

A THERMOMECHANICAL MODEL FOR ENERGETIC MATERIALS WITH PHASE TRANSFORMATIONS*

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Abstract. A model is developed to describe energetic materials with phase transformations from solid to liquid to gas with an exothermic chemical reaction. The model uses a phase variable and a reaction progress variable as thermodynamically independent state variables. A configurational force balance is used to derive an evolution law for the phase variable. The evolution equation for the reaction progress variable is posed as a basic law. In various limits the material is a classical elastic solid, a Newtonian viscous liquid, and a compressible gas. The model is examined in relation to classical equilibrium thermodynamics in a quasi-static limit. The model formulation is specialized to simple motions which are analyzed in a companion paper.

Key words. combustion, phase transformations, energetic materials

AMS subject classifications. 74A50, 74F10, 74F25, 74A15, 80A22, 80A25

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1. Introduction. This paper presents a thermodynamically self-consistent model that can describe a material that undergoes phase transitions from solid to liquid to gas with an exothermic chemical reaction. The model development is quite basic and is likely to have wider applications, but the motivation for the study is to describe the behavior and properties of energetic materials such as those used in pyrotechnic materials such as condensed explosives and solid propellants.

Condensed phase energetic materials (EMs) are most typically room temperature organic solids that bind substantial chemical energy in molecular bonds. Upon initiation of chemical reaction between submolecular constituents within the solid, energy is released that is subsequently available to do work or is converted into heat. The advantage of the condensed phase explosive is that the energy per unit volume is approximately a thousand times higher than its premixed, gaseous counterpart.

For the purposes of illustration and to help us develop a conceptual framework, we will consider the energetic material HMX, $[CH_2 - N(NO_2)]_4$, [1] (a solid explosive compound) to be a base-line energetic material. HMX is solid at room temperature and pressure, and when fully chemically decomposed, its gaseous products are simple gases like water vapor, carbon dioxide, and molecular nitrogen. There are thousands of known energetic (explosive) compounds, so our choice of HMX is both practical (because of its wide use) and representative, in that nearly all of the modeling issues considered here apply to similar materials. Fundamental scientific questions surround the phenomena of ignition and release of energy in these materials (EMs) subsequent to impact with a piston or due to a rapid shearing motion. At high impact speeds, (typically on the order of 1000 *m/sec*), simple hydrodynamic models give an adequate

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description for both ignition and transition to detonation. Hydrodynamic models are expressed in the form of the Euler equations for reactive gas dynamics [2], which balance kinetic energy, elastic potential energy, and the chemical energy released by the reaction. By virtue of the speed of collision and the short duration of the ignition event, one can justify the neglect of other types of energy and their transfer. However, at lower impact speeds (typically below 1000 m/sec) one must fully take into account the solid nature of the material. In contrast, models for lower-speed impact must reflect a large number of types of energy and mechanisms by which energy in the condensed phases can be transformed, localized, and dissipated. A successful model must be able to describe three-dimensional stress distributions, heat conduction, phase transformations, and chemical reaction as the material changes from solid to liquid to gas.

Thus, accounting for the change in phase and chemical reaction are essential parts of modeling the ignition of energetic solids. In order to do this in a continuum modeling framework, one must add additional thermodynamic state variables that reflect the internal degrees of freedom that measure the extent of reaction and phase change in the material. Necessarily, one must posit additional balance laws and provide the required constitutive theory to complete a model formulation. One does this by using physical considerations (that may lie in the proposed model's subscale physics) to pose the required additional balance laws. For example, in the case of classical combustion theory (see Williams [3] for a representative discussion of the derivation of the commonly used equations of combustion theory), the additional state variables that correspond to the internal degrees of freedom are the mass fractions of all the independent chemical species. The additional balance laws are literal statements of molecular mass balance for each independent species. Other constitutive forms required to describe the evolution of the mass fraction variable are based on well-known laws of collisional reaction (in the case of gaseous chemical reaction), Fickian diffusion, and so on. Importantly, the added balance laws themselves have an identifiable, *molecular origin* and are directly related to physically unambiguous statements of mass balance. However, while the physics at the molecular subscale is clear, the continuum-scale formulation embraces the added (partial) mass conservation statements as primitive, physical laws that must be given by ansatz.

When modeling the phase changes from solid to liquid to gas it is also important to have a physical understanding of the molecular origins of state variables and constitutive forms that describe the phase change. On the molecular scale, a typical EM solid like HMX is comprised of nitrated hydrocarbon molecules that reside in a highly ordered crystal lattice. Large quantities of energy are released only if there is a chemical reaction between smaller pieces of the molecule, juxtaposed or dislodged by deformation, which subsequently release their chemical energy through elementary exothermic reactions typical of those for the gas-phase chemistry. For example, the liquid phase of HMX is known to be very reactive and short-lived compared to the solid phase; likewise HMX vapor is extremely reactive [4], [5]. The liquid phase is molecularly less well ordered than the solid, with larger average intermolecular distances than the solid. If correlated to the average intermolecular spacing (say), the gas phase is less ordered than the liquid. Thus a state variable (sometimes called an order parameter or a phase field variable) can be introduced to reflect a continuum measure of molecular order of the condensed phases (solid crystalline and liquid phases) and the gaseous phase. We will call the order parameter, or phase field variable, simply the phase variable ϕ and assume that it is normalized in such a way so that $\phi = 0$

corresponds to a solid, $\phi = 1$ a liquid, and $\phi = 2$ a gas.

In this formulation, the precise relationship of noninteger values of a phase variable like ϕ to the molecular subscale structure of the material is somewhat ambiguous in contrast to the unambiguous meaning of reactant mass fractions in combustion theory. In a more advanced theory it is anticipated that ϕ will be assigned to specific molecular coordinates. Advances in molecular dynamics of condensed phase systems do promise to eventually provide a more substantial basis for physical assignment of the phase variables, possibly based on the average molecular spacing (say) or other molecularly based kinematic variables [6], [7].

Despite possible ambiguity in its precise physical interpretation, if a phase variable is to be used in a model to represent an independent degree of freedom, it should be constrained by standard principles found in the theory of continuum mechanics. In the regions where the phase is pure (i.e., $\phi = 0, 1,$ or 2) the material properties and the constitutive relations must describe the pure material with the properties of that phase. We require that the formulation has a sense in which it is thermodynamically and tensorially consistent. This allows further developments in a rational and systematic manner in three dimensions. We consider a simplified model of an EM (HMX, say) which we suppose has three relevant phases: a solid phase, a liquid phase, and a gas phase. We assume that the path from solid to gas goes through the successive phase transformations, solid \rightarrow liquid \rightarrow gas. Phase boundaries are to be represented by (typically thin) regions across which the value of the phase variable changes from one constant to another. Also, we will use a single (lumped chemistry) progress variable λ , to describe the extent of exothermic chemical reaction λ with value $\lambda = 0$ when no reaction has occurred and $\lambda = 1$ when the reaction is completed. The model allows chemical reactions in any phase.

A key aspect of the model is explicit partitioning of the energy associated with specific internal (thermal) energy, chemical reaction energy, elastic potential (deformational) energy, and energies associated with phase change, such as the enthalpies associated with melting of the solid and evaporation of the liquid, and potential energies stored at phase boundaries. The partitioning of the energy is represented by a decomposition of the Helmholtz free energy ψ into the various parts associated with the energies listed above, such that $\psi = \psi_{thermal} + \psi_{elastic} + \psi_{reaction} + \psi_{phase} + \psi_{grad(phase)}$. The constitutive forms used for $\psi_{thermal}$ and $\psi_{elastic}$ are found in discussions of thermo-elastic materials. The constitutive forms for ψ_{phase} and $\psi_{grad(phase)}$ contain the energies of phase change and energies stored near phase change interfaces. The constitutive form for $\psi_{reaction}$ can be found in a discussion of premixed combustible materials. The free energies and other constitutive variables are allowed to depend on both the phase variable ϕ and the reaction progress variable λ as well as the temperature T and the deformation gradient \mathbf{F} and the gradient of ϕ , $\vec{\nabla}\phi$. The governing equations are formulated by statements of conservation of mass, momentum, energy, evolution equations for the change in phase, and the progress of the chemical reaction.

The treatment we use to describe the evolution of the phase variable follows classical treatments that arose in the discussion of solidification (for example, see [8]) but specifically follows a consistent formulation pioneered by Gurtin [9]. Gurtin has argued for a separate continuum balance of configurational forces acting near the boundaries separating pure phases in the volumetric bulk. The arguments for including these additional forces may be justified by consideration of short-range van der Waals forces that typically are generated near phase boundaries due to local changes in the intermolecular distances. The arguments for such configurational forces

are similar to those used to explain classical surface tension forces. The hypothesis is that if the configurational forces act in the vicinity of the boundary near the change in phase and in the bulk, they can be in balance, and if so, they must not effect the overall (conventional) momentum balances. Hence the force balance is posited as a basic law. However, with the postulate of a balance of configurational forces comes the consequence that those forces do work. The working rate is accounted for explicitly in the overall energy balance.

The second law of thermodynamics (the Clausius–Duhem inequality) restricts the form of the constitutive theory so that the rate processes are dissipative and entropy is increasing. An important outcome of these arguments is the derivation of an evolution equation for the phase variable ϕ that is essentially a Ginzburg–Landau equation with additional forcing terms. The evolution equation for ϕ is a time-dependent, reaction–diffusion equation which is amply capable of describing the pattern formation associated with phase transformation. The richness of the resulting theory becomes evident in the energy equation. Due to the decomposition of the Helmholtz free energy, the energy equation contains contributions from all the different terms in the partition and reflects the fact that in the energetic material, energy is converted and distributed to many different forms such as elastic, kinetic, internal, and phase gradient energy (stored in interfaces).

In the sections that follow, the development of the model is given, based on the continuum-thermodynamic formulation described above. In section 2 we review the continuum-thermodynamic formulation consistent with conventional combustion theory [3], [10], [11], [12] that specifically includes a reaction progress variable. A (nonstandard) presentation of the Helmholtz energy decomposition is given and the attendant standard arguments for restrictions placed by the second law are given. In section 3 we present a model for a material that changes from solid to liquid to gas and present a Helmholtz free-energy decomposition that is suitable to describe such a material, subject to second law restrictions. In section 4, the combined model for an EM (with both phase change and chemical reaction) is then presented. In section 5 we discuss various limiting cases of the model. We discuss the relationship of the model to classical quasi-static thermodynamics and illustrate examples based on fits to HMX properties to illustrate the dynamics of a phase change that would be calculated in the classical theory. Section 6 presents special formulations of the model equation for three important simple motions. These cases are (i) constant volume evolution (which is a generalization of the classical constant volume explosion formulation found in combustion theory), (ii) one-dimensional, time-dependent longitudinal compression (expansion), and (iii) one-dimensional, time-dependent shear motion. The solution of the equations for these three important cases for an HMX-like material is the subject of the companion paper [13].

In what follows, a “c” subscript denotes a condensed phase, either solid or liquid, an “f” subscript denotes fluid, either liquid or gas, an “s” subscript denotes solid, an “l” subscript denotes liquid, and a “g” subscript denotes gas. The spelled out subscripts “solid,” “liquid,” and “gas” refer to constant values for that pure phase. The notation is kept as simple as possible in an attempt make the paper easier to read. Bold face quantities can either be vectors or tensors. If obvious, the constant arguments during differentiation are dropped. Our notation is standard, insofar as is possible and follows a well-known text like Bowen [12].

1.1. Kinematics. Let the Eulerian (spatial) coordinates of position in the lab-frame be given by \mathbf{x} and the Lagrangian (material) coordinates (or particle coordi-

nates) be given by \mathbf{X} . For simplicity we will assume that \mathbf{X} represent the initial position of material particles. Then the mapping of the deformations that define the particle trajectory paths is given by

$$(1.1) \quad \mathbf{x} = \mathbf{x}(\mathbf{X}, t).$$

The deformation gradient \mathbf{F} is defined by the derivative

$$(1.2) \quad \mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}},$$

and the velocity of particles \mathbf{v} is defined by the time derivative of the particle trajectories $\mathbf{v} = (\partial \mathbf{x} / \partial t)_{\mathbf{X}}$. The velocity gradient is $\mathbf{L} = \vec{\nabla} \mathbf{v}$. Let the dot notation, $\dot{}$, refer to the material derivative. A standard identity that can be verified by the previous definitions and the chain rule gives the material (particle-fixed) time derivative of the deformation gradient as $\dot{\mathbf{F}} = \mathbf{L}\mathbf{F}$. A statement of conservation of mass in the material frame is that the ratio of the instantaneous density, ρ , of the particle to a reference (ambient) density of the solid, ρ_0 , is equal to the determinant of the deformation gradient

$$(1.3) \quad \det(\mathbf{F}) = \frac{\rho_0}{\rho}.$$

2. Review of the thermomechanics for a simple model of a reactive flow. The standard combustion model, for a premixed mixture that can explode or burn, can be derived from a simple mixture theory; see references [3], [10], [11], [12]. The combined model that we introduce later incorporates the features of the standard combustion model, so we review its derivation. Importantly, the reaction progress variable λ represents a product mass flux. Hence λ is treated differently from the phase variable ϕ , which is introduced later to describe the change in phase from solid to liquid to gas.

