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RPPR Final Report

as of 14-Aug-2023

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Title: Theoretical Investigation of Mechanically Coupled Chemical Kinetics and Phase Transitions in Energetic Materials

Begin Performance Period: 13-May-2019

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STEM Degrees: 3

STEM Participants:

Major Goals: In this work we aim to understand how the mechanical response of energetic materials effects the chemical kinetics and to determine in what scenarios this effect is significant. Through the development of theoretical models that are validated by experimental observations, we aim to expose new phenomena.

Accomplishments: - Theoretical model now published in Proceedings of the Royal Society, captures fully coupled dynamic cavity expansion, with the embedded explosive modeled as a reactive mixture, and can explain multi-stage explosions. Model explains the short timescale temperature spike reported in experiments and also confirms that for high activation energies the mechanical deformation can interfere with the chemical kinetics to essentially switch the explosion on and off at a frequency that is of the order on the natural elastic frequency.

- Experimental work was extended to softer materials softer materials. Overall it shows that long time response, which exhibits multiple peaks of cavity size, cannot be explained by existing chemical kinetics models nor by mechanics. It appears to be governed by experimental artifacts such as blocking of the laser light by the cavity. This decelerates the heating as the cavity expands and accelerates it again after the cavity retracts.

- From our experiments we can estimate the amount of energy released in the micro-explosion. This energy measure can then be used to assess the stability of an aggregate polymer bounded explosive, using theory of phase transitions, as detailed next.

- Theoretical model reveals a threshold value for onset of instability of the reaction – thus providing a clear (fully couple chemo-mechanical) approach to estimate the criteria for initiation from a hot spot.

- Experimental work captures the effect of rate dependence on fracture patterns.

- Work to understand shock waves is published in PRL and also featured in Nature Reviews Physics.

Training Opportunities: Nothing to Report

Results Dissemination: This work was presented at an international conference - The 19th U.S. National Congress on Theoretical and Applied Mechanics (USNCTAM), and has been published in the Proceedings of The Royal Society A.

Chockalingam, S., Lem, J. and Cohen, T., 2022. Thermo-chemo-mechanically coupled cavity dynamics and the emergence of multi-phase bursts. Proceedings of the Royal Society A, 478(2264), p.20220247.

RPPR Final Report

as of 14-Aug-2023

Honors and Awards: Chockalingam Senthilnathan - Received prestigious postdoc fellowship at Perdue (Lillian Gilbreth Postdoctoral Fellowship)
Tal Cohen - Received Tenure at MIT and received teaching award.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Xuanhe Li

Person Months Worked: 6.00

Funding Support:

Project Contribution:

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Participant Type: PD/PI

Participant: Tal Cohen

Person Months Worked: 1.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Jet Lem

Person Months Worked: 1.00

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Date Submitted: 8/15/19 12:00AM

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Article Title: Capturing strain stiffening using Volume Controlled Cavity Expansion

Authors: Shabnam Raayai-Ardakani, Tal Cohen

Keywords: Volume Controlled Cavity Expansion; PDMS properties; Strain stiffening; Shear modulus; Mooney–Rivlin; Gent; Ogden

Abstract: Strain-stiffening is a well-documented behavior in soft biological materials such as liver and brain tissue. Measuring and characterizing this nonlinear response, which is commonly considered as a mechanism for damage prevention, is of great interest to engineers for design of better biomimetic materials, and to physicians for diagnostic purposes. However, probing the elastic response of soft or biological materials at large deformation in their natural habitat, is an arduous task. Here, we present the Volume Controlled Cavity Expansion (VCCE) technique as a measurement method that offers the ability of characterizing the local stiffening response of materials in addition to identifying their shear modulus. By employing minimal constitutive representations involving only two constants (Mooney–Rivlin, Gent, and Ogden) we show that for the conventional PDMS samples, this technique and an accompanying data analysis method capture the shear modulus, as well as providing reliable measures.

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Article Title: The intimate relationship between cavitation and fracture

Authors: Raayai-Ardakani, Shabnam and Earl, Darla Rachelle and Cohen, Tal

Keywords: Fracture, Cavitation

Abstract: Nearly three decades ago, the field of mechanics was cautioned of the obscure nature of cavitation processes in soft materials [A. Gent, Cavitation in rubber: a cautionary tale, Rubber Chem. Technol., 1990, 63, 49–53]. Since then, the debate on the mechanisms that drive this failure process is ongoing. Using a high precision volume controlled cavity expansion procedure, this paper reveals the intimate relationship between cavitation and fracture. Combining a Griffith inspired formulation for crack propagation, and a Gent inspired formulation for cavity expansion, we show that despite the apparent complexity of the fracture patterns, the pressure–volume response follows a predictable path. In contrast to available studies, both the model and our experiments are able to track the entire process including the unstable branch, by controlling the volume of the cavity.

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Article Title: Observation of Ultraslow Shock Waves in a Tunable Magnetic Lattice
Authors: Jian Li, S Chockalingam, and Tal Cohen
Keywords: shock waves, particle physics
Abstract: The combination of fast propagation speeds and highly localized nature has hindered the direct observation of the evolution of shock waves at the molecular scale. To address this limitation, an experimental system is designed by tuning a one-dimensional magnetic lattice to evolve benign waveforms into shock waves at observable spatial and temporal scales, thus serving as a “magnifying glass” to illuminate shock processes. An accompanying analysis confirms that the formation of strong shocks is fully captured. The exhibited lack of a steady state induced by indefinite expansion of a disordered transition zone points to the absence of local thermodynamic equilibrium and resurfaces lingering questions on the validity of continuum assumptions in the presence of strong shocks.
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Journal: Journal of the Mechanics and Physics of Solids
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Article Title: Probing local nonlinear viscoelastic properties in soft materials
Authors: Chockalingam Senthilnathan, Christine Roth, Thomas Henzel, Tal Cohen
Keywords: Viscoelasticity, Soft materials, Volume controlled cavity expansion
Abstract: Minimally invasive experimental methods that can measure local rate dependent mechanical properties are essential in understanding the behaviour of soft and biological materials in a wide range of applications. Needle based measurement techniques such as Cavitation Rheology (Zimmerlin et al., 2007) and Volume Controlled Cavity Expansion (VCCE, Raayai-Ardakani et al. (2019a)), allow for minimally invasive local mechanical testing, but have been limited to measuring the elastic material properties. Here, we propose several enhancements to the VCCE technique to adapt it for characterisation of viscoelastic response at low to medium stretch rates. Through a carefully designed loading protocol, the proposed technique performs several cycles of expansion–relaxation at controlled stretch rates in a cavity expansion setting and then employs a large deformation viscoelastic model to capture the measured material response.
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Article Title: Thermo-chemo-mechanically coupled cavity dynamics and the emergence of multi-phase bursts

