has led to emerging research opportunities at the forefront of the field. Theoretically and computationally, recent advances in finite-temperature *ab initio* electronic structure methods beyond mean-field theories, coupled with the unprecedented surge in compute power afforded by ultra-scale computing platforms, have led to important new developments in our ability to predict the thermodynamic properties of warm states of matter.

- **Relevant research needs:** The development of simulation tools that provide a predictive treatment of the EOS of materials in the warm dense matter regime.

Because different EOS models are used in different physical regimes of stress, temperature, and density, technical improvements in interpolation schemes and numerical issues to ensure thermodynamic consistency across models and regimes would be of significant interest. Accurate information spanning all relevant states of stress, temperature, and strain rate, whether obtained from theory/simulation or experiment, is also required in order to improve the equation of state for a given material. As typical numerical simulations of interest involve multiple materials, as important as attaining predictive accuracy for single material’s EOS is developing reliable methods for representing the (effective) EOS of a mixture of materials, or equivalently, mixing EOSs in given simulation. Ultimately, the goal is the formulation of a unified EOS model that captures all of the important physics in all relevant regimes of thermodynamic state space.

- ***Optical, electrical, and transport properties:***

Other materials properties of interest include optical, electrical, and transport properties of materials under extreme conditions. Since experimental probes often involve the measurements of the optical, electrical, and/or transport properties of materials, the predictions of these properties as a function of stress and/or temperature is an area of great importance. For example, temperature in shock physics experiments is usually extracted from the measurement of emissivity of the materials under dynamic compression. The first-principles development of predictive simulations of the optical properties of materials under high-stress/high-temperature conditions is of great interest. Similarly the design and analysis of dynamic high-stress experiments using pulsed power technology requires physics-based models of the materials electrical conductivity at high temperature.

- **Relevant research needs:** The development of quantum-based simulation tools that provide a predictive treatment of the optical, electrical, and/or transport properties of materials under extreme conditions.

- ***Kinetics and metastability:***

As has already been noted, there is often a competition between thermodynamics and kinetics that leads to geometric frustration, or trapping of materials in non-equilibrium metastable states (geometric, magnetic, etc.). This is true whether one considers “simple” metals (grain size, texture) or complex fluids such as microphase separating multi-component polymeric systems. In such cases, straightforward atomistic simulation methods will usually fail to capture even the most dominant morphological motifs for systems with realistic geometric dimensions, due to limitations of accessible simulation times. Nevertheless, it is imperative for a genuine predictive capability on the macroscale that physics-based mesoscale models capture the essence of the detailed chemical interactions (bonding in metals; chain topology, chemical composition) at microscopic scales. Field theoretic models are often useful in such situations, as they can, in principle, provide a connection between microscopic physics and continuum behaviors; and the “dynamics” of phase evolution can be followed for much longer times for field models than with a particle-based model. However, there are few examples where realistic field descriptions have been formulated and parameterized for specific materials. Another key ingredient is the ability to incorporate the effects of a given materials processing history on the final morphology/properties that result.

- **Relevant research needs:** Development of improved models for composites, which may range from “standard” materials such as filler-reinforced polymer foams or high-explosive formulations to highly novel, functional nanomaterials (see white paper on *Novel Materials*).

### 3. Constitutive properties of materials:

Of interest to the NNSA programs are applications that anticipate and accommodate material or structural failure occurring in the course of normal operation because material response in a ‘failed state’ can control how the entire body continues to respond in an on-going process. Accordingly, material properties well beyond the linear response regime need to be accurately described. This gives rise to strong interest in plasticity and failure, the full range of phase transformations, chemical transformations, and coupled physics behaviors, which can become pronounced for strongly-driven conditions.

As important as the science needed to create accurate material models, the ultimate goal of achieving predictive *simulations* cannot be reached without algorithmic advances that enable transforming successful materials research into robust, efficient, and codable models. Codability would be helped by good interfaces between the host code and material models that facilitate

implementation of material models, particularly when a host code is incompatible with the underlying equations of the model. [For an example, see: *MIG version 0.0: Model interface guidelines: rules to accelerate installation of numerical models into any compliant parent code*, R.M. Brannon, M.K. Wong. SAND96-2000, Sandia National Laboratories, Albuquerque, NM (1996).]

- **Elasticity:**

The elastic response of a pure material is a fundamental property that can be obtained directly from appropriate derivatives of the free energy with respect to change in volume (or applied strain). Higher derivatives correspond to nonlinearities in the stress-strain curve, up to the elastic limit (beyond which permanent inelastic deformation occurs). The forms of the various terms in the elastic free energy — second- and third-order elastic constants, etc. — reflect the inherent symmetry of the material, for example, cubic, monoclinic, or triclinic. Elasticity is generally a sensitive function of thermodynamic state (temperature, stress, material phase), and in the case of certain materials such as polymers strain rate effects can be large. In the case of polycrystalline or composite materials the elastic response must be calculated as an appropriate average over a suitably large representative volume element (RVE) in the material that captures any possible anisotropies due for example to texture. This generally involves either a formal or an empirical homogenization procedure. Knowledge of the tensoral and isotropic elastic response is a key ingredient in specification of an EOS; which, as noted earlier, is fundamental to the reliable description of material response. The ability to predict and utilize the elastic behaviors of metals, organics, piezo- and ferroelectrics, and both random and ordered composite materials is of significant interest.