For the purpose of discussion, one assumes that there are only two distinct species, fuel and product (say). The corresponding chemical reaction is written as $F \rightarrow P + Q_{hc}$ (*heat*). All physical properties of the two species such as the molecular weights, specific heats, conductivities, etc. are assumed to be identical, save the heats of formation, the weighted difference of which is the heat of combustion.

We start with the balance laws for conservation of mass, linear momentum (without body forces), and energy:

$$(2.1) \quad \dot{\rho} + \rho(\vec{\nabla} \cdot \mathbf{v}) = 0,$$

$$(2.2) \quad \rho \dot{\mathbf{v}} = \vec{\nabla} \cdot \boldsymbol{\sigma} + \rho \mathbf{f},$$

$$(2.3) \quad \rho \dot{e} = \boldsymbol{\sigma} : \vec{\nabla} \mathbf{v} - \vec{\nabla} \cdot \mathbf{q} + \rho r.$$

In the energy equation, r is a volumetric energy production term that typically represents radiation or volumetric heating (or cooling) in combustion theory. The body force is given by \mathbf{f} . In addition, we invoke a primitive evolution law for the reaction progress variable λ :

$$(2.4) \quad \rho \dot{\lambda} = \vec{\nabla} \cdot \mathbf{s} + \rho \Omega.$$

The vector \mathbf{s} is the flux of mass of reacted species per unit area per unit time and $\rho \Omega$ is the instantaneous rate of creation of mass of the reacted species per unit volume.

Then λ is recognized as the mass fraction of the product species. Further, by direct correspondence with the standard combustion equations, one can interpret $\mathbf{s} = \rho\lambda\mathbf{V}$, where \mathbf{V} is the diffusion velocity of the product species (say), and where $\rho\lambda$ is the partial density fraction of the same product.

To these basic laws we add the second law of thermodynamics, the Clausius–Duhem inequality

$$(2.5) \quad \rho\dot{\eta} \geq -\vec{\nabla} \cdot \left(\frac{\mathbf{q}}{T} \right) + \vec{\nabla} \cdot \left(\frac{Q_{hc}\mathbf{s}}{T} \right) + \frac{\rho r}{T},$$

where Q_{hc} , the heat of combustion, is the exothermic energy release per unit mass and the term $\vec{\nabla} \cdot (Q_{hc}\mathbf{s}/T)$ represents the gradient of the entropy flux associated with the chemical reaction.

2.1. Constitutive forms and restrictions. Next consider the classical forms and assumptions that lead to the combustion equations of premixed materials found in texts like [3] or [10]. The formulation uses the Helmholtz free energy, which is defined in terms of the internal energy and entropy as $\psi = e - T\eta$. We start with the assumption that ψ is specified by

$$(2.6) \quad \psi = \psi(\mathbf{F}, T, \lambda),$$

and we assume similar dependencies for e , η , and all other thermodynamic variables. Next we consider the implication of the entropy inequality and deduce various restriction imposed by it on the constitutive formulation.

If we use the definition of the Helmholtz free energy to get an expression for the entropy, as $\eta = (e - \psi)/T$, and take the material derivative, we obtain $\dot{\eta} = (\dot{e} - \dot{\psi} - \eta\dot{T})/T$. In particular the derivative $\dot{\psi}$ appears and, using the form assumed above, it is calculated as

$$(2.7) \quad \dot{\psi} = \frac{\partial\psi}{\partial\mathbf{F}}\mathbf{F}^T : \vec{\nabla}\mathbf{v} + \frac{\partial\psi}{\partial T}\dot{T} + \frac{\partial\psi}{\partial\lambda}\dot{\lambda}.$$

Using this expression for $\dot{\psi}$ and using the energy equation to replace \dot{e} in the entropy inequality leads to an intermediate result:

$$(2.8) \quad \left(\boldsymbol{\sigma} - \rho \frac{\partial\psi}{\partial\mathbf{F}}\mathbf{F}^T \right) : \vec{\nabla}\mathbf{v} - \rho \left(\eta + \frac{\partial\psi}{\partial T} \right) \dot{T} - (\mathbf{q} - Q_{hc}\mathbf{s}) \cdot \frac{\vec{\nabla}T}{T} - \rho \frac{\partial\psi}{\partial\lambda} \dot{\lambda} - Q_{hc} \vec{\nabla} \cdot \mathbf{s} \geq 0.$$

We restrict our choice in constitutive theory to forms that will automatically satisfy this dissipation inequality as the physical processes in the material range over all admissible deformations and temperature fields. For example, since $\vec{\nabla}\mathbf{v}$ can be regarded as an independent field, then in the standard way we restrict the form of the stress tensor such that

$$(2.9) \quad \boldsymbol{\sigma} = \rho \frac{\partial\psi}{\partial\mathbf{F}}\mathbf{F}^T + \boldsymbol{\sigma}^{diss},$$

where the dissipative stress $\boldsymbol{\sigma}^{diss}$ satisfies $\boldsymbol{\sigma}^{diss} : \vec{\nabla}\mathbf{v} \geq 0$. This last requirement is clearly satisfied by the classical choice for a viscous fluid,

$$(2.10) \quad \boldsymbol{\sigma}^{diss} = \nu_g (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_g \mathbf{D},$$

where $\mathbf{D} = (\vec{\nabla}\mathbf{v} + \vec{\nabla}\mathbf{v}^T)/2$ and ν_g, μ_g are positive and are identified as the gas-phase bulk and shear viscosities. The assumed form of the stress becomes

$$(2.11) \quad \boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \nu_g (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_g \mathbf{D}.$$

In a similar fashion, since \dot{T} is independent, we require that the Helmholtz free energy must satisfy Gibbs' relation

$$(2.12) \quad \frac{\partial \psi}{\partial T} = -\eta.$$

The entropy inequality is now satisfied if the following reduced inequality is satisfied:

$$(2.13) \quad -(\mathbf{q} - Q_{hc}\mathbf{s}) \cdot \frac{\vec{\nabla}T}{T} - \rho \frac{\partial \psi}{\partial \lambda} \dot{\lambda} - Q_{hc} \vec{\nabla} \cdot \mathbf{s} \geq 0.$$

If we assume that the change in the Helmholtz free energy with respect to the progress variable is related to the heat of combustion (which also can be verified and put into direct correspondence with forms derived in mixture theory of reacting gases; see [10], [11], [12]),

$$(2.14) \quad \frac{\partial \psi}{\partial \lambda} = -Q_{hc},$$

and we use the evolution equation for the progress variable $\rho \dot{\lambda} - \vec{\nabla} \cdot \mathbf{s} = \rho \Omega$, then the reduced inequality can be recast as

$$(2.15) \quad -(\mathbf{q} - Q_{hc}\mathbf{s}) \cdot \frac{\vec{\nabla}T}{T} + \rho Q_{hc} \Omega \geq 0.$$

Finally we make the choice that the energy flux vector is the sum of a Fourier heat conductive flux and an energy flux associated with the diffusion of the product species,

$$(2.16) \quad \mathbf{q} = -k \vec{\nabla}T + Q_{hc} \mathbf{s},$$

and we require that for an exothermic chemical reaction with $Q_{hc} > 0$, the reaction rate must be positive with $\Omega \geq 0$. With these restrictions the second law is automatically satisfied. Recall that \mathbf{s} represented the mass flux vector of the product species, $\mathbf{s} = \rho \lambda \mathbf{V}$, where \mathbf{V} is the diffusion velocity of that species. Without further restriction we can make a standard assumption that the diffusion velocity is related to the gradient of the species concentration through a Fick's law relation,

$$(2.17) \quad \mathbf{s} = \rho \lambda \mathbf{V} = d \vec{\nabla} \lambda,$$

where $d \geq 0$ is a diffusion coefficient.

2.2. Temperature form of the energy equation. We present the temperature form of the energy equation in terms of a specification of the Helmholtz free energy, in order to set the stage for later discussions. We use the definition of the specific internal energy in terms of the temperature and the entropy, $e = \psi + T\eta$, to obtain $\dot{e} = \dot{\psi} + \eta \dot{T} + T\dot{\eta}$. Next we use the form of the Helmholtz energy $\psi(\mathbf{F}, T, \lambda)$ and Gibbs' relation $\eta = -\partial\psi/\partial T$ to generate expressions for $\dot{\psi}$ and $\dot{\eta}$ as

$$(2.18) \quad \dot{e} = \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v} + \frac{\partial \psi}{\partial T} \dot{T}, \quad \dot{\eta} = -\frac{\partial^2 \psi}{\partial T \partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v} - \frac{\partial^2 \psi}{\partial T^2} \dot{T}.$$

We then insert these expression into (2.3) and make some further simplifications. A collection of terms appears that is associated with the stress-related dissipation

$$\left(\boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T \right) : \vec{\nabla} \mathbf{v} = \boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v}.$$

Using the classical definition of the specific heat at constant deformation (volume),

$$(2.19) \quad c_v \equiv T \left. \frac{\partial \eta}{\partial T} \right|_{\mathbf{F}} = -T \left. \left(\frac{\partial^2 \psi}{\partial T^2} \right) \right|_{\mathbf{F}},$$

the energy equation can be rewritten as follows:

$$(2.20) \quad \rho c_v \dot{T} = -\vec{\nabla} \cdot \mathbf{q} + \boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v} + \rho T \frac{\partial^2 \psi}{\partial T \partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v}.$$

The term $\rho T (\partial^2 \psi / \partial T \partial \mathbf{F}) \mathbf{F}^T : \vec{\nabla} \mathbf{v}$ is a stress work term classically associated with thermal stresses. As we will see below in the case of gaseous combustion for ideal gases, this term is proportional to the pressure work term $-p (\vec{\nabla} \cdot \mathbf{v})$, where $p = \rho R_g T$ and R_g is the ideal gas constant.

2.2.1. The form of the Helmholtz free energy from classical combustion theory. To complete the classical formulation for premixed combustion, one must specify the form of the Helmholtz free energy. The forms can be extracted from the correct forms found in the binary mixture theory of premixed gases; see [12], [3], [10], [11]. Let $\mathbf{B} = \mathbf{F} \mathbf{F}^T$ be the left Cauchy–Green tensor and let $III_{\mathbf{B}} = (\rho_0 / \rho)^2$ be the third invariant of \mathbf{B} . Then the form of the Helmholtz free energy for a thermally ideal material, with the additional term required for the change in enthalpy associated with combustion, is comprised of three parts: a thermal energy density $\psi_1 = c_v [(T - T_0) - T \ln(T/T_0)]$, a strain energy density associated with the temperature (that defines the pressure in terms of the density and temperature) $\psi_2 = -1/2 R_g T \ln(III_{\mathbf{B}})$, and the chemical enthalpy $\psi_3 = -Q_{hc} \lambda$. Thus the total free energy $\psi = \psi_1 + \psi_2 + \psi_3$ is

$$(2.21) \quad \psi = c_v (T - T_0) - c_v T \ln \left(\frac{T}{T_0} \right) - \frac{1}{2} R_g T \ln(III_{\mathbf{B}}) - Q_{hc} \lambda.$$

It follows that the elastic part of the stress can be computed from this form of the free energy and identifies the classical thermodynamic pressure p . In particular, we have that $\rho (\partial \psi / \partial \mathbf{F}) \mathbf{F}^T = 2\rho (\partial \psi / \partial \mathbf{B}) \mathbf{B} = -\rho R_g T \mathbf{I} \equiv -p \mathbf{I}$, which leads to the identification of the pressure p by the ideal gas law, $p = \rho R_g T$. Also, the thermal stress work term is rewritten $\rho (\partial \psi / \partial \mathbf{F}) \mathbf{F}^T : \vec{\nabla} \mathbf{v} = -p (\vec{\nabla} \cdot \mathbf{v})$. The corresponding form of the entropy and the internal energy (obtained from the definition of the Helmholtz free energy and Gibbs' relation) are given by

$$(2.22) \quad e = c_v (T - T_0) - Q_{hc} \lambda, \quad \eta = c_v \ln \left(\frac{T}{T_0} \right) + \frac{R}{2} \ln(III_{\mathbf{B}}).$$

2.3. Summary of the governing equations for a premixed reactive fluid.

Here we summarize the results of the last section that reduce to the classical form of the combustion equations for a premixed combustible fluid. These equations incorporate the various restrictions and constitutive forms that we assumed and are suitable for solving initial value problems ordinarily associated with the theory of premixed

combustion. The entropy (dissipation) inequality is not included in our list since it is automatically satisfied by construction of the model. The equations for ρ , \mathbf{v} , T , and λ are

$$(2.23) \quad \dot{\rho} + \rho \vec{\nabla} \cdot \mathbf{v} = 0,$$

$$(2.24) \quad \rho \dot{\mathbf{v}} = \vec{\nabla} \cdot \boldsymbol{\sigma} + \rho \mathbf{f},$$

$$(2.25) \quad \rho c_v \dot{T} = \vec{\nabla} \cdot (k \vec{\nabla} T) + \boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v} - p(\vec{\nabla} \cdot \mathbf{v}) + \rho Q_{hc} \Omega,$$

$$(2.26) \quad \rho \dot{\lambda} = \vec{\nabla} \cdot (d \vec{\nabla} \lambda) + \rho \Omega,$$

with the constitutive relation for the stress given by $\boldsymbol{\sigma} = -\rho R_g T \mathbf{I} + \nu_g \vec{\nabla} \cdot \mathbf{v} \mathbf{I} + 2\mu_g \mathbf{D}$, with $\boldsymbol{\sigma}^{diss} = \nu_g \vec{\nabla} \cdot \mathbf{v} \mathbf{I} + 2\mu_g \mathbf{D}$, and with $\mathbf{D} = (\vec{\nabla} \mathbf{v} + \vec{\nabla} \mathbf{v}^T)/2$.