Authors: Chockalingam Senthilnathan, Jet Lem, Tal Cohen

Keywords: cavity dynamics, soft solids, energetic materials

Abstract: Understanding the dynamics induced by confined thermo-chemical processes occurring inside a solid medium is a fundamental problem of interest in several applications, such as hotspot formation and micro-explosions in energetic materials and laser-induced cavitation for energy focusing and material characterization. In recent years, advanced experimental capabilities have uncovered elusive behaviours in such systems, including temperature spikes that emerge at short timescales, and multiphase explosions. By coupling the mechanics of the solid, the thermodynamics, and the chemical kinetics of the decomposition reactions, the theoretical model developed here explains and demonstrates these phenomena. The dimensionless response of the system is studied numerically and analytical expressions for the mechanical response limits are derived. These results should be useful in guiding future experiments and in explaining phenomena that may emerge at various length and timescales.

Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
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Partners

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I certify that the information in the report is complete and accurate:

Signature: Tal Cohen

Signature Date: 8/10/23 2:16PM

Research



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Thermo-chemo-mechanically coupled cavity dynamics and the emergence of multi-phase bursts

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Understanding the dynamics induced by confined thermo-chemical processes occurring inside a solid medium is a fundamental problem of interest in several applications, such as hotspot formation and micro-explosions in energetic materials and laser-induced cavitation for energy focusing and material characterization. In recent years, advanced experimental capabilities have uncovered elusive behaviours in such systems, including temperature spikes that emerge at short timescales, and multi-phase explosions. By coupling the mechanics of the solid, the thermodynamics, and the chemical kinetics of the decomposition reactions, the theoretical model developed here explains and demonstrates these phenomena. The dimensionless response of the system is studied numerically and analytical expressions for the mechanical response limits are derived. These results should be useful in guiding future experiments and in explaining phenomena that may emerge at various length and timescales.

1. Introduction

The dynamic expansion and collapse of a cavity that is mechanically deformed by thermo-chemical processes occurring inside it, is a fundamental problem of interest in several applications, such as hotspot formation [1–10] and micro-explosions in energetic materials

[11,12], underground explosions for excavation and weapons testing [13,14], cavity dynamics-based material characterization techniques [15–18] and sonochemical or hydrodynamic cavitation reactors for chemical processing [19].

Recent observations in energetic materials emphasize the need to understand the coupling between the deformation of the confining body and the chemical kinetics [11]. Energetic materials are a class of materials that can release high amounts of stored chemical energy through an exothermic chemical reaction beyond that necessary to self-sustain the reaction; they find applications in propellants, explosives and pyrotechnics [20,21], and are often used in the form of energetic crystals that are embedded in a polymer binder. Recent experiments demonstrate that the mechanical properties of the confining inert binder material can significantly affect the explosion behaviour and can thus impact their sensitivity to premature explosions [11,22]. Models that can explain the explosion behaviour and its sensitivity to external stimuli are thus crucial to determine standards for safe handling and transportation of energetic materials. However, despite considerable efforts during the last decades, current understanding is still limited [23,24].

Understanding the local explosion behaviour at the scale of individual crystals confined in an elastic binder material provides a pathway to elucidate the thermo-chemo-mechanical behaviour of energetic materials. Such *micro-explosions* can also serve as a representative unit to describe the multi-scale response of the aggregate explosion behaviour. The highly nonlinear coupled phenomena that may emerge in such systems are demonstrated by recent experimental observations of micro-explosions [11,12], which report the emergence of *two-phase* and *two-stage* explosion behaviour. Theoretical models are thus needed to explain and predict the broad range of possible phenomena that may emerge in such systems, as well as the constitutive sensitivities, and their potential relevance at different scales.

Another example of chemical reactions being coupled with dynamic cavity motion is in cavitation phenomena [25–28]. Collapsing fluid cavitation bubbles result in high temperatures, pressures and generation of free radicals, and have been used to drive chemical reactions in cavitation reactors [19]. There have been extensive studies on cavitation in fluids [29–37] accounting for several factors including heat and mass transfer, fluid compressibility, and even chemical reactions inside the cavity [25–28,38,39]. On the contrary, study of cavity dynamics in solids has typically been restricted to accounting for either prescribed mechanical loading [40–43] or thermo-mechanical modelling inside the cavity [15,16,44–48] without accounting for chemical reactions, even in studies of underground explosions [13,49,50]. Inertial microcavitation rheometry is a material characterization technique that uses a focused pulsed laser to generate inertial cavitation bubbles in soft solids that are subsequently imaged and analysed to extract the high strain-rate viscoelastic properties. While chemical reactions in the cavity might be potentially important in understanding the evolution of cavity dynamics, current modelling treats the cavity contents as a non-reactive two-phase mixture of inter-diffusing condensible water vapour and non-condensable gas with the vapour undergoing equilibrium phase change at the bubble wall [15,16].

Overall, current modelling frameworks of cavity dynamics in solids omit the influence of chemical reactions inside the cavity that might be relevant to studying the problems described above. This manuscript is an attempt at addressing this gap by developing a thermo-chemo-mechanically coupled model for a cavity undergoing motion with a chemical reaction occurring inside it. The model is then used to investigate the coupling between mechanical motion and chemical kinetics, with a focus on solid decomposition reactions to study the micro-explosion behaviour in energetic materials and to expose different possible physical phenomena that may emerge, including multi-explosive behaviour.

The paper is organized as follows. In §2, we set up the coupled governing equations, which are then numerically and analytically investigated at progressively increasing levels of coupling—mechanical, thermal and chemical, for different problems of interest in §3. We provide some concluding remarks in §4.

2. Theory

We consider a cavity in an infinite solid medium undergoing dynamic motion resulting from thermal and chemical processes occurring inside it. In this section, we develop the governing equations that describe the mechanics of the confining soft solid, the thermodynamics and chemical kinetics within the cavity, and the coupling between all of them, while describing the simplifying assumptions that are employed for analytical tractability.