- **Relevant research needs:** Development of simulation tools to compute the aforementioned properties reliably at elevated temperatures and pressures, for systems large enough that finite-size effects do not dominate; to formulate approaches that account for defects and damage that serve to modify the elastic response from that corresponding to perfect material; and to develop reliable methods for satisfying the preceding needs within the context of structurally complex, highly anisotropic functional materials.

- **Plasticity:**

Among the outstanding challenges in plasticity and inelasticity theory that are of interest to NNSA include plastic behavior of metals subjected to complex load paths and/or high strain rates; the mechanical response of polymers used as encapsulants; the vibration and impact response of foams – in bulk and as encapsulants; and creep of solders and brazes subjected to cyclic thermal loading.

The observed ability for a solid to support deviatoric stresses under compression to high stress is of significant scientific and practical interest. It is important in several applications, including shock, quasi-isentropic, and isothermal compression for equation-of-state measurements.



- **Relevant research needs:** Theoretical developments that build on and unify the variety of relevant experimental observations to develop a basic understanding of this aspect of material response.

Such efforts would be aided by computational methods for estimating high-stress strength properties, including molecular dynamics and dislocation dynamics simulations, developed in tandem with mesoscopic models that capture the essence of the microscopic physics in ways that can be expressed in engineering-scale simulation codes (for example by formulation of sub-grid models for inhomogeneous inelastic deformation). Then the acquired understanding will need to be represented in physics-based models of material strength at high stress and high strain rates and for complicated, non-monotonic load histories.

Under dynamic loading conditions, a brittle material transitions, suddenly, from small strains to large deformations. However, existing methods for treating large deformations corrupt the representation of the constitutive response. Hence, further development is needed of numerical methods that can treat large deformations while tracking Lagrangian state variables.

Verification remains a large need in material modeling. Renewed effort is needed in defining “patch tests” for constitutive models. These should include tests to match the expected single-element responses for idealized plasticity; and, taking a rather broad view of what is included in “constitutive behavior, failure models such as von Mises and Mohr-Coulomb under complicated stress histories.

- **Relevant research needs:** Established and implementation of procedures into frameworks for automated testing of frame- and basis-invariance, thermodynamic consistency, and material stability. Such procedures would be exercised by host codes to ensure that all constitutive models meet these verification tests.

- *Interfacial phenomena:*

Material interfaces often dominate constitutive behavior, whether they be grain boundaries in metals or a liquid-solid interface as for polymer wetting. In some cases, such as metallic or intermetallic alloys, interfaces are “sharp” – only several atomic diameters in extent; whereas in others, such as polymers on a surface, the range of the “interphase” between substrate material, “surface” polymer, and “bulk” polymer can be quite large. In addition, significant stress localization can occur at incommensurate interfaces, and have large effects on mechanical properties and material stability/compatibility. Thus, understanding physical and chemical processes peculiar to interfacial regions in materials is a key component to developing quantifiable predictive capability. Given the importance of interface phenomena and the current limits of predictive modeling of them, interests extends to understanding the behavior nearly any material interface. Example systems of interest include adhesive bonds formed by epoxies or elastomers; adhesion of encapsulating foams to metals or integrated

circuit boards, with prediction of initiation and nature of bond failure; adhesion and slipping between concrete and reinforcing bar.

- **Relevant research needs:** Development of theoretical/computational approaches to capture the underlying phenomenology for the range of materials of interest (including interfaces among metals, insulators, organics/polymers, and liquids, in all combinations), and development of multi-scale approaches to describe the disparity between atomic dimensions and interfacial layer thicknesses.

- ***Homogenized treatment of damage, cracking, and failure:***

While localization and failure behavior entails far more than just constitutive properties (see white papers on *Material Stability* and *Material Failure*), a homogenized treatment of damage can provide a useful local description of the material state approaching or in failure on a spatial scale that cannot be resolved in practical simulations, and is therefore often an important “sub model” that appears explicitly or implicitly within a constitutive formulation. Making damage models predictive requires establishing direct connection of their phenomenology to underlying degradation mechanisms and ensuring the models’ thermodynamic consistency. This is inherently a complex, multiscale problem.

- **Relevant research needs:** Establishment of physically based, quantifiable and measurable connections between atomistic simulations, mesoscopic dislocation dynamics and rate-dependent, anisotropic continuum-scale plasticity models.

Comments similar to those immediately above for damage apply more generally to any material in which localization occurs due to (any kind of) material heterogeneity on a sub-grid spatial scale. Although the details will surely differ from application to application, this type of connection among disparate scales and dominant physical processes, involving one or more homogenizations to yield a constitutive model suitable for macroscale simulation, is needed whether the specific target is a single- or poly-crystal metal, or a complicated, multi-component organic material. However, in order to be reliable and of real predictive power, each of these up-scalings and homogenization steps needs to be performed in the most rigorous way possible, taking care on a case-by-case basis to capture the essential physics or chemistry that drives the observed phenomenology on a given spatio-temporal scale.

Prediction of strength behavior that is dependent on ‘weakest link’ failure requires characterizing and representing variability of strength in a material and sample size effects. Both micro-scale and macro-scale simulations can contribute to determining good representations of strength distributions.

- **Relevant research needs:** Development of stochastic modeling methods to predict strength behavior and provide reliable representations of strength distributions .

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