3. Thermomechanics of a model of a material with phase changes from solid to liquid to gas. Here we develop a model for a material that can undergo a phase change from solid to liquid to gas in preparation for the development of the combined model, which includes chemical reaction and exothermic energy release. The important difference in the development in this section from that in section 2 is the introduction of a phase variable that is used to describe and delineate the separate phases. In order to describe the phase transitions we introduce the (normalized) variable ϕ so that $\phi = 0$ corresponds to the solid phase, $\phi = 1$ to the liquid phase, and $\phi = 2$ to the vapor phase. In its pure phases, solid, liquid, and gas, the material is prescribed by classical models for that pure phase, i.e., a compressible elastic solid and a compressible Newtonian liquid and gas.

A consistent thermodynamic formulation for the model is developed through an extension of a formulation proposed by Gurtin [9]. Energy expended by the system during a phase change is associated with configurational forces of two types—a configurational stress that acts at or near the boundaries between phases which is balanced by a configurational force distributed in the bulk. The power expenditure of these forces must be accounted for in the energy balance. If one assumes that the configurational forces in the material are balanced separately (this is a posited balance), then the evolution of the phase field ϕ is constrained by the entropy inequality to be dissipative and further considerations lead to the derivation of an evolution law for ϕ . This is in contrast to the formulation of the last section, which considered the evolution law for the progress variable λ as posited. Presumably (and we have considered this in some detail that is not presented here), an alternative to deriving the equation for ϕ is to pose an evolution equation as fundamental and then derive the consequence of local balance for the configurational forces. Either way, one comes to similar physical conclusions. The consequences of this choice, in absence of better, physically based arguments, need to be judged against the forms of the equations that result that allow us to solve interesting initial value problems.

The starting point is the form of the general laws. The differential form of the general law for mass, (2.1), and momentum, (2.2), are unchanged from the previous section. We turn to the more unfamiliar considerations of the force balance law associated with the phase change and corresponding changes in the energy balance next.

3.0.1. Force balances associated with the change in phase. Associated with the evolution of the phase variable ϕ , we introduce a balance of configurational stress $\boldsymbol{\xi}$, a configurational internal force density π_ϕ . The integral form of the balance

law for a body in region \mathcal{B} with boundary $\partial\mathcal{B}$ is

$$(3.1) \quad \int_{\partial\mathcal{B}} \boldsymbol{\xi} \cdot \mathbf{n} \, dA + \int_{\mathcal{B}} (\pi_\phi) \, dV = 0,$$

and with the use of the divergence theorem, the corresponding differential form of the balance law is

$$(3.2) \quad \vec{\nabla} \cdot \boldsymbol{\xi} + \pi_\phi = 0.$$

3.0.2. Rate of work. The rate of work expended on \mathcal{B} is due to the external forces acting on the surface and within the volume of \mathcal{B} . Gurtin [9] shows that the correct form for the rate of work due to all stresses is

$$(3.3) \quad \mathcal{W} \equiv \int_{\partial\mathcal{B}} (\boldsymbol{\sigma} \mathbf{n} \cdot \mathbf{v} + \boldsymbol{\xi} \cdot \dot{\phi} \mathbf{n}) \, dA + \int_{\mathcal{B}} \mathbf{b} \cdot \mathbf{v} \, dV.$$

The integral form of the energy balance can be written in the standard way as the material derivative of the total energy (internal and kinetic) equated to the rate of work minus the energy flux out of the body plus the rate of heating by any other source; thus

$$(3.4) \quad \frac{D}{Dt} \int_{\mathcal{B}} \rho \left(e + \frac{1}{2} |\mathbf{v}|^2 \right) \, dV = \mathcal{W} - \int_{\partial\mathcal{B}} \mathbf{q} \cdot \mathbf{n} \, dA + \int_{\mathcal{B}} \rho r \, dV.$$

To obtain the differential form we convert the surface integrals into volume integrals and use the divergence theorem. The resulting integral must hold everywhere for all subvolumes, so the resulting integrand is set to zero, which leads to an intermediate differential form (not shown). We then use the momentum equation and take its dot product with the velocity \mathbf{v} to get the standard work-energy statement on a material path and subtract that result from the above-mentioned intermediate form to get the following form of the energy equation:

$$(3.5) \quad \rho \dot{e} = -\vec{\nabla} \cdot \mathbf{q} + \boldsymbol{\sigma} : \vec{\nabla} \mathbf{v} + \boldsymbol{\xi} \cdot \vec{\nabla}(\dot{\phi}) - \pi_\phi \dot{\phi} + \rho r.$$

The main difference from the classical form is the appearance of the two work terms $\boldsymbol{\xi} \cdot \vec{\nabla}(\dot{\phi})$ and $-\pi_\phi \dot{\phi}$ that derive from the configurational forces. For upcoming considerations of the entropy inequality, it is useful to use identities (which can be verified easily in Cartesian index notation) to rewrite the term $\boldsymbol{\xi} \cdot \vec{\nabla}(\dot{\phi})$ as

$$(3.6) \quad \boldsymbol{\xi} \cdot \vec{\nabla}(\dot{\phi}) = \overline{\vec{\nabla} \dot{\phi}} \cdot \boldsymbol{\xi} + \vec{\nabla} \dot{\phi} \otimes \boldsymbol{\xi} : \mathbf{L},$$

so that the revised energy equation reads as

$$(3.7) \quad \rho \dot{e} = -\vec{\nabla} \cdot \mathbf{q} + \boldsymbol{\sigma} : \vec{\nabla} \mathbf{v} + \overline{\vec{\nabla} \dot{\phi}} \cdot \boldsymbol{\xi} + \vec{\nabla} \dot{\phi} \otimes \boldsymbol{\xi} : \vec{\nabla} \mathbf{v} - \pi_\phi \dot{\phi} + \rho r.$$

3.0.3. The entropy inequality. Finally, to these basic laws we must add the second law of thermodynamics, the Clausius–Duhem inequality

$$(3.8) \quad \rho \dot{\eta} \geq -\vec{\nabla} \cdot \left(\frac{\mathbf{q}}{T} \right) + \frac{\rho r}{T}.$$

Note that since ϕ is not assumed to be related to a partial mass density of material, there is no entropy flux term like $\vec{\nabla} \cdot (Q_{hc} \mathbf{s}/T)$ that appears in the combustion-based entropy inequality (2.5). Equation (3.8) is the classical (inert) form of the entropy inequality.

3.0.4. Constitutive forms and restrictions from the entropy inequality.

We restrict our attention to a general class of constitutive equations and start with a very general assumption that the free energy density ψ , the Cauchy stress $\boldsymbol{\sigma}$, the configurational stresses $\boldsymbol{\xi}$, and the internal configurational force π_ϕ , the entropy density η , and the heat flux \mathbf{q} at any point (\mathbf{x}, t) are dependent on the deformation gradient \mathbf{F} , the temperature T , the phase field ϕ , the gradients $\vec{\nabla}T$, $\vec{\nabla}\phi$, and the velocity gradient \mathbf{L} , such that we can write

$$(3.9) \quad \psi = \psi(\mathbf{F}, T, \phi, \vec{\nabla}T, \vec{\nabla}\phi, \mathbf{L}).$$

We assume that $\boldsymbol{\sigma}$, $\boldsymbol{\xi}$, π_ϕ , η , and \mathbf{q} all depend on the same argument list, $(\mathbf{F}, T, \phi, \vec{\nabla}T, \vec{\nabla}\phi, \mathbf{L})$. We use the definition of the Helmholtz free energy to get an expression for the entropy, $\eta = (e - \psi)/T$, take the material derivative, and then use the energy equation to replace \dot{e} and use the chain rule to replace $\dot{\psi}$. These substitutions into the entropy inequality lead to the intermediate result:

$$(3.10) \quad \left(\boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \vec{\nabla}\phi \otimes \boldsymbol{\xi} \right) : \vec{\nabla}\mathbf{v} - \rho \left(\eta + \frac{\partial \psi}{\partial T} \right) \dot{T} - \left(\pi_\phi + \rho \frac{\partial \psi}{\partial \phi} \right) \dot{\phi} \\ - \rho \frac{\partial \psi}{\partial \vec{\nabla}T} \cdot \dot{\vec{\nabla}T} - \left(\rho \frac{\partial \psi}{\partial \vec{\nabla}\phi} - \boldsymbol{\xi} \right) \cdot \dot{\vec{\nabla}\phi} - \rho \left(\frac{\partial \psi}{\partial \mathbf{L}} \right) : \dot{\mathbf{L}} - \mathbf{q} \cdot \frac{\vec{\nabla}T}{T} \geq 0.$$

Again we restrict our choice of constitutive forms to those that automatically satisfy this dissipation inequality as the physical process in the material ranges over all admissible deformations and temperature and phase fields. We restrict the form of the stress tensor such that

$$(3.11) \quad \boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T - \vec{\nabla}\phi \otimes \boldsymbol{\xi} + \boldsymbol{\sigma}^{diss},$$

where again $\boldsymbol{\sigma}^{diss}$ must be chosen to satisfy $\boldsymbol{\sigma}^{diss} : \vec{\nabla}\mathbf{v} \geq 0$. Later we will take $\boldsymbol{\sigma}^{diss}$ to be given by (2.10), where the shear and bulk viscosities are taken to be functions of the phase field variable ϕ . We require that Gibbs' relation be satisfied and that the configurational force $\boldsymbol{\xi}$ be defined by the derivative of the Helmholtz free energy with respect to the gradient of ϕ such that

$$(3.12) \quad \eta = -\frac{\partial \psi}{\partial T} \quad \text{and} \quad \boldsymbol{\xi} = \rho \frac{\partial \psi}{\partial \vec{\nabla}\phi}.$$

We also assume that the Helmholtz free energy is independent of $\mathbf{L} = \vec{\nabla}\mathbf{v}$ and the temperature gradient $\vec{\nabla}T$ so that

$$(3.13) \quad \frac{\partial \psi}{\partial \mathbf{L}} = 0 \quad \text{and} \quad \frac{\partial \psi}{\partial \vec{\nabla}T} = 0$$

hold. We also suppose that the energy flux vector is described by a Fourier heat conduction law, $\mathbf{q} = -k\vec{\nabla}T$, and insist that k is a positive constant that can be a function of the temperature and the order parameter, i.e., $k(\phi, T) \geq 0$. Then the reduced dissipation inequality now has the form

$$(3.14) \quad - \left(\pi_\phi + \rho \frac{\partial \psi}{\partial \phi} \right) \dot{\phi} \geq 0.$$

The final form of the reduced dissipation inequality is satisfied if we require that the phase changes be dissipative and if we allow π_ϕ to take the form

$$(3.15) \quad - \left(\pi_\phi + \rho \frac{\partial \psi}{\partial \phi} \right) = B \dot{\phi},$$

where $B \geq 0$. Equation (3.15) is an evolution equation for the phase variable ϕ . Note that the configurational force balance (3.2) defines $\pi_\phi = -\vec{\nabla} \cdot \boldsymbol{\xi}$ and with the configurational force identified by $\boldsymbol{\xi} = \rho(\partial\psi/\partial\vec{\nabla}\phi)$ leads to $\pi_\phi = -\vec{\nabla} \cdot (\rho\partial\psi/\partial\vec{\nabla}\phi)$. Thus (3.15) can be re-expressed as

$$(3.16) \quad B \dot{\phi} = \vec{\nabla} \cdot \left(\rho \frac{\partial \psi}{\partial \vec{\nabla} \phi} \right) - \rho \frac{\partial \psi}{\partial \phi}.$$

Given appropriate forms for ψ (such as quadratic dependence of ψ on $\vec{\nabla}\phi$), (3.16) is recognized as an advection, reaction-diffusion equation, which, given an assumed form for ψ , can generate a Ginzburg–Landau equation. The coefficient B^{-1} is then recognized as a kinetic rate constant for the phase transformation.