(a) Dynamics of the confining solid

We first develop the governing equations that describe the large deformation mechanics of the confining solid, which we assume to be incompressible. Accounting for the compressibility of the confining medium will lead to loss of energy through acoustic waves and thus damping of the cavity motion [15,32,34], which we neglect in our modelling here. A detailed derivation of the governing equations can be found in several earlier studies [42,43,51] and is provided for a general constitutive model in appendix A, for completeness. We consider a spherical cavity embedded in the confining solid, subjected to internal pressure p and an externally applied remote tension p_{ext} . Assuming that the size of the cavity is small compared with the dimensions of the body, the motion of the solid can be fully described by the time-dependent cavity radius $a(t)$ whose undeformed value is A . Assuming that the confining solid is incompressible, the mechanical power expended on it by the loading on its surfaces can be written as

$$\dot{W} = p\dot{V}_c - p_{\text{ext}}\dot{V}_c = P\dot{V}_c, \quad P = p - p_{\text{ext}} \quad (2.1)$$

where $V_c = (4/3)\pi a^3$ is the volume of the cavity. We neglect thermal conduction and inelasticity such as viscosity, damage and fracture in the confining solid so that the first law of thermodynamics yields

$$\dot{T}_E + \dot{U}_E = \dot{W}, \quad (2.2)$$

where $\dot{T}_E$ and $\dot{U}_E$ are the rate of change of total kinetic energy and total elastic energy in the confining solid, respectively. Accounting for heat transfer and inelasticity in the solid medium will lead to energy losses and damping in the cavity motion. The results for our model here can be considered a conservative extreme limit for cavity motion (the maximum cavity size and stretches will be higher than if the damping sources were accounted for).

The rate of change of the total kinetic energy in the confining solid can be written as

$$\dot{T}_E = \rho \left(\frac{3}{2} \dot{a}^2 + a\ddot{a} \right) \dot{V}_c, \quad (2.3)$$

where ρ is the constant mass density of the confining solid. We specialize our equations using the neo-Hookean free energy function to describe the constitutive response of the confining material. Defining a circumferential stretch at the cavity wall λ_a as

$$\lambda_a = \frac{a}{A}, \quad (2.4)$$

the total elastic energy in the confining solid U_E can be written as

$$U_E = U_E^* \bar{H}, \quad \bar{H} = \mu V_{c_0}, \quad U_E^*(\lambda_a) = \frac{1}{2}(\lambda_a - 1)^2(4 + 5\lambda_a + 3\lambda_a^{-1}), \quad (2.5)$$

where μ is the shear modulus of the material, V_{c_0} is the undeformed volume of the cavity and $\bar{H}$ is the characteristic dimensional energy. The rate of change of total elastic energy stored in the

confining solid is thus

$$\dot{U}_E = P_m \dot{V}_c, \quad \text{where } P_m = \frac{\mu}{2}(5 - 4\lambda_a^{-1} - \lambda_a^{-4}). \quad (2.6)$$

Using (2.1), (2.3) and (2.6) in (2.2), we can write the following equation that relates the cavity motion to the loading on the solid

$$P(t) = \rho \left(\frac{3}{2} \dot{a}^2 + a \ddot{a} \right) + \frac{\mu}{2}(5 - 4\lambda_a^{-1} - \lambda_a^{-4}), \quad (2.7)$$

where the first term on the right-hand side is the pressure that results from inertia of cavity motion and the second term is the pressure arising from the elastic material resistance.

In a purely mechanical problem setting where $P(t)$ is a prescribed function that is not coupled to any other thermal and chemical processes, the motion of the cavity can be obtained by integrating (2.7), given the initial conditions

$$a(t=0) = a_0 \quad \text{and} \quad \dot{a}(t=0) = \dot{a}_0. \quad (2.8)$$

In this paper, we employ $a_0 = A$ and $\dot{a}_0 = 0$ in all our analysis.

In this section, the dynamic motion of the cavity has been linked to the pressure applied on the solid. Next, we describe the evolution of the pressure inside the cavity for thermo-mechanical processes described by a prescribed power supply to the cavity.

(b) Thermodynamics of cavity content

The pressure on the cavity wall is generated by the gas inside the cavity. We neglect the heat and mass transfer effects in the gas,¹ and thus the pressure p , temperature T and mass density ρ_g in the gas are taken to be spatially uniform.² We further approximate the gas behaviour using the ideal gas law

$$pV_g = n_g RT \quad \text{or} \quad pv_g = RT, \quad (2.9)$$

where V_g is the volume occupied by the gases, n_g is the number of moles of gas, R is the ideal gas constant and $v_g = V_g/n_g$ is the molar volume of the gas. We choose an effective heat capacity ratio $\gamma (> 1)$ so that the internal energy in the gas U_g can be written as

$$U_g = n_g C_v T = \frac{pV_g C_v}{R} = \frac{pV_g}{\gamma - 1}. \quad (2.10)$$

For the analysis in this paper, we set $\gamma = 1.4$, the value for diatomic gases.

In this section, we will first develop the governing equation for a thermo-mechanical process where the cavity is supplied a known prescribed heat power as a function of time. In the following section, the chemical coupling will be introduced where the power supply arises from a chemical decomposition reaction. The mechanical power expended by the gas on the confining solid is given by

$$\dot{W}_g = p \dot{V}_c = 4\pi a^2 \dot{a} p. \quad (2.11)$$

Assuming a heat power supply rate of $\dot{Q}$ to the gases, the first law of thermodynamics in rate form can be written inside the cavity as

$$\dot{Q} = \dot{U}_g + \dot{W}_g. \quad (2.12)$$

Combining equations (2.10)–(2.12), the evolution of pressure in the gas can be expressed through the differential equation

$$\dot{p} = \frac{\gamma - 1}{V_g} (\dot{Q} - p \dot{V}_c) - p \frac{\dot{V}_g}{V_g}. \quad (2.13)$$

¹See [47] for a comprehensive investigation of the effect of heat and mass transfer effects on cavity dynamics.

²Cavitation studies in fluids usually employ a homobaric assumption (spatially uniform pressure) [37] and account for spatial variation of temperature. However, for the energetic materials systems we want to study, accounting for spatial distribution of energy release and heat and mass transfer within the cavity is infeasible since there is not necessarily any spatial symmetry or regularity in the decomposition reaction.

For the thermo-mechanical problem, we have $V_g = V_c = (4/3)\pi a^3$ and thus (2.13) simplifies as

$$\dot{p} = 3 \left[(\gamma - 1) \frac{\dot{Q}}{4\pi a^3} - \gamma p \frac{\dot{a}}{a} \right]. \quad (2.14)$$

Thus, the evolution of pressure inside the cavity can be linked to the dynamic cavity motion and the heat power supply per unit volume of gas. For a given heat power supply rate, $\dot{Q}(t)$, (2.14) can be integrated along with the equation of motion (2.7) to solve for the cavity motion and evolution of pressure inside the cavity, given the initial pressure $p(t=0) = p_i$, external pressure p_{ext} and initial conditions in (2.8).

(c) Chemical kinetics

In the previous section, we included the heat supply as an external source term and have considered the volume of the gas as equal to that of the cavity. In the fully coupled problem heat is a product of a chemical reaction, and the fraction of cavity volume occupied by the gas can change as the reaction proceeds. Although the decomposition of most energetic materials is a highly complicated chemical process with multiple possible chemical pathways [52–57], our model simplifies the process to write the overall solid decomposition reaction in the following form:



where we denote the solid reactants by X , and the gas products by Y , with ϕ being the stoichiometric ratio, and q is the heat energy released per unit volume consumption of the solid crystal, which we assume to be incompressible. This form applies to a broad class of solid decomposition reactions, and will be later specialized to investigate micro-explosions. Nonetheless, the framework can be extended to any arbitrary chemical reaction.

For the reaction in (2.15), the consumption rate can be written as

$$\dot{n}_g = -\phi \dot{n}_s = -\phi \frac{\dot{V}_s}{v_s}, \quad (2.16)$$

where n_g is the number of moles of the gas, n_s is the number of moles of the solid crystal, V_s is the volume of the solid crystal and v_s is its molar volume. It can be shown that the evolution of the pressure inside the cavity is described by the same equation (2.13) developed for the thermo-mechanical problem setting (see appendix B) except that the volume of gas and the cavity are no longer the same but instead related as

$$V_g = V_c - V_s, \quad (2.17)$$

and the heat power takes the form,

$$\dot{Q}(t) = -q \dot{V}_s. \quad (2.18)$$

Thus, we have the following equation for the evolution of the pressure inside the cavity,

$$\dot{p} = (\gamma - 1) \frac{\dot{Q}}{V_g} - \gamma p \frac{\dot{V}_c}{V_g} + p \frac{\dot{V}_s}{V_g}, \quad (2.19)$$

where the volumetric consumption rate of the solid crystal will depend on the chemical kinetics.

The chemical kinetics of decomposition of energetic materials is highly non-trivial. Nevertheless, several models have been proposed in the literature based on experiments and molecular dynamics simulations [56,58–64]. We describe the reaction progress in terms of the

extent of conversion α , which is defined as³

$$\alpha = \frac{n_{s_0} - n_s}{n_{s_0}} = \frac{V_{s_0} - V_s}{V_{s_0}}, \quad (2.20)$$

where V_{s_0} and $n_{s_0} = V_{s_0}/v_s$ are the initial volume and number of moles of solid [65–67]. A broad class of reaction kinetics can be described by the general form

$$\dot{\alpha} = f(\alpha)k(T)h(P) \Rightarrow \frac{\dot{V}_s}{V_{s_0}} = -f\left(1 - \frac{V_s}{V_{s_0}}\right)k(T)h(P), \quad (2.21)$$

where $k(T)$ is the temperature-dependent reaction rate constant, expressed in SI units s^{-1} ; $f(\alpha)$ is the dimensionless reaction model describing the mechanism such as contracting area/volume, diffusion, Avrami–Erofev (nucleation), fixed reaction order, etc.; and $h(P)$ is the dimensionless pressure dependence term. Different functional forms for f , g and h can be found in [66,67]. For the results in the next section, we employ the following functional forms⁴

$$f(\alpha) = 1 - \alpha, \quad k(T) = A_r e^{-(E_a/RT)}, \quad h(P) = 1, \quad (2.22)$$

where $1 - \alpha$ describes a first order reaction kinetics, A_r is the Arrhenius constant and $E_a > 0$ is the activation energy for the reaction. Other common forms for the reaction model preserve the key conclusions that are made in the next section.⁵ Note that the assumed Arrhenius form for $k(T)$ implies that the higher the temperature the faster the reaction rate and the higher the activation energy the stronger the temperature dependence of the reaction rate. For high activation energies, the temperature dependence can be strong enough that the reaction can effectively ‘switch off’ at low temperatures and ‘switch on’ at high temperatures. The kinetics models employed here have several well-known limitations, especially with fitting them to experimental data [63,65,68], but they are nevertheless the current standard for kinetics modelling and are also conducive to our qualitative analysis here.

This completes the development of the governing equations for the fully thermo-chemo-mechanically coupled problem. The evolution equations (2.16) for moles of gas, (2.19) for pressure, (2.21) for extent of conversion and (2.7) for cavity motion can be integrated given the initial pressure $p(t=0) = p_i$, external pressure p_{ext} , initial volume of solid crystal V_{s_0} , initial number of moles of gas n_{g_0} and the initial conditions for cavity motion (2.8). The temperature can be evaluated using the ideal gas law (2.9). In the next section, we will numerically integrate the governing equations for different problem scenarios of interest and analytically solve for the response limits wherever possible.

3. Results

In this section, we examine solutions of the governing equations developed previously, to study the dynamics of the cavity motion and its coupling to the evolution of the thermodynamic and chemical parameters. To understand the role of the coupling, we will progressively introduce the different levels of complexity: (a) to understand the mechanical response, we first solve a purely mechanical problem by considering step loading of the applied pressure; (b) to analyse the influence of the gas thermodynamics we consider adiabatic cavity oscillations (i.e. with $\dot{Q} = 0$); (c) we examine the different limits of the response induced by energy release over different characteristic timescales, through specified heat power $\dot{Q}(t)$; (d) finally, we investigate the fully thermo-chemo-mechanically coupled solid decomposition reaction.

³Note that α is typically defined in experiments such that it is equal to 1 at the end of the chemical process irrespective of whether the entire mass of reactant was consumed. Here we use a slightly modified definition to make it amenable to numerical modelling where the leftover reactant is not known *a priori*.