3.1. Temperature form of the energy equation. In order to show the coupling between the thermal (temperature) field, the stress field, and the phase field, we present an alternative form of the energy equation. Starting with the energy balance (3.7) we use the definition of the specific internal energy in terms of the temperature and the entropy, $e = \psi + T\eta$, to obtain $\dot{e} = \dot{\psi} + \eta\dot{T} + T\dot{\eta}$. Next we use the form of the Helmholtz energy $\psi(\phi, T, \vec{\nabla}\phi, \mathbf{F})$ and Gibbs' relation, $\eta = -\partial\psi/\partial T$, to generate expressions for $\dot{\psi}$ and $\dot{\eta}$:

$$(3.17) \quad \dot{\psi} = \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v} + \frac{\partial \psi}{\partial T} \dot{T} + \frac{\partial \psi}{\partial \phi} \dot{\phi} + \frac{\partial \psi}{\partial \vec{\nabla} \phi} \cdot \dot{\vec{\nabla}} \phi,$$

$$(3.18) \quad \dot{\eta} = -\frac{\partial^2 \psi}{\partial T \partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v} - \frac{\partial^2 \psi}{\partial T^2} \dot{T} - \frac{\partial^2 \psi}{\partial T \partial \phi} \dot{\phi} - \frac{\partial^2 \psi}{\partial T \partial \vec{\nabla} \phi} \cdot \dot{\vec{\nabla}} \phi.$$

We then insert these expressions into (3.7) and make some further simplifications. In the resulting collection, terms proportional to \dot{T} drop out because of Gibb's relation $\eta = -\partial\psi/\partial T$. Likewise, terms proportional to $\dot{\vec{\nabla}}\phi$ drop out because of the relation for the configurational stress $\boldsymbol{\xi} = \rho(\partial\psi/\partial\vec{\nabla}\phi)$. A collection of terms appear that is associated with the stress-related dissipation

$$\left(\boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \vec{\nabla} \phi \otimes \boldsymbol{\xi} \right) : \vec{\nabla} \mathbf{v} = \boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v},$$

and a collection of terms associated with the dissipation induced by the phase transformation appears,

$$- \left(\rho \frac{\partial \psi}{\partial \phi} + \pi_\phi \right) \dot{\phi} = B \dot{\phi}^2.$$

Using the classical definition of the specific heat at constant deformation (volume), $c_v \equiv T(\partial\eta/\partial T)_{\mathbf{F}} = -T(\partial^2\psi/\partial T^2)_{\mathbf{F}}$, the energy equation can be rewritten as follows:

$$(3.19) \quad \rho c_v \dot{T} = -\vec{\nabla} \cdot \mathbf{q} + \boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v} + B \dot{\phi}^2 + \rho T \frac{\partial^2 \psi}{\partial T \partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v} \\ + \rho T \frac{\partial^2 \psi}{\partial T \partial \phi} \dot{\phi} + \rho T \frac{\partial^2 \psi}{\partial T \partial \vec{\nabla} \phi} \cdot \dot{\vec{\nabla}} \phi + \rho r.$$

Some straightforward physical interpretations can be made for the various terms. The term $\boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v}$ is the viscous dissipation associated with the stress. The term $B\dot{\phi}^2$ is a dissipation associated with the phase change. The term $\rho T(\partial^2 \psi / \partial T \partial \phi) \dot{\phi}$ is an energy source term that is associated with enthalpic changes in phase (similar to those associated with the heat of combustion for reacting flows). The term $\rho T(\partial^2 \psi / \partial T \partial \mathbf{F}) \mathbf{F}^T : \vec{\nabla} \mathbf{v}$ is (again) a stress work term classically associated with thermal stresses. Similarly, the term $\rho T(\partial^2 \psi / \partial T \partial \vec{\nabla} \phi) \cdot \vec{\nabla} \dot{\phi}$ is a thermal stress work term associated with the configurational stress of the phase change.

3.1.1. Invariance requirements and isotropy. Most energetic solids are encountered as fine-grained polycrystalline aggregates and are often modeled with conventional isotropic liquid and gaseous forms. We now restrict our attention to isotropic materials, and we ignore possible anisotropic properties in this model. As is conventional we require that the material response is invariant under superposed rigid changes of observer. It can be shown in a standard way that the constitutive dependence on the deformation gradient \mathbf{F} can be replaced by the left Cauchy–Green tensor $\mathbf{B} = \mathbf{F}\mathbf{F}^T$ and that the dependence on the velocity gradient is replaced by the symmetric stretching tensor $\mathbf{D} = (\mathbf{L} + \mathbf{L}^T)/2$. Furthermore, isotropy requires that the dependence on \mathbf{B} appears through its principal scalar invariants $I_{\mathbf{B}} = \text{trace} \mathbf{B}$, $II_{\mathbf{B}} = \frac{1}{2}((\text{trace} \mathbf{B})^2 - \text{trace}(\mathbf{B}^2))$, and $III_{\mathbf{B}} = \det \mathbf{B}$.

3.1.2. Constitutive specification of the Helmholtz free energy. Having made arguments that constrain the general form of the constitutive description, we next specialize the forms to extend the phase field constitutive forms and to capture commonly used classical forms for the pure solid, liquid, and gas phases. Without regard to exothermic chemical reaction, we will assume that the Helmholtz free energy is composed of four parts, such that we can write

$$(3.20) \quad \psi = \psi_1 + \psi_2 + \psi_3 + \psi_4.$$

The first two, ψ_1, ψ_2 , are to be associated with the formulation of the phase transformations—the phase gradient energy density and the enthalpies associated with the phase transition. The latter two, ψ_3, ψ_4 , are of classical origins—the thermal energy density and the strain energy density.

We assume that the Helmholtz free energy depends on $\vec{\nabla} \phi$ only through ψ_1 and that the phase gradient energy density is specified with the explicit quadratic dependence by

$$(3.21) \quad \psi_1 = \frac{1}{2} \gamma_\phi |\vec{\nabla} \phi|^2.$$

It follows from (3.12) that the configurational force $\boldsymbol{\xi}$ is determined by the formula

$$(3.22) \quad \boldsymbol{\xi} = \rho \frac{\partial \psi}{\partial \vec{\nabla} \phi} = \rho \gamma_\phi \vec{\nabla} \phi.$$

The physical interpretation of the phase-configurational stress $\boldsymbol{\xi}$ is as a traction that acts near or in the phase transition region in the direction of the gradient of $\vec{\nabla} \phi$, i.e., perpendicular to contours of constant ϕ .

Next we consider the contribution ψ_2 , the phase transition energy density which reflects enthalpy changes during phase transition and is specified as

$$(3.23) \quad \psi_2 = \frac{1}{2} \Psi^{well} \mathcal{F}(\phi) + \beta_m(\phi) Q_m \left(\frac{T}{T_m} - 1 \right) + \beta_v(\phi) Q_v \left(\frac{T}{T_v} - 1 \right).$$

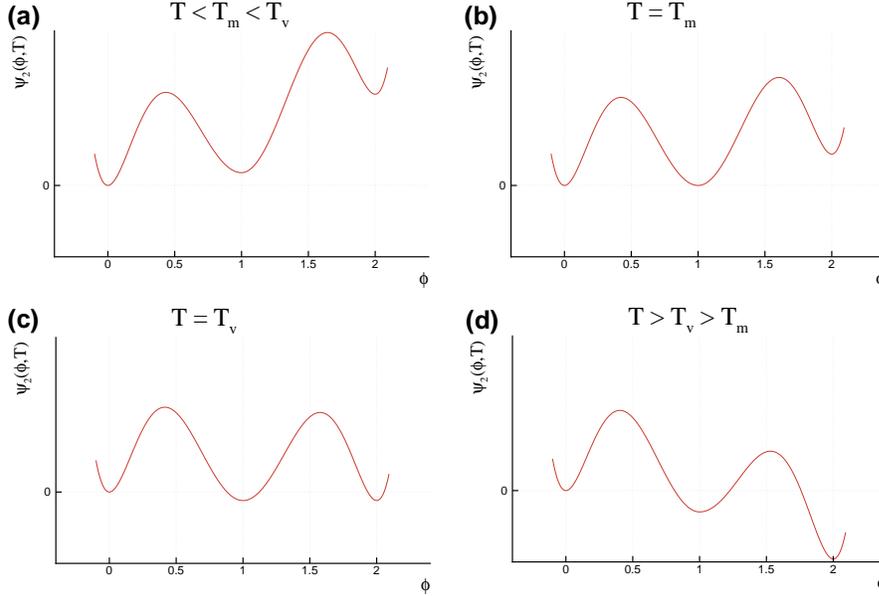


FIG. 1. Plot of ψ_2 as a function of ϕ with T variation.

The constants $\Psi^{well} > 0$, $Q_m < 0$, and $Q_v < 0$ represent a potential well depth and the heats of melting and vaporization. The constants $T_m > 0$ and $T_v > 0$ represent temperatures of melting and vaporization. The triple-well potential $\mathcal{F}(\phi)$ can be described by a smooth positive definite function whose isolated zeros are at $\phi = 0, 1$, and 2 , representing three local minima. In addition, $\mathcal{F}(\phi)$ is assumed to be locally quadratic near the zeros at $\phi = 0, 1$, and 2 , i.e., near $\phi = 0$, $\mathcal{F} \sim \phi^2$, near $\phi = 1$, $\mathcal{F} \sim (\phi - 1)^2$, and near $\phi = 2$, $\mathcal{F} \sim (\phi - 2)^2$. As an illustration, $\mathcal{F} = [\phi(\phi - 1)(\phi - 2)]^2$ has this property. The function $\beta_m(\phi)$ is assumed to be smooth and monotonically increasing and has values from 0 to 1 on the range $0 \leq \phi \leq 1$ with zero derivative elsewhere. The function $\beta_v(\phi)$ is similarly assumed to be monotonically increasing with values from 0 to 1 on the range $1 \leq \phi \leq 2$. Note that the derivative of transition energy density $\partial\psi_2/\partial\phi$ generates source terms in both the energy and phase equations represented as

$$(3.24) \quad \frac{\partial\psi_2}{\partial\phi} = \frac{1}{2}\Psi^{well}\frac{\partial\mathcal{F}}{\partial\phi}(\phi) + \beta'_m(\phi)Q_m\left(\frac{T}{T_m} - 1\right) + \beta'_v(\phi)Q_v\left(\frac{T}{T_v} - 1\right).$$

Figure 1 illustrates the assumed dependence of $\psi(\phi, T)$ on ϕ and T . Starting from (a) through (d), temperature T is raised from below T_m to above T_v , representing a standard melting-evaporation process. The transition energy density in case (a) has its minimum at $\phi = 0$. As T is increased through T_m and then T_v , we see a shift in the global minima from pure solid to solid-liquid and to liquid-vapor. As T eventually exceeds T_v as shown in (d), the energy minimizing well shifts to a vapor state at $\phi = 2$. The coefficients and functions Ψ^{well} , β_m , β_v can be adjusted (if needed) to reflect more accurately the physical properties observed in accordance with the phase transformation. Here we have chosen very simple forms.

We again assume the classical form for the thermal energy density and choose ψ_3

(which has the same form as ψ_1 in section 2) to be

$$(3.25) \quad \psi_3 = c_v [(T - T_0) - T \ln(T/T_0)],$$

where c_v is the specific heat at constant deformation. This is consistent with simple ideal models for solids, liquids, and gases.

Finally we choose a form for ψ_4 , the strain energy density. We assume that it is composed of three subparts. The first part is associated with the thermal expansion stresses commonly identified in the condensed phase:

$$(3.26) \quad \psi_{4a} = -\frac{\alpha_c(\phi)K}{2\rho_0}(T - T_0) \ln(III_{\mathbf{B}}),$$

where K is the solid bulk modulus and α_c is the linear coefficient of thermal expansion. We again take $\alpha_c(\phi)$ to be a smooth, nonzero function in the condensed phases, solid and liquid, and zero in the gas phase. For example, $\alpha_c(0) = \alpha_{solid}$, $\alpha_c(1) = \alpha_{liquid}$, and $\alpha_c(2) = 0$. The second part of ψ_4 is associated with the pressure commonly identified in an ideal gas that we encountered in the previous section on gaseous combustion:

$$(3.27) \quad \psi_{4b} = -\frac{1}{2}R_g(\phi)T \ln(III_{\mathbf{B}}).$$

Here $R_g(\phi)$ plays the role of the ideal gas constant except that it is assumed to be nonzero in the gas phase and at or near zero in the solid and liquid condensed phase such that $R_g(0) = 0$, $R_g(1) = 0$, $R_g(2) = R_{gas}$.