⁴We employ $h(P) = 1$ since unlike the temperature dependence, there is no consensus on the pressure dependence of the reaction rate for decomposition of energetic materials [59,61].

⁵We confirmed this for reaction models of the form $f(\alpha) = (1 - \alpha)^N$, such as contracting volume ($N = 2/3$), second-order ($N = 2$) and third-order ($N = 3$) kinetics.

Our results will be presented in non-dimensional form, with the characteristic velocity taken as the linear shear wave-speed, and with the corresponding characteristic time, volume and energy defined, respectively, as

$$c_s = \sqrt{\frac{\mu}{\rho}}, \quad \bar{t} = \frac{A}{c_s}, \quad V_{c_0} = \frac{4}{3}\pi A^3, \quad \bar{H} = \mu V_{c_0} \quad (3.1)$$

Oscillation stretch limits. For the considered cases, it will be seen that the cavity performs oscillatory motion in the stretch range $\lambda_a \in [\lambda_a^{\text{lb}}, \lambda_a^{\text{ub}}]$ where the cavity velocity vanishes at the limits. These stretch limits qualify the extremes of the mechanical response of the system and can be analytically evaluated using the integrated form of the governing equations and the fact that the kinetic energy of the confining medium vanishes at the oscillation limits. We first write the integrated form of (2.12) using (2.4), (2.10) and (2.11) as

$$\Delta Q = \Delta U_g + \Delta W_g, \quad \Delta U_g = \frac{V_{c_0}}{\gamma - 1} \left(p^f \lambda_a^{f3} - p^i \lambda_a^{i3} \right), \quad \Delta W_g = 3V_{c_0} \int_{\lambda_a^i}^{\lambda_a^f} p \lambda_a^2 d\lambda_a, \quad (3.2)$$

where the superscript i denotes the quantity at an initial time $t = t_i$, the superscript f denotes the quantity at a final time $t = t_f$ and ΔQ is the net heat energy supplied to the cavity in the time period $t \in [t_i, t_f]$. Here we take $t_i = 0$ and consider an initially stress-free state, such that $\lambda_a^i = 1$.

Next, we write the integrated form of (2.2) using (2.1), (2.4), (2.5), and the fact that we assume zero initial kinetic and elastic energy, as

$$T_E^f + U_E^f = \Delta W = \Delta W_g - \Delta W_{\text{ext}}, \quad \Delta W_{\text{ext}} = p_{\text{ext}} V_{c_0} \left(\lambda_a^{f3} - 1 \right), \quad U_E^f = U_E^*(\lambda_a^f) \bar{H}, \quad (3.3)$$

where we have assumed a constant external pressure. We can combine (3.2) and (3.3) to write the following integrated equation:

$$\Delta Q = U_E^*(\lambda_a^f) \bar{H} + \Delta U_g + \Delta W_{\text{ext}} + T_E^f. \quad (3.4)$$

The values of λ_a^f that satisfy the above equations along with requirement $T_E^f = 0$, are the stretch limits λ_a^b . We will soon use these analytical limits, to understand the predicted dynamic response.

(a) Constant pressure loading

We first consider the purely mechanical problem described in §2a by considering a constant pressure loading, such that $P (= p - p_{\text{ext}})$ is constant. The dynamic motion of the cavity is independent of the material and geometric parameters when described in dimensionless quantities (i.e. the stretch λ_a , dimensionless time $t/\bar{t}$ and dimensionless pressure P/μ), as shown in figure 1. Oscillation induced by positive values of P , namely when the internal pressure is higher than the external pressure, is shown in figure 1a,b, and oscillation induced by negative cavity gauge pressure is shown in figure 1c,d.

For positive values of P , the cavity undergoes expansion oscillations between the stretches of $\lambda_a^{\text{lb}} = 1$ and λ_a^{ub} , with increasing values of time period t_p and maximum stretch λ_a^{ub} with increasing value of the dimensionless pressure, up to a critical value of 2.5. Above the critical pressure loading, which represents the dynamic cavitation limit [40,41,69] (the dynamic and static cavitation limits are equal), the cavity expands unstably without oscillations ($t_p, \lambda_a^{\text{ub}} \rightarrow \infty$). For negative values of P , the cavity undergoes contraction oscillations between the stretches of λ_a^{lb} and $\lambda_a^{\text{ub}} = 1$, with decreasing values of the time period and minimum stretch limit with increasing magnitude of the dimensionless pressure. There is, however, no unstable contraction of the cavity.

The stretch limits ($\lambda_a^b = \{\lambda_a^{\text{lb}}, \lambda_a^{\text{ub}}\}$) where the cavity velocity vanishes, and the dimensionless time period $t_p/\bar{t}$ of oscillations, are plotted in figure 2. The stretch limits can be analytically evaluated using (3.3), the definitions in (3.1), (3.2), and the fact that p is constant, as the solutions

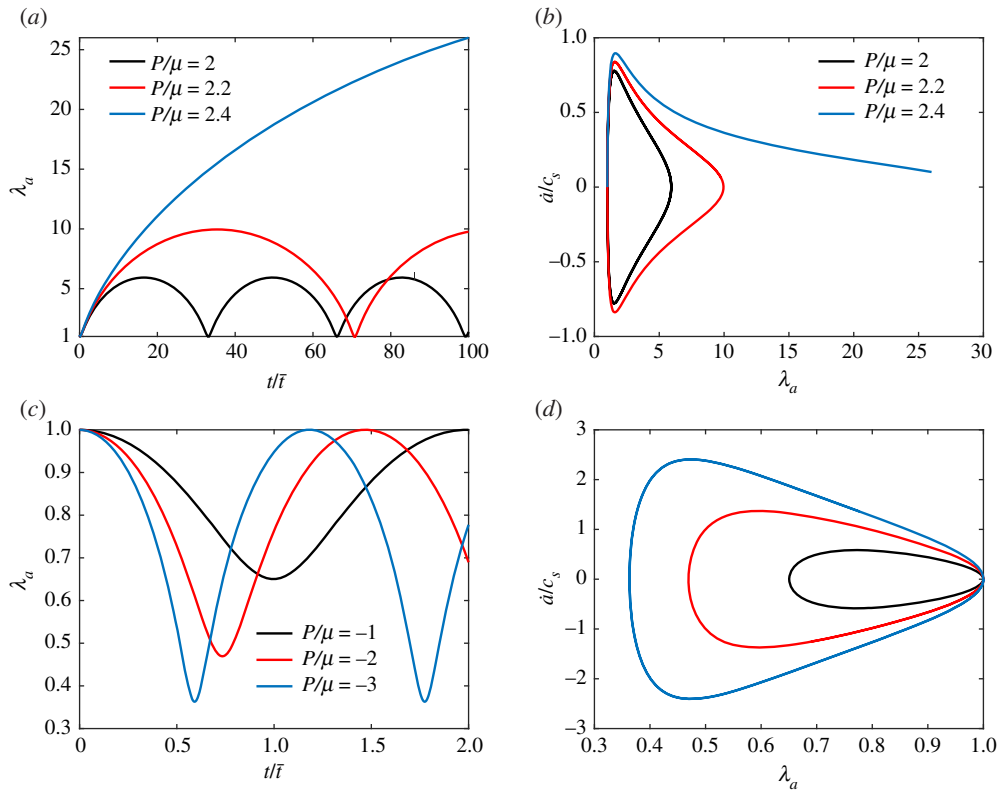


Figure 1. (a–d) Plots of the mechanical response of confining solid for a constant pressure process described by the pressure $P = p - p_{\text{ext}}$. (Online version in colour.)

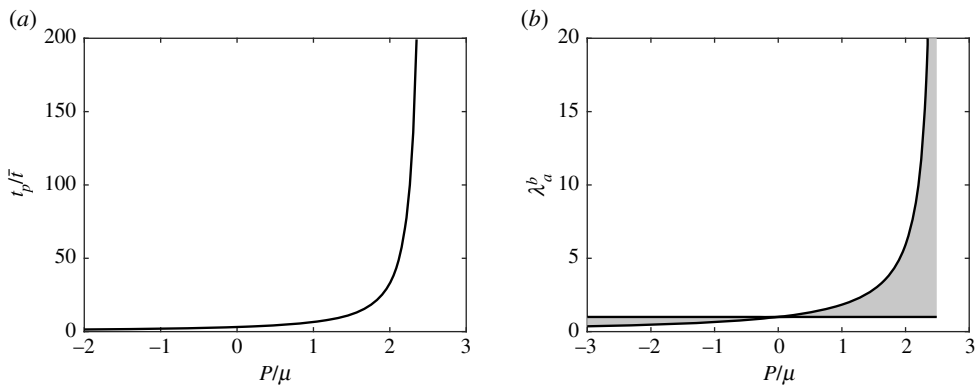


Figure 2. Cavity oscillation (a) time periods and (b) stretch limits for a constant pressure process described by the pressure $P = p - p_{\text{ext}}$. In (b), $P/\mu = 2.5$ is the dynamic cavitation limit, above which the cavity expands unstably.

to the equation

$$\frac{P}{\mu} \left(\lambda_a^{b3} - 1 \right) = U_E^*(\lambda_a^b). \quad (3.5)$$

It can be seen that $\lambda_a^b = 1$ is one of the trivial solutions of the equation. The analytically calculated limits coincide with the numerical results shown here.

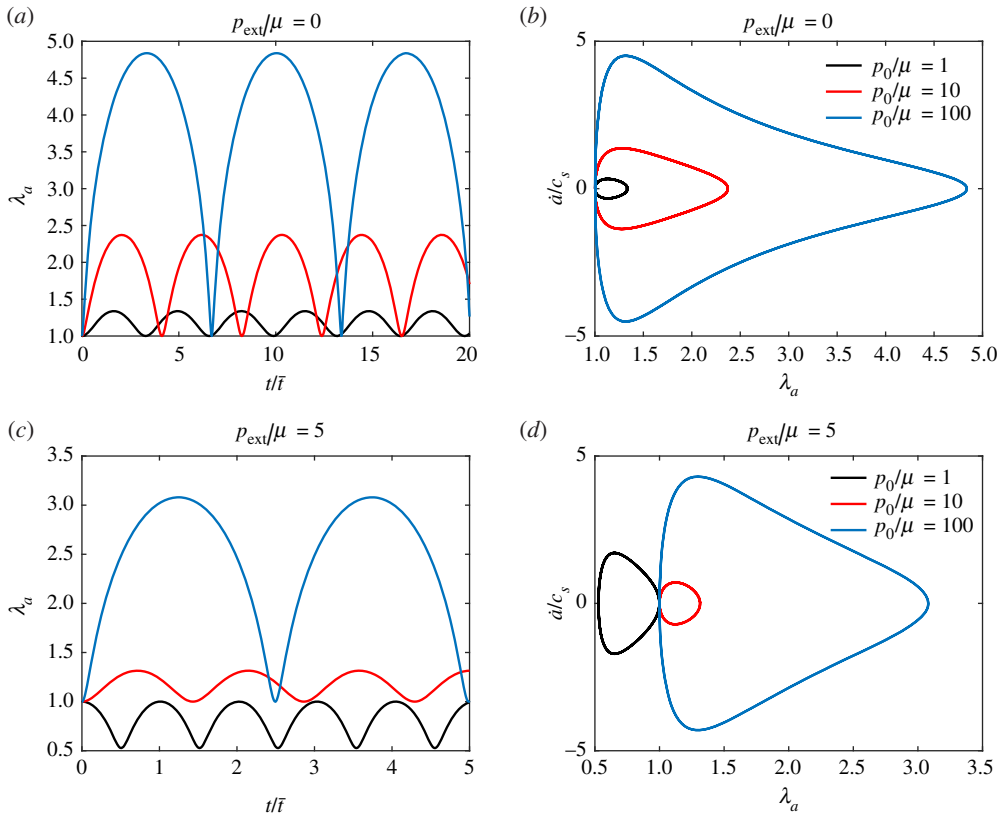


Figure 3. (a–d) Plots of the mechanical response of confining solid for an adiabatic process described by initial pressure p_0 and external pressure p_{ext} . (Online version in colour.)