The third part, ψ_{4c} , is based on properties of a compressible neo-Hookean, Blatz-Ko solid [15] which is given as

$$(3.28) \quad \psi_{BK} = \frac{\mu}{2\rho_0}(I_{\mathbf{B}} - 3) + \frac{\mu(1 - 2\nu)}{2\rho_0\nu} \left(III_{\mathbf{B}}^{-\nu/(1-2\nu)} - 1 \right).$$

The constants ν and μ here represent the Poisson ratio of the material and the elastic Lamé parameter, μ . The contribution to the stress associated with this potential is

$$(3.29) \quad \boldsymbol{\sigma}_{BK} = 2\rho \frac{\partial \psi_{BK}}{\partial \mathbf{B}} \mathbf{B} = \mu_s \frac{\rho}{\rho_0} \mathbf{B} - \mu \frac{\rho}{\rho_0} III_{\mathbf{B}}^{-\nu/(1-2\nu)} \mathbf{I}.$$

We use this to model the elastic deformation of the solid, but for the liquid we pose a slightly altered form of this potential based on purely isotropic deformations. Consider the isotropic (either uniform contraction or expansion) given by $\mathbf{x} = s\mathbf{X}$, where s is the stretch ratio of material line segments. It follows simply that $\mathbf{F} = s\mathbf{I}$, $\mathbf{B} = s^2\mathbf{I}$, $III_{\mathbf{B}} = \det(\mathbf{B}) = (\rho_0/\rho)^2 = s^6$, $s = (\rho_0/\rho)^{1/3}$, $\mathbf{B} = (\rho_0/\rho)^{1/3}\mathbf{I}$, and $(\rho_0/\rho)^{1/3} = III_{\mathbf{B}}^{1/6}$. For the Blatz-Ko solid, the isotropic stress is related to the volume ratio by

$$(3.30) \quad \boldsymbol{\sigma} = -\mu \frac{\rho}{\rho_0} \left[\left(\frac{\rho}{\rho_0} \right)^{-\frac{2\nu}{1-2\nu}} - \left(\frac{\rho}{\rho_0} \right)^{-\frac{1}{3}} \right] \mathbf{I}.$$

We choose our model for the strain energy of the liquid to have the same functional form for the isotropic stress dependence on the density ratio as that for the solid, and

merely note that we replace the dependence on ρ_0/ρ by $III_{\mathbf{B}}^{1/2}$ and work backwards. The corresponding Helmholtz free energy for the liquid would take the form

$$(3.31) \quad \psi_{BK(liquid)} = \frac{3}{2} \frac{\mu}{\rho_0} III_{\mathbf{B}}^{1/3} + \frac{\mu(1-2\nu)}{2\rho_0\nu} \left(III_{\mathbf{B}}^{-\nu/(1-2\nu)} - 1 \right).$$

We can combine the two potentials for the solid and the liquid in the following way. Let $\mu_s(\phi)$ be a coefficient such that $\mu_s(0) = \mu_{solid}$ and it is zero for $\phi \geq 1$. Let $\mu_l(\phi)$ be a smooth function such that $\mu_l(1) = \mu_{liquid}$ with $\mu_l(0) = \mu_l(2) = 0$. One makes similar definitions for ν_s and ν_l . Let μ_c be defined as the sum $\mu_c = \mu_l + \mu_s$, and $\nu_c = \nu_l + \nu_s$. Then the combined solid, liquid, elastic potential can be written as

$$(3.32) \quad \psi_{4c} = \frac{\mu_s}{2\rho_0} (I_{\mathbf{B}} - 3) + \frac{3}{2} \frac{\mu_l}{\rho_0} III_{\mathbf{B}}^{1/3} + \frac{\mu_c(1-2\nu_c)}{2\rho_0\nu_c} \left(III_{\mathbf{B}}^{-\nu_c/(1-2\nu_c)} - 1 \right).$$

Note that other functional forms for the strain energy density could have been chosen for ψ_{4c} , but we chose the Blatz–Ko form since it has a simple reduction to compressible linear elasticity in the limit of small strain, which is deemed convenient for our purposes. We anticipate that as the solid become significantly nonlinearly elastic, we expect that a phase transformation will occur so that the specific choice of Blatz–Ko is not a sensitive one for the properties of the model. The deformational portion of stress associated with this strain energy is ψ_{4c} ,

$$(3.33) \quad \boldsymbol{\sigma}^{def} \equiv 2\rho \frac{\partial \psi_{4c}}{\partial \mathbf{B}} \mathbf{B} = \mu_s \frac{\rho}{\rho_0} \mathbf{B} - \mu_c \frac{\rho}{\rho_0} III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} \mathbf{I} + \mu_l \frac{\rho}{\rho_0} III_{\mathbf{B}}^{1/3} \mathbf{I}.$$

3.2. Total free-energy density and summary of constitutive forms. The form of $\psi = \psi_1 + \psi_2 + \psi_3 + \psi_{4a} + \psi_{4b} + \psi_{4c}$ is written as

$$(3.34) \quad \begin{aligned} \psi &= \frac{\mu_s(\phi)}{2\rho_0} (I_{\mathbf{B}} - 3) + \frac{\mu_c(\phi)(1-2\nu_s)}{2\rho_0\nu_s} \left(III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} - 1 \right) + \frac{3\mu_l(\phi)}{2\rho_0} III_{\mathbf{B}}^{1/3} \\ &\quad - \frac{\alpha_c(\phi)K}{2\rho_0} (T - T_0) \ln(III_{\mathbf{B}}) - \frac{1}{2} R_g(\phi) T \ln(III_{\mathbf{B}}) && \text{strain energy density} \\ &\quad - c_v(\phi) \left[T \ln \left(\frac{T}{T_0} \right) - (T - T_0) \right] && \text{thermal energy density} \\ &\quad + \frac{1}{2} \Psi^{well} \mathcal{F}(\phi) + \beta_m(\phi) \left(\frac{T}{T_m} - 1 \right) Q_m + \beta_v(\phi) \left(\frac{T}{T_v} - 1 \right) Q_v && \text{phase transition} \\ &\quad + \frac{1}{2} \gamma_\phi |\vec{\nabla} \phi|^2. && \text{gradient energy density} \end{aligned}$$

The constitutive theory is essentially complete. The stress is given by the general expression

$$(3.35) \quad \boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \mathbf{B}} \mathbf{B} - \vec{\nabla} \phi \otimes \boldsymbol{\xi} + \boldsymbol{\sigma}^{diss},$$

with $\boldsymbol{\xi}$ given by $\boldsymbol{\xi} = \rho \gamma_\phi \vec{\nabla} \phi$ and $\boldsymbol{\sigma}^{diss}$ given by $\boldsymbol{\sigma}^{diss} = \mu_f (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_f \mathbf{D}$. The stress formula becomes

$$(3.36) \quad \begin{aligned} \boldsymbol{\sigma} &= \mu_s \frac{\rho}{\rho_0} \mathbf{B} - \mu_c \frac{\rho}{\rho_0} III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} \mathbf{I} + \mu_l \frac{\rho}{\rho_0} III_{\mathbf{B}}^{1/3} \mathbf{I} \\ &\quad - \alpha_c(\phi) K \frac{\rho}{\rho_0} (T - T_0) \mathbf{I} - \rho R_g(\phi) T \mathbf{I} \\ &\quad - \rho \gamma_\phi \vec{\nabla} \phi \otimes \vec{\nabla} \phi + \nu_f (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_f \mathbf{D}. \end{aligned}$$

The energy flux vector remains $\mathbf{q} = -k\vec{\nabla}T$. The various source terms in the energy and phase equations can be computed from the forms given in (3.34).

We can now summarize the governing equations for the phase change model as

$$(3.37) \quad \dot{\rho} + \rho\vec{\nabla} \cdot \mathbf{v} = 0,$$

$$(3.38) \quad \rho\dot{\mathbf{v}} = \vec{\nabla} \cdot \boldsymbol{\sigma} + \rho\mathbf{f},$$

$$(3.39) \quad \begin{aligned} \rho c_v \dot{T} = & \vec{\nabla} \cdot (k\vec{\nabla}T) + \boldsymbol{\sigma}^{diss} : \vec{\nabla}\mathbf{v} + B\dot{\phi}^2 + \rho T \frac{\partial^2 \psi}{\partial T \partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla}\mathbf{v} \\ & + \rho T \frac{\partial^2 \psi}{\partial T \partial \phi} \dot{\phi} + \rho T \frac{\partial^2 \psi}{\partial T \partial \vec{\nabla}\phi} \cdot \vec{\nabla}\dot{\phi} + \rho r, \end{aligned}$$

$$(3.40) \quad B\dot{\phi} = \vec{\nabla} \cdot (\rho\gamma_\phi \vec{\nabla}\phi) - \rho \frac{\partial \psi}{\partial \phi},$$

$$(3.41) \quad \dot{\mathbf{F}} = \mathbf{L}\mathbf{F},$$

where B, c_v, γ_ϕ, k , etc. are constitutive scalars which could be regarded as functions of both ϕ and T . We have added the kinematic identity (3.41) in order to compute the evolution of the displacement gradients.

4. The combined model: Modifications to include chemical reaction.

Here we list the modifications required to combine both models into one. First we take the phase change model as the starting point and we retain all the assumptions and assumed forms of the previous section, specifically in regards to the appearance of ϕ . The configurational force balance (3.2) is retained as a fundamental balance law (the consequence of which leads to the derivation of the evolution equation for ϕ , equation (3.40)).

Next we assume that, in addition to ϕ , which measures the molecular order of the phase, the mass fraction λ simultaneously measures the amount of exothermic chemical reaction that has taken place. So λ is added to all the argument lists; in particular, in the expression for ψ we assume the dependence

$$(4.1) \quad \psi = \psi(\mathbf{F}, T, \phi, \lambda, \vec{\nabla}\phi, \mathbf{L}).$$

A statement of conservation of λ is added in the form of (2.4), which reflects a molecularly based conservation of species. The second law must be modified to include the entropy flux associated with the heat of combustion (so it takes the same form as (2.5)),

$$(4.2) \quad \rho\dot{\eta} \geq -\vec{\nabla} \cdot \left(\frac{\mathbf{q}}{T} \right) + \vec{\nabla} \cdot \left(\frac{Q_{hc}\mathbf{s}}{T} \right) + \frac{\rho r}{T}.$$

One argues the entropy inequality in exactly the same manner as in the previous section, with the same assumptions and conclusions of section 3, with the additional exception that one uses the evolution equation for λ , (2.4), to reduce the dissipation inequality in the manner explained in section 2. The energy flux vector is identified by the requirement of positivity of the left-hand side of (2.15), which leads to

$$(4.3) \quad \mathbf{q} = -k\vec{\nabla}T + Q_{hc}\mathbf{s}.$$

The vector \mathbf{s} can be chosen according to Fick's law such that

$$(4.4) \quad \mathbf{s} = d\vec{\nabla}\lambda.$$

The Helmholtz free energy is designated as $\psi = \psi_1 + \psi_2 + \psi_3 + \psi_{4a} + \psi_{4b} + \psi_{4c} + \psi_5$, where ψ_{1-4c} are defined in the previous section and ψ_5 is the chemical enthalpy $\psi_5 = -Q_{hc}\lambda$. The configurational stress is again of the form $\boldsymbol{\xi} = \rho\gamma_\phi \vec{\nabla}\phi$. The representation of the stress is

$$(4.5) \quad \begin{aligned} \boldsymbol{\sigma} = & \mu_s \frac{\rho}{\rho_0} \mathbf{B} - \mu_c \frac{\rho}{\rho_0} III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} \mathbf{I} + \mu_l \frac{\rho}{\rho_o} III_{\mathbf{B}}^{1/3} \mathbf{I} \\ & - \alpha_c(\phi) K \frac{\rho}{\rho_0} (T - T_0) \mathbf{I} - \rho R_g(\phi) T \mathbf{I} \\ & - \rho \gamma_\phi \vec{\nabla}\phi \otimes \vec{\nabla}\phi + \nu_f (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_f \mathbf{D}. \end{aligned}$$

The various scalar material properties identified previously, such as c_v, γ_ϕ, \dots , now can also have explicit dependence on λ as well as ϕ and T .