(b) Adiabatic oscillations

We now numerically solve the thermo-mechanically coupled problem described in §2b for $\dot{Q}(t) = 0$ (adiabatic process) with an initial pressure inside the cavity $p_i = p_0$ and constant external pressure p_{ext} . Analysing the adiabatic case can be useful in several settings. For example, consider that an explosion sets up an initial pressure p_0 in the cavity. The subsequent motion of the cavity can be described using an adiabatic process if no more heat power is being supplied to the cavity. The dimensionless mechanical response of the system is invariant for a given pair of $\{p_0/\mu, p_{\text{ext}}/\mu\}$ and some sample results are plotted in figure 3. It can be seen that the response is always oscillatory with time period t_p and, similar to the constant pressure case, the cavity undergoes expansion oscillations when $P_0 = p_0 - p_{\text{ext}}$ is positive and contraction oscillations when P_0 is negative. However, unlike the constant pressure case, there is never unstable cavity expansion as there is no external agent to supply the increasing energy required for continued elastic deformation.

Furthermore, for $p_{\text{ext}}/\mu = 0$, the time periods and deformation limits are greatly reduced for a given value of P_0/μ in the adiabatic oscillations in comparison with those for the same value of P/μ in the constant pressure case. This is because the pressure in the cavity drops rapidly with increasing expansion of the cavity: for an adiabatic process, the pressure and temperature evolution is linked to the cavity motion using (2.9) and (2.14), while setting $\dot{Q} = \dot{n}_g = 0$, as follows:

$$p = p_0 \lambda_a^{-3\gamma}, \quad T = T_0 \lambda_a^{3(1-\gamma)}, \quad (3.6)$$

where T_0 is the initial temperature in the undeformed cavity.

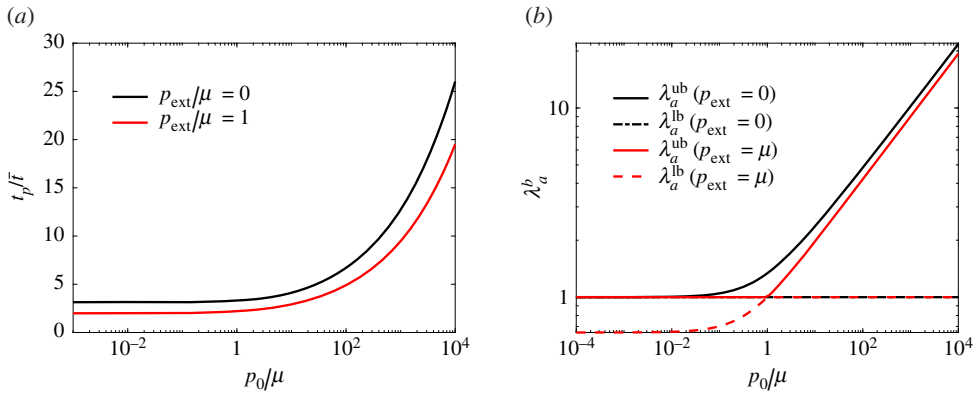


Figure 4. Cavity oscillation (a) time periods and (b) stretch limits for an adiabatic process described by initial pressure p_0 and external pressure p_{ext} . (Online version in colour.)

The time periods and stretch limits are plotted for select values of $\{p_0/\mu, p_{\text{ext}}/\mu\}$ in figure 4. It can be seen that the time period and amount of deformation increase with increasing magnitude of $P_0 = p_0 - p_{\text{ext}}$, and especially rapidly when $P_0 > 0$. Further, the external pressure has a non-negligible effect on the time period and stretch limits of the adiabatic oscillations even when $p_0 \gg p_{\text{ext}}$ and thus external atmospheric pressure is an essential part of modelling the dynamic cavity motion for thermo-mechanical processes. The stretch limits can be analytically evaluated using (3.4), (3.6), the definitions in (3.1)–(3.3), and $\Delta Q = 0$, as the solutions to the equation

$$\frac{1}{\gamma - 1} \frac{p_0}{\mu} \left(\lambda_a^{b^{3(1-\gamma)}} - 1 \right) + \frac{p_{\text{ext}}}{\mu} \left(\lambda_a^{b^3} - 1 \right) + U_E^*(\lambda_a^b) = 0. \quad (3.7)$$

Once again, $\lambda_a^b = 1$ is a trivial solution and the analytical stretch limits coincide with the numerical results.

(c) Specified heat energy with differing energy supply rates

In this section, we solve another thermo-mechanically coupled problem using the formulation in §2b by specifying a functional form for $\dot{Q}(t)$ such that a given amount of heat energy H is supplied over a characteristic time τ . Here we choose the following functional form for the heat power supply (plotted in figure 5a),

$$\dot{Q}(t) = \begin{cases} \frac{2H}{\tau} \sin^2\left(\frac{\pi t}{\tau}\right) & 0 \leq t \leq \tau \\ 0 & t > \tau \end{cases}, \quad (3.8)$$

such that $\int_0^{\tau} \dot{Q}(t) dt = H$. We note that we have confirmed that the qualitative conclusions in this section hold for other functional forms of $\dot{Q}(t)$, such as a Gaussian function and a hat function. Here we set $p_i = p_{\text{ext}}$ so that there is no cavity motion before the power supply begins, and identify the following two extreme cases of power supply that merit scrutiny:

- (i) $\tau/\bar{t} \rightarrow 0$ – the explosive limit, in which the energy is supplied faster to the cavity than it can mechanically respond.
- (ii) $\tau/\bar{t} \rightarrow \infty$ – the quasi-static limit, in which no inertial effects are present ($\dot{a}, \ddot{a} = 0$).

The dimensionless mechanical response is invariant for a given set of $\{p_i/\mu, p_{\text{ext}}/\mu, H/\bar{H}, \tau/\bar{t}\}$.

From the results shown in figure 5, it is seen that faster energy release of the same amount of dimensionless heat energy (i.e. smaller $\tau/\bar{t}$) leads to more violent mechanical oscillations.

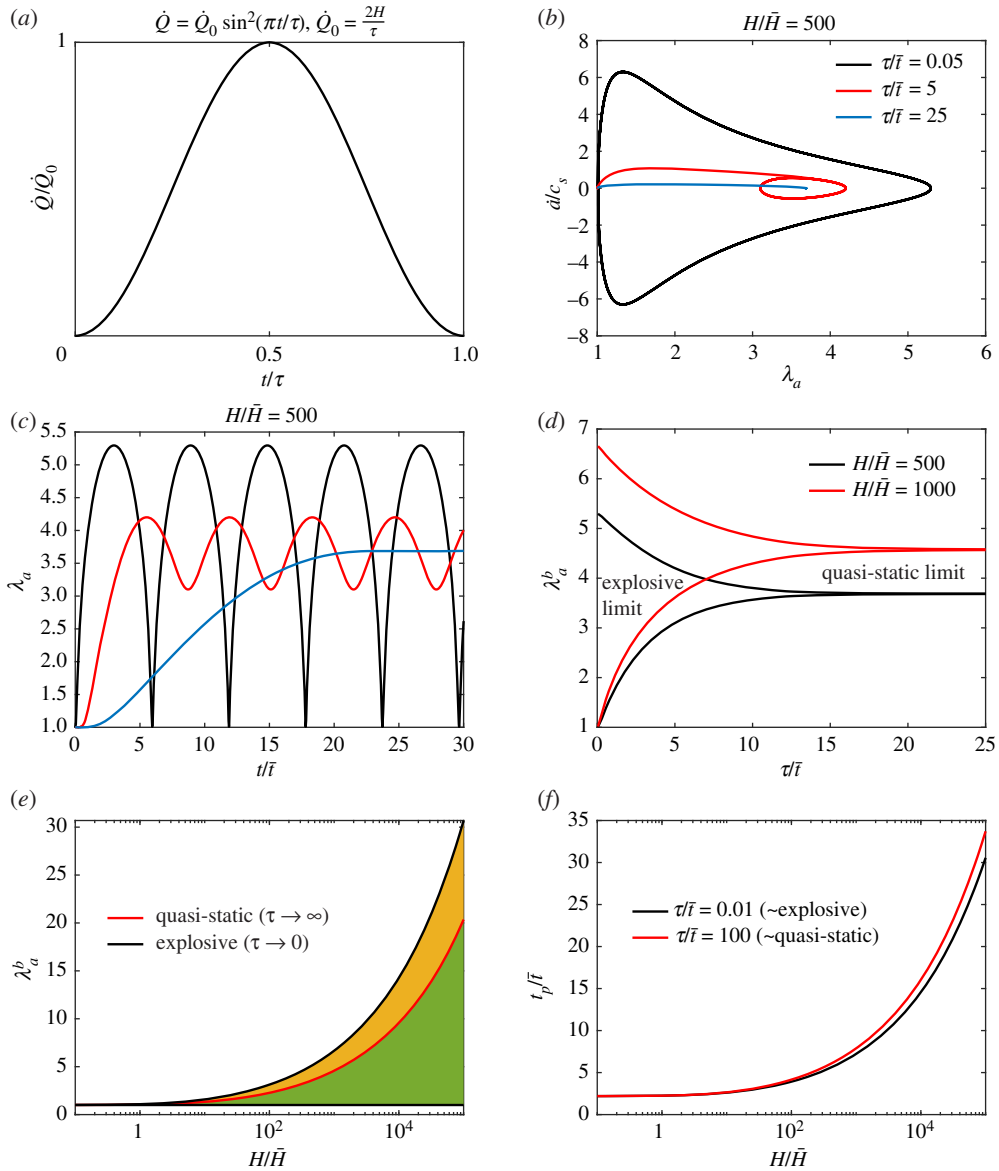


Figure 5. Plots of the mechanical response of confining solid for a specified heat power supply to the cavity: (a) Chosen form for the heat power supply as a function of time, a total heat energy of H units is supplied to the cavity over time τ where the maximum heat power is $\dot{Q}_0 = 2H/\tau$. (b,c) Mechanical response for $H/\bar{H} = 500$. (d) Steady-state oscillation stretch limits as a function of rate of energy release for given $H/\bar{H}$. (e) Analytical stretch limits (numerically validated) of the steady-state oscillations for the case of quasi-static and explosive heat energy supply. Yellow and green shaded regions represent the stretch regimes in which upper and lower bound stretch limits lie, respectively, for any rate of energy supply. (f) Steady-state oscillation time period as a function of $H/\bar{H}$. For (b–e), $p_i = p_{\text{ext}} = \mu$. (Online version in colour.)

After the power supply stops, the cavity oscillates between stretch limits $\lambda_a^b = \{\lambda_a^{\text{lb}}, \lambda_a^{\text{ub}}\}$ with time period t_p . These steady oscillation stretch limits are plotted as a function of the parameter $\tau/\bar{\tau}$ that characterizes the rate of energy release, in figure 5d. The explosive limit produces the most violent mechanical oscillations with $\lambda_a^{\text{lb}} = 1$ and in the quasi-static limit $\lambda_a^{\text{lb}} = \lambda_a^{\text{ub}}$. The upper and lower bounds for the stretch limits demonstrate monotonic trends with the rate of energy release

and are each bounded between their respective values for the explosive limit and the quasi-static stretch limit. Thus, the explosive and quasi-static limits for a problem with a known amount of dimensionless heat energy serve as extremes between which we can qualitatively expect the response to lie for any other energy supply rate.

The stretch limits for the explosive and quasi-static case are plotted as a function of $H/\bar{H}$ in figure 5e, it can be observed that the larger the supplied dimensionless energy the larger the maximum stretch. The green and yellow shaded regions represent the stretch regimes in which λ_a^{lb} and λ_a^{ub} lie, respectively, for any rate of energy supply. The time period of steady oscillations however shows little dependence on the energy supply rate and instead depends primarily on the dimensionless energy released, as shown in figure 5f for two extremes of power supply. This is because the time period of oscillations for the nonlinear mechanical response of the confining solid depends on the stretch regime in which the oscillations are occurring and the upper bound of the stretch is of similar order for any energy supply rate given $H/\bar{H}$.

The stretch limits for the quasi-static power supply can be analytically evaluated using equations (3.2)–(3.4), along with $\Delta Q = H$, $p_i = p_{\text{ext}}$, and setting $\dot{a}, \ddot{a} = 0$ in (2.7), as the solutions to the equation

$$\frac{H}{\bar{H}} = U_E^*(\lambda_a^b) + \frac{1}{\gamma - 1} \frac{P_m(\lambda_a^b)}{\mu} \lambda_a^{b3} + \frac{\gamma}{\gamma - 1} \frac{p_{\text{ext}}}{\mu} (\lambda_a^{b3} - 1). \quad (3.9)$$

There is only one solution to the above equation and thus $\lambda_a^{\text{lb}} \rightarrow \lambda_a^{\text{ub}}$ in the quasi-static limit.

As discussed previously, the explosive power supply will set up a pressure p_0 in the cavity which will then adiabatically oscillate as described in §3b. Since the