A revised list of the governing equations for the combined model with reaction and phase change is

$$(4.6) \quad \dot{\rho} + \rho \vec{\nabla} \cdot \mathbf{v} = 0,$$

$$(4.7) \quad \rho \dot{\mathbf{v}} = \vec{\nabla} \cdot \boldsymbol{\sigma} + \rho \mathbf{f},$$

$$(4.8) \quad \begin{aligned} \rho c_v \dot{T} = & \vec{\nabla} \cdot (k \vec{\nabla} T) + \boldsymbol{\sigma}^{diss} : \vec{\nabla} \mathbf{v} + B \dot{\phi}^2 + \rho T \frac{\partial^2 \psi}{\partial T \partial \mathbf{F}} \mathbf{F}^T : \vec{\nabla} \mathbf{v} \\ & + \rho T \frac{\partial^2 \psi}{\partial T \partial \phi} \dot{\phi} + \rho T \frac{\partial^2 \psi}{\partial T \partial \vec{\nabla} \phi} \cdot \vec{\nabla} \dot{\phi} + \rho Q_{hc} \Omega + \rho r, \end{aligned}$$

$$(4.9) \quad B \dot{\phi} = \vec{\nabla} \cdot (\rho \gamma_\phi \vec{\nabla} \phi) - \rho \frac{\partial \psi}{\partial \phi},$$

$$(4.10) \quad \rho \dot{\lambda} = \vec{\nabla} \cdot (d \vec{\nabla} \lambda) + \rho \Omega,$$

$$(4.11) \quad \dot{\mathbf{F}} = \mathbf{L} \mathbf{F}.$$

With the specific constitutive forms chosen for ψ , the energy equation becomes

$$(4.12) \quad \begin{aligned} \rho c_v \dot{T} = & \vec{\nabla} \cdot (k \vec{\nabla} T) + \nu_f (\vec{\nabla} \cdot \mathbf{v})^2 + 2\mu_f \mathbf{D} : \mathbf{D} + B \dot{\phi}^2 - \alpha_c(\phi) K \frac{\rho}{\rho_0} T (\vec{\nabla} \cdot \mathbf{v}) - \rho R_g(\phi) T (\vec{\nabla} \cdot \mathbf{v}) \\ & + \left\{ -\frac{\alpha'_c(\phi)}{2} K \frac{\rho}{\rho_0} T \ln(III_{\mathbf{B}}) - \rho \frac{R'_g(\phi)}{2} T \ln(III_{\mathbf{B}}) - \rho c'_v(\phi) T \ln\left(\frac{T}{T_0}\right) \right. \\ & \left. + \rho \left[\beta'_m(\phi) \frac{T}{T_m} Q_m + \beta'_v(\phi) \frac{T}{T_v} Q_v \right] \right\} \dot{\phi} + \rho Q_{hc} \Omega + \rho r, \end{aligned}$$

and the evolution law for ϕ becomes

$$(4.13) \quad \begin{aligned} B \dot{\phi} = & \vec{\nabla} \cdot (\rho \gamma_\phi \vec{\nabla} \phi) + \rho c'_v(\phi) \left[T \ln\left(\frac{T}{T_0}\right) - (T - T_0) \right] \\ & - \frac{\mu'_s(\phi)}{2} \frac{\rho}{\rho_0} (I_{\mathbf{B}} - 3) - \frac{\mu'_c(\phi)}{2} \frac{\rho}{\rho_0} \frac{(1 - 2\nu_s)}{\nu_s} \left(III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} - 1 \right) + \frac{3\mu'_l(\phi)}{2} \frac{\rho}{\rho_o} III_{\mathbf{B}}^{1/3} \\ & + \frac{\alpha'_c(\phi)}{2} K \frac{\rho}{\rho_0} (T - T_0) \ln(III_{\mathbf{B}}) + \frac{1}{2} \rho R'_g(\phi) T \ln(III_{\mathbf{B}}) \\ & - \rho \frac{1}{2} \Psi^{well} \frac{\partial \mathcal{F}}{\partial \phi} - \rho \left[\beta'_m(\phi) \left(\frac{T}{T_m} - 1 \right) Q_m + \beta'_v(\phi) \left(\frac{T}{T_v} - 1 \right) Q_v \right]. \end{aligned}$$

4.1. Material transition functions. An important ingredient of our model is the use of ϕ -dependent material properties or material transition functions. Earlier in section 2.4.2, we encountered $\beta_m(\phi), \beta_v(\phi)$ in the specification of the phase transition energy density, $\mu_c(\phi), \mu_l(\phi), \mu_s(\phi), \alpha_c(\phi), R_g(\phi)$ in the specification of the strain energy density, $c_v(\phi)$ in the specification of the thermal energy density, as well as functions associated with dissipative processes like $\nu_f(\phi)$. The model assumes that these functions have limiting pure phase values when $\phi = 0, 1, 2$. The structure of these functions has an influence on the exact details of the spatial structure of the transition layers and their dynamics when particular problems are solved. However, one makes an implicit assumption that when the transitions occur in thin layers relative to other geometric lengths, the structure within the layer does not strongly influence the information transmitted across the layer. This modeling precept is consistent with the use of viscous dissipation to describe continuum shock structure when the shock is molecularly thin.

For illustration sake, Figures 2 and 3 show typical transition functions that we have used to carry out representative simulations discussed in the companion paper [13]. These functions are constructed from simple polynomials in ϕ and their smooth extensions. The figures clearly show the basic properties that are required. For example, in Figure 2(c), the representation of the thermal expansion parameter $\alpha_c(\phi)$, which has the same (constant) value in the solid and liquid phase, is zero in the gas phase. Another example is that $\beta'_m(\phi)$ is zero for all values of ϕ except for those between 0 and 1, and terms that multiply $\beta'_m(\phi)$ are only involved in the solid to liquid transitions of melting or freezing and are totally absent in the liquid-gas transition of evaporation and condensation.

5. Some limiting cases.

5.1. Pure phases. The results for pure phases can be identified by the constitutive forms for the stress tensor. First we will consider the solid, $\phi = 0$, in the additional limit of small strain. The small strain limit is represented in terms of the displacement gradient $\mathbf{H} = \mathbf{F} - \mathbf{I}$, where $|\mathbf{H}| \ll 1$. Define the small strain tensor $\mathbf{E} = (\mathbf{H} + \mathbf{H}^T)/2$, and the left Cauchy–Green tensor can be written as $\mathbf{B} = \mathbf{F}\mathbf{F}^T = \mathbf{I} + 2\mathbf{E} + \mathbf{H}\mathbf{H}^T$. Our limiting form for the stress relation reduces to

$$(5.1) \quad \boldsymbol{\sigma} = -\alpha_{solid} \frac{\rho}{\rho_0} K(T - T_0) \mathbf{I} + \frac{2\mu_{solid} \nu_{solid}}{1 - 2\nu_{solid}} I_{\mathbf{E}} \mathbf{I} + 2\mu_{solid} \mathbf{E},$$

When one considers the limit of a liquid, $\phi = 1$, the expression for the stress becomes

$$(5.2) \quad \boldsymbol{\sigma} = -\alpha_{liquid} K \frac{\rho}{\rho_0} (T - T_0) \mathbf{I} - \mu_{liquid} \frac{\rho}{\rho_0} \left(\left(\frac{\rho}{\rho_0} \right)^{2\nu_{liquid}/(1-2\nu_{liquid})} - \left(\frac{\rho}{\rho_0} \right)^{-2/3} \right) \mathbf{I} \\ + \nu_{liquid} (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_{liquid} \mathbf{D};$$

similarly for the limit of the gas, $\phi = 2$, the expression for the stress becomes

$$(5.3) \quad \boldsymbol{\sigma} = -\rho R_{gas} T \mathbf{I} + \nu_{gas} (\vec{\nabla} \cdot \mathbf{v}) \mathbf{I} + 2\mu_{gas} \mathbf{D}.$$

5.2. Motionless phase transition. In this case we simply assume that the system is nearly motionless with $\mathbf{v} \approx 0$ and consider the pure phase change from solid

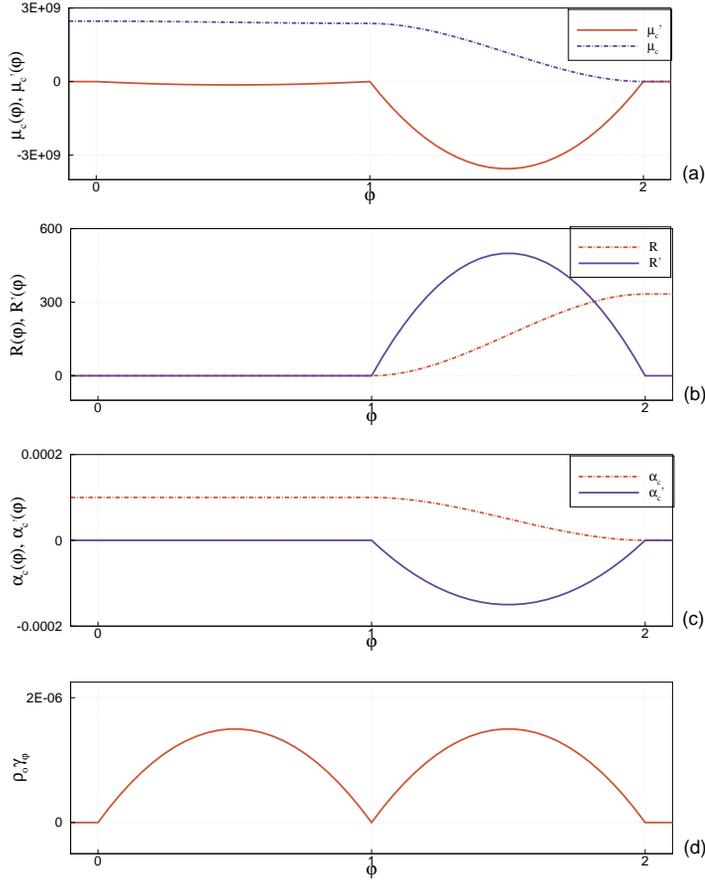


FIG. 2. Plots of transition functions for HMX simulation and their derivatives with respect to the phase variable. Shear modulus, ideal gas constant, thermal expansion coefficient, and phase diffusion coefficient are shown from top to bottom.

to liquid with no chemical reaction. In addition, we neglect the thermal expansion configurational forces, consistent with a nearly zero velocity field, and the thermal dissipation associated with the phase transition. Further we assume that ϕ is in the range $0 \leq \phi \leq 1$ and $\mathcal{F}(\phi)$ is effectively a double-well potential. We take the specific heat to be constant and are left with a thermal-diffusional model for the temperature and phase field given by the equations

$$(5.4) \quad \rho c_v \dot{T} = \vec{\nabla} \cdot (k \vec{\nabla} T) + \rho \beta'_m(\phi) \frac{T}{T_m} Q_m \dot{\phi}$$

and

$$(5.5) \quad B \dot{\phi} = \vec{\nabla} \cdot (\rho \gamma_\phi \vec{\nabla} \phi) - \rho \frac{1}{2} \Psi^{well} \frac{\partial \mathcal{F}}{\partial \phi} - \rho \beta'_m(\phi) \left(\frac{T}{T_m} - 1 \right) Q_m.$$

These equations are a generalized form of a thermally dependent Ginzburg–Landau theory of phase transitions often cited in discussions of solidification of binary alloys (see, for example, Wheeler, Boettinger, and McFadden [14].) Simple systems

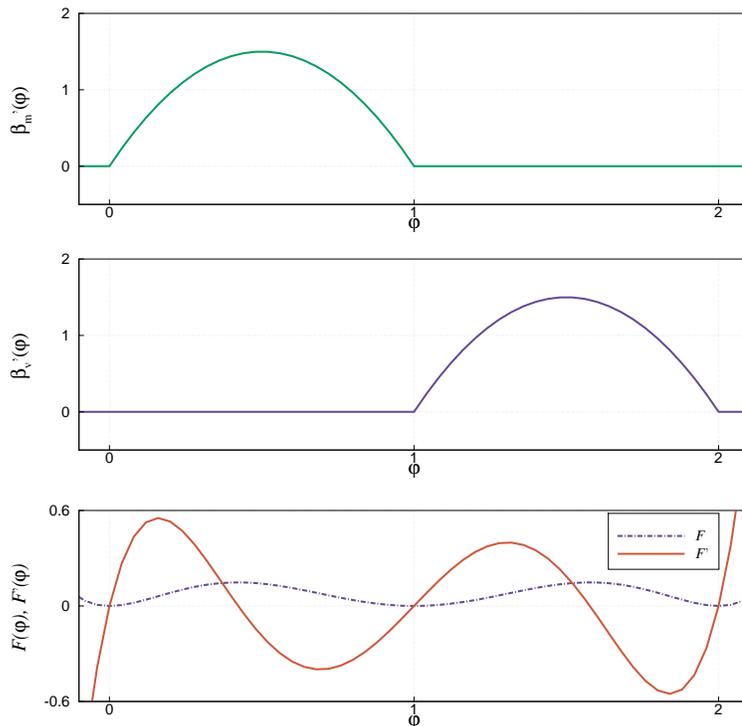


FIG. 3. φ -dependent transfer functions (derivatives) for heat of phase transformations, β'_m and β'_v . The third figure depicts the triple-well Ginzburg–Landau potential function and its derivative.

of this form, with a double-well potential and a single latent heat term, that have been analyzed in the literature have been shown to correspond to various forms of the classical (sharp interface) description of phase transitions. Further analysis leads to modified Stefan problems that incorporate surface tension and kinetic undercooling [8].

5.3. Relation to the simpler theory of quasi-static phase transformation. Here we briefly discuss the manner in which our model relates to the theory of quasi-static phase transformations that are a part of classical equilibrium thermodynamics. We assume that the changes in the state in the material happen so slowly that all inertial effects can be neglected and that the material undergoes only isotropic volume changes that are measured by changes in the density. The stress is spherical so that $\boldsymbol{\sigma} = -p\mathbf{I}$. The deformation is homogeneous such that $\mathbf{x} = s\mathbf{X}$, with $\mathbf{F} = s\mathbf{I}$, $\det(\mathbf{F}) = s = (\rho_0/\rho)$, $\mathbf{B} = (\rho_0/\rho)^2\mathbf{I}$, and strain invariants $III_{\mathbf{B}} = (\rho_0/\rho)^2$ and $I_{\mathbf{B}} - 3 = 3[(\rho_0/\rho)^2 - 1]$. One neglects all spatial gradients.

Next we consider the volume changes that occur as the temperature rises when the material is subjected to constant volumetric heating (given by constant r), under isobaric (constant pressure) conditions. For simplicity, we will also assume that the specific heat is constant in all phases. Then the change in the thermodynamic states would be controlled by a simplified version of the energy equation (for the

temperature) and the phase evolution equation. These are written as

$$(5.6) \quad \rho c_v \frac{\partial T}{\partial t} = \rho \left(\beta'_m(\phi) \frac{T}{T_m} Q_m + \beta'_v(\phi) \frac{T}{T_v} Q_v \right) \frac{\partial \phi}{\partial t} + \rho r,$$

$$(5.7) \quad B \frac{\partial \phi}{\partial t} = -\rho \frac{1}{2} \Psi^{well} \frac{\partial \mathcal{F}}{\partial \phi} - \rho \left[\beta'_m(\phi) \frac{T - T_m}{T_m} Q_m + \beta'_v(\phi) \frac{T - T_v}{T_v} Q_v \right],$$

and for the purpose of illustration, (4.5) is simplified by linearizing ρ about ρ_0 in the solid and liquid phases to obtain the thermal equation of state, a relation between p , ρ , T , and ϕ ,

$$(5.8) \quad p = \frac{6 \mu_c(\phi) \nu_s}{1 - 2 \nu_s} \left(\frac{\rho}{\rho_0} - 1 \right) + \alpha_c K \frac{\rho}{\rho_0} (T - T_0) - \rho R_g T.$$

The above equations are solved subject to the initial condition that the material is initially solid and, at the reference temperature, $\phi(0) = 0$ and $T(0) = T_0$. For constant pressure, a specified temperature, and ϕ , (5.8) determines the specific volume, $V = 1/\rho$. The solution of the initial value problem for T and ϕ determines a trajectory in T, V, ϕ -space at fixed p . A typical solution shows that as the temperature rises in the solid, the volume increases along the isobar. A phase transition (change in ϕ) does not take place till the temperature nears the melting temperature, T_m . Above that temperature local analysis shows that a change in stability of the state $\phi = 0$ occurs and then the transition from $\phi = 0$ to $\phi = 1$ occurs. Since the volumetric change is small (4% or less), the deviation in a T, v isobar is not large in some sense. As the temperature continues to rise, the second phase transition occurs near the vaporization temperature, T_v . Since the thermal equation of state is effectively modeled by the ideal gas law, a rather large change in the specific volume occurs. Finally, after the phase transition to vapor is completed and $\phi = 2$ is reached, the temperature continues to climb on the gas phase isobar with increasing volume. Figure 4 show plots of a T, V -trajectory for a isobaric phase transition for the HMX-like material described in [13]. Figure 5 shows the corresponding ϕ, V -trajectory at different pressures. Again, the purpose here is simply to illustrate that conventional notions of quasi-static phase transformations described in classical thermodynamics are embedded in this model.

6. Special forms of the model for three simple motions. In this concluding section we write out special and exact forms of the differential equations for the model when the material undergoes three simple motions: (i) evolution at constant volume, (ii) one-dimensional, time-dependent, longitudinal motion, and (iii) one-dimensional, time-dependent shear motion. All three are very important in the analysis of ignition of EMs. The three cases are the exclusive subject of the companion paper [13], in which numerical simulation and the properties of the model are discussed further.

6.1. Constant volume evolution and thermal explosion. A simple but extremely important subcase that is studied extensively in combustion theory describes the constant volume thermal explosion, where the velocity \mathbf{v} and all spatial gradients are exactly zero. The density is constant hence the volume of a material particle is constant. For illustration, we neglect thermal expansion and assume constant specific heat and gas constants. We are left with three ODEs in time for the temperature, phase change, and reaction progress:

$$(6.1) \quad \rho c_v \frac{\partial T}{\partial t} = \rho \left(\beta'_m(\phi) \frac{T}{T_m} Q_m + \beta'_v(\phi) \frac{T}{T_v} Q_v \right) \frac{\partial \phi}{\partial t} + \rho Q_{hc} \Omega + \rho r,$$

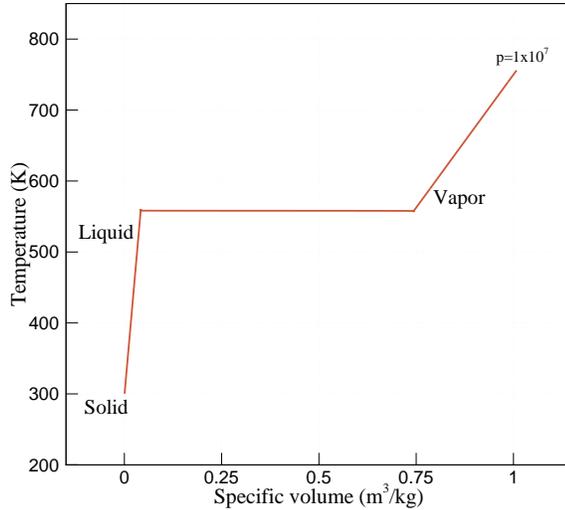


FIG. 4. T, V -trajectory on an isobar ($p = 10^7$ Pa) under the quasi-static assumptions. The large volume jump from liquid to gas happens at nearly constant temperature T_v .

$$(6.2) \quad B \frac{\partial \phi}{\partial t} = -\rho \frac{1}{2} \Psi^{well} \frac{\partial \mathcal{F}}{\partial \phi} - \rho \left[\beta'_m(\phi) \frac{T - T_m}{T_m} Q_m + \beta'_v(\phi) \frac{T - T_v}{T_v} Q_v \right],$$

$$(6.3) \quad \frac{\partial \lambda}{\partial t} = \Omega.$$

If one discards phase change, we recover the equations from standard combustion theory for constant volume thermal explosion, $c_v(\partial T/\partial t) = Q_{hc} \Omega$, $(\partial \lambda/\partial t) = \Omega$. Of course, the more interesting behavior occurs when phase change is included. The typical dynamics of these ODEs are discussed at length in [13].

6.2. Longitudinal motion. Next we turn to specializations of the equations to simplified motions that lead to PDEs in one space dimension and one time dimension; this is particularly suited to the study of ignition phenomena in EMs (which is one of our main concerns). First we consider longitudinal compression associated with a flyer-plate impact test. In this idealization, an infinite slab experiences a displacement loading normal to its surface. Specifically we consider the following one-dimensional motion:

$$(6.4) \quad x_1 = X_1 + f_1(X_1, t), \quad x_2 = X_2, \quad x_3 = X_3,$$

where f_1 is the 1-displacement.

For this motion, there is one nonzero velocity component, $v_1 = \partial f_1/\partial t|_{\mathbf{X}}(X_1, t)$, \mathbf{F} is diagonal with $F_{11} = \partial x_1/\partial X_1 = 1 + f'_1$, and $F_{22} = F_{33} = 1$. The density is related to the single strain gradient by $1 + f'_1 = \rho_0/\rho$. Also, \mathbf{B} is diagonal with $B_{11} = (1 + f'_1)^2$, $B_{22} = 1$, $B_{33} = 1$. The first and third invariants of \mathbf{B} are $I_{\mathbf{B}} =$

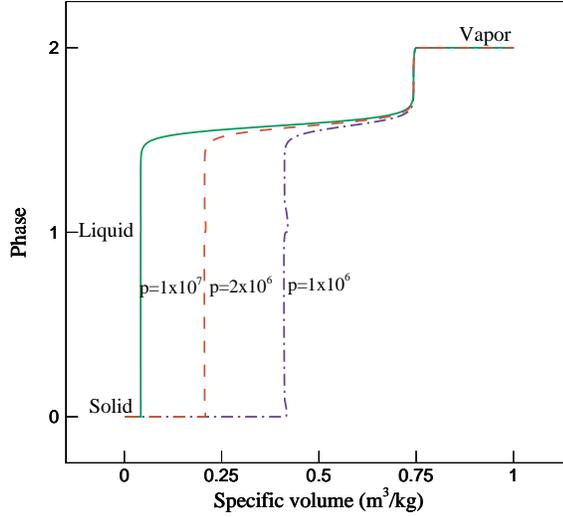


FIG. 5. Phase-V trajectory of constant pressure under the thermo-quasistatic assumption.

$2 + (1 + f'_1)^2$ and $III_{\mathbf{B}} = (1 + f'_1)^2$, with $III_{\mathbf{B}} = (\rho_0/\rho)^2$ and $I_{\mathbf{B}} - 3 = (\rho_0/\rho)^2 - 1$. Hence we use the density as the independent strain measure and replace f'_1 . The one nonzero component of the velocity gradient and rate of strain tensor are, respectively, $L_{11} = D_{11} = \partial v_1/\partial x_1$. Also, $(\vec{\nabla}\phi \otimes \vec{\nabla}\phi)_{11} = (\partial\phi/\partial x_1)^2$. It then follows that all the shear stresses are zero, $\sigma_{12} = \sigma_{23} = \sigma_{13} = 0$, and the normal stresses σ_{11} are given by

$$(6.5) \quad \sigma_{11} = -\mu_c \left(\frac{\rho}{\rho_0} \right) \left[\left(\frac{\rho}{\rho_0} \right)^{\frac{2\nu_s}{1-2\nu_s}} - \left(\frac{\rho}{\rho_0} \right)^{-2} \right] - \alpha_c K \frac{\rho}{\rho_0} (T - T_0) \\ - \rho R_g T - \rho \gamma_\phi \left(\frac{\partial\phi}{\partial x_1} \right)^2 + (\nu_f + 2\mu_f) \frac{\partial v_1}{\partial x_1}.$$

The other normal stress are the same as the σ_{11} stress, minus the phase stress, i.e., $\sigma_{22} = \sigma_{33} = \sigma_{11} + \rho \gamma_\phi (\partial\phi/\partial x_1)^2$.

The specific governing equations for longitudinal compression are the mass and momentum equations

$$(6.6) \quad \frac{\partial \rho}{\partial t} + v_1 \frac{\partial \rho}{\partial x_1} + \rho \frac{\partial v_1}{\partial x_1} = 0,$$

$$(6.7) \quad \rho \left(\frac{\partial v_1}{\partial t} + v_1 \frac{\partial v_1}{\partial x_1} \right) = \frac{\partial}{\partial x_1} \left\{ -\mu_c \left(\frac{\rho}{\rho_0} \right) \left[\left(\frac{\rho}{\rho_0} \right)^{\frac{2\nu_s}{1-2\nu_s}} - \left(\frac{\rho}{\rho_0} \right)^{-2} \right] \right. \\ \left. - \alpha_c K \frac{\rho}{\rho_0} (T - T_0) - \rho R_g T - \rho \gamma_\phi \left(\frac{\partial\phi}{\partial x_1} \right)^2 + (\nu_f + 2\mu_f) \frac{\partial v_1}{\partial x_1} \right\}$$

and the energy balance, phase evolution, and reaction progress evolution equations that take the specific forms

$$\begin{aligned}
 \rho c_v \left(\frac{\partial T}{\partial t} + v_1 \frac{\partial T}{\partial x_1} \right) &= \frac{\partial}{\partial x_1} \left(k \frac{\partial T}{\partial x_1} \right) + (\nu_f + 2\mu_f) \left(\frac{\partial v_1}{\partial x_1} \right)^2 \\
 &+ B \dot{\phi}^2 - \left[\alpha_c K \frac{\rho}{\rho_0} T + \rho R_g(\phi) T \right] \frac{\partial v_1}{\partial x_1} \\
 &+ \left\{ -\frac{1}{2} \alpha'_c(\phi) K \frac{\rho}{\rho_0} T \ln(III_{\mathbf{B}}) - \frac{1}{2} \rho R'_g(\phi) T \ln(III_{\mathbf{B}}) - \rho c'_v(\phi) T \ln(T/T_0) \right. \\
 (6.8) \quad &+ \left. \rho \left[\beta'_m(\phi) \frac{T}{T_m} Q_m + \beta'_v(\phi) \frac{T}{T_v} Q_v \right] \right\} \dot{\phi} + \rho Q_{hc} \Omega + \rho r,
 \end{aligned}$$

$$\begin{aligned}
 (6.9) \quad B \left(\frac{\partial \phi}{\partial t} + v_1 \frac{\partial \phi}{\partial x_1} \right) &= \frac{\partial}{\partial x_1} \left(\rho \gamma_\phi \frac{\partial \phi}{\partial x_1} \right) + \rho c'_v(\phi) \left[T \ln \left(\frac{T}{T_0} \right) - (T - T_0) \right] \\
 &- \frac{\mu'_s(\phi)}{2} \frac{\rho}{\rho_0} (I_{\mathbf{B}} - 3) - \frac{\mu'_c(\phi)}{2} \frac{\rho}{\rho_0} \frac{(1 - 2\nu_s)}{\nu_s} \left(III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} - 1 \right) - \frac{3\mu'_1(\phi)}{2} \frac{\rho}{\rho_0} III_{\mathbf{B}}^{1/3} \\
 &+ \frac{\alpha'_c(\phi)}{2} K \frac{\rho}{\rho_0} (T - T_0) \ln(III_{\mathbf{B}}) + \frac{1}{2} \rho R'_g(\phi) T \ln(III_{\mathbf{B}}) \\
 &- \frac{1}{2} \rho \Psi^{well} \frac{\partial \mathcal{F}}{\partial \phi} - \rho \left[\beta'_m(\phi) \frac{T - T_m}{T_m} Q_m + \beta'_v(\phi) \frac{T - T_v}{T_v} Q_v \right],
 \end{aligned}$$

and

$$(6.10) \quad \rho \left(\frac{\partial \lambda}{\partial t} + v_1 \frac{\partial \lambda}{\partial x_1} \right) = \frac{\partial}{\partial x_1} \left(d \frac{\partial \lambda}{\partial x_1} \right) + \rho \Omega.$$

6.3. Shear motion. Now we turn to specialization of the equations to shear motion, which again leads to PDEs in one space dimension, transverse to the motion, and one time dimension. A nominal geometry is a slab of fixed thickness loaded on one surface with constant velocity while the other is fixed. The bottom surface is taken to be fixed (zero displacement) for the entire duration of the test. Specifically, we consider the following one-dimensional motion:

$$(6.11) \quad x_1 = X_1 + f_1(X_2, t), \quad x_2 = X_2 + f_2(X_2, t), \quad x_3 = X_3,$$

where f_1 and f_2 are the in-plane displacements, which can also be regarded as functions of the spatial coordinate and time x_2, t . Corresponding to this motion, one has the velocities with dependencies $v_1(x_2, t), v_2(x_2, t)$, and $v_3 = 0$ and $\partial/\partial x_1 = \partial/\partial x_3 = 0$. The expression of the material time derivative is given by $\dot{(\)} = \partial/\partial t + v_2 \partial/\partial x_2$.

The shear deformation is described by

$$\begin{aligned}
 (6.12) \quad (\mathbf{F})_{ij} = \frac{\partial x_i}{\partial X_j} &= \begin{bmatrix} 1 & f'_1 & 0 \\ 0 & 1 + f'_2 & 0 \\ 0 & 0 & 1 \end{bmatrix}_{ij}, \\
 (\mathbf{B})_{ij} = (\mathbf{F}\mathbf{F}^T)_{ij} &= \begin{bmatrix} 1 + f_1'^2 & f_1'(1 + f_2') & 0 \\ f_1'(1 + f_2') & (1 + f_2')^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}_{ij},
 \end{aligned}$$

$$(6.13) \quad (\mathbf{L})_{ij} = (\vec{\nabla} \mathbf{v})_{ij} = \frac{\partial v_i}{\partial x_j} = \begin{bmatrix} 0 & \frac{\partial v_1}{\partial x_2} & 0 \\ 0 & \frac{\partial v_2}{\partial x_2} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (\mathbf{D})_{ij} = \begin{bmatrix} 0 & \frac{1}{2} \frac{\partial v_1}{\partial x_2} & 0 \\ \frac{1}{2} \frac{\partial v_1}{\partial x_2} & \frac{\partial v_2}{\partial x_2} & 0 \\ 0 & 0 & 0 \end{bmatrix}_{ij}.$$

The invariants of \mathbf{B} are computed as $I_{\mathbf{B}} = 1 + f_1'^2 + (1 + f_2')^2 + 1$ and $III_{\mathbf{B}} = (1 + f_2')^2 = (\rho_0/\rho)^2$ with $1 + f_2' = \rho_0/\rho$. Also $I_{\mathbf{B}} - 3 = (\rho_0/\rho)^2 - 1 + f_1'^2$. In addition, from the kinematic identity, $\dot{\mathbf{F}} = \mathbf{L}\mathbf{F}$, we obtain two nontrivial relations $\dot{f}_1' = (1 + f_2')\partial v_1/\partial x_2$ and $\dot{f}_2' = (1 + f_2')\partial v_2/\partial x_2$, where the material derivative is $\dot{(\cdot)} = \partial/\partial t + v_2 \partial/\partial x_2$. The second of the two results just restates mass conservation and is equivalent to replacing $1 + f_2'$ with ρ_0/ρ . But the first is an independent expression for the shear strain, which can be recast in terms of the density and transverse velocity gradient as

$$(6.14) \quad \dot{(f_1')} = \left(\frac{\rho_0}{\rho}\right) \frac{\partial v_1}{\partial x_2}.$$

Finally, the contribution to the configurational stress has only one nonzero component, $(\vec{\nabla} \phi \otimes \vec{\nabla} \phi)_{22} = (\partial \phi / \partial x_2)^2$.

Using the density ρ and the shear strain f_1' as the two independent kinematic variables, we can now write down expressions for the components of the stress tensor. The cross-plane shear stresses are zero, i.e., $\sigma_{13} = \sigma_{23} = 0$. The in-plane shear stress σ_{12} is given by the expression

$$(6.15) \quad \sigma_{12} = \mu_s f_1' + \mu_f \frac{\partial v_1}{\partial x_2}.$$

The in-plane normal stress σ_{22} is given by

$$(6.16) \quad \sigma_{22} = -\mu_c \left(\frac{\rho}{\rho_0}\right) \left[\left(\frac{\rho}{\rho_0}\right)^{\frac{2\nu_s}{1-2\nu_s}} - \left(\frac{\rho}{\rho_0}\right)^{-2} \right] - \alpha_c K \frac{\rho}{\rho_0} (T - T_0) - \rho R_g T \\ - \rho \gamma_\phi \left(\frac{\partial \phi}{\partial x_2}\right)^2 + (\nu_f + 2\mu_f) \frac{\partial v_2}{\partial x_2}.$$

The specific governing equations for the shear motion for the full model are

$$(6.17) \quad \frac{\partial \rho}{\partial t} + v_2 \frac{\partial \rho}{\partial x_2} + \rho \frac{\partial v_2}{\partial x_2} = 0,$$

$$(6.18) \quad \rho \left(\frac{\partial v_1}{\partial t} + v_2 \frac{\partial v_1}{\partial x_2} \right) = \frac{\partial}{\partial x_2} \left[\mu_s f_1' + \mu_f \frac{\partial v_1}{\partial x_2} \right],$$

$$(6.19) \quad \rho \left(\frac{\partial v_2}{\partial t} + v_2 \frac{\partial v_2}{\partial x_2} \right) = \frac{\partial}{\partial x_2} \left\{ -\mu_c \left(\frac{\rho}{\rho_0}\right) \left[\left(\frac{\rho}{\rho_0}\right)^{\frac{2\nu_s}{1-2\nu_s}} - \left(\frac{\rho}{\rho_0}\right)^{-2} \right] \right. \\ \left. - \alpha_c(\phi) K \frac{\rho}{\rho_0} (T - T_0) - \rho R_g(\phi) T - \rho \gamma_\phi \left(\frac{\partial \phi}{\partial x_2}\right)^2 + (\nu_f + 2\mu_f) \frac{\partial v_2}{\partial x_2} \right\},$$

$$\begin{aligned}
(6.20) \quad \rho c_v \left(\frac{\partial T}{\partial t} + v_2 \frac{\partial T}{\partial x_2} \right) &= \frac{\partial}{\partial x_2} \left(k \frac{\partial T}{\partial x_2} \right) + \left[\mu_f \left(\frac{\partial v_1}{\partial x_2} \right)^2 + (\nu_f + 2\mu_f) \left(\frac{\partial v_2}{\partial x_2} \right)^2 \right] \\
&\quad + B \dot{\phi}^2 - \left[\alpha_c K \frac{\rho}{\rho_0} T + \rho R_g T \right] \frac{\partial v_2}{\partial x_2} \\
&\quad + \left\{ -\frac{1}{2} \alpha'_c(\phi) K \frac{\rho}{\rho_0} T \ln(III_{\mathbf{B}}) - \frac{1}{2} \rho R'_g(\phi) T \ln(III_{\mathbf{B}}) - \rho c'_v(\phi) T \ln(T/T_0) \right. \\
&\quad \left. + \rho \left[\beta'_m(\phi) \frac{T}{T_m} Q_m + \beta'_v(\phi) \frac{T}{T_v} Q_v \right] \right\} \dot{\phi} + \rho Q_{hc} \Omega + \rho r,
\end{aligned}$$

$$\begin{aligned}
(6.21) \quad B \left(\frac{\partial \phi}{\partial t} + v_2 \frac{\partial \phi}{\partial x_2} \right) &= \frac{\partial}{\partial x_2} \left(\rho \gamma_\phi \frac{\partial \phi}{\partial x_2} \right) + \rho c'_v(\phi) [T \ln(T/T_0) - (T - T_0)] \\
&\quad - \frac{\mu'_s(\phi)}{2} \frac{\rho}{\rho_0} (I_{\mathbf{B}} - 3) - \frac{\mu'_c(\phi)}{2} \frac{\rho}{\rho_0} \frac{(1 - 2\nu_s)}{\nu_s} \left(III_{\mathbf{B}}^{-\nu_s/(1-2\nu_s)} - 1 \right) - \frac{3\mu'_1(\phi)}{2} \frac{\rho}{\rho_0} III_{\mathbf{B}}^{1/3} \\
&\quad + \frac{\alpha'_c(\phi)}{2} K \frac{\rho}{\rho_0} (T - T_0) \ln(III_{\mathbf{B}}) + \frac{1}{2} \rho R'_g(\phi) T \ln(III_{\mathbf{B}}) \\
&\quad - \frac{1}{2} \rho \Psi^{well} \frac{\partial \mathcal{F}}{\partial \phi} - \rho \left[\beta'_m(\phi) \frac{T - T_m}{T_m} Q_m + \beta'_v(\phi) \frac{T - T_v}{T_v} Q_v \right]
\end{aligned}$$

and for chemical reaction are

$$(6.22) \quad \rho \left(\frac{\partial \lambda}{\partial t} + v_2 \frac{\partial \lambda}{\partial x_2} \right) = \frac{\partial}{\partial x_2} \left(d \frac{\partial \lambda}{\partial x_2} \right) + \rho \Omega.$$

Finally, the kinematic relation (6.14) for the shear strain (which must be included) is expressed as

$$(6.23) \quad \frac{\rho}{\rho_0} \left(\frac{\partial f'_1}{\partial t} + v_2 \frac{\partial f'_1}{\partial x_2} \right) = \frac{\partial v_1}{\partial x_2}.$$

7. Conclusions. We have posed a three-dimensional model for a representative energetic material with two independent state variables that represent the change in phase and the extent of exothermic reaction. The model has a context and formulation in which it is thermodynamically consistent. This is in contrast to other models which may not be self-consistent because the constitutive theory is invoked a posteriori. Gurtin's notion of a fundamental balance of configurational forces leads to evolution laws for the phase variable. Limiting forms of this model are consistent with classical theories, but the model also yields limiting forms that can describe the transition between two phases, if desired. The combined model is very rich in the sense that the coupling between phase evolution and the energy equations is complex, due in part to the necessary partition of the Helmholtz free energy.

In [13] we use experimental data based on the behavior and properties of HMX to study representative dynamics of the three simple motions discussed in section 6. The examples we develop show a variety of behavior observed over many time and length scales. Strain localization and phase transition phenomena are observed, as well as many other complex phenomena.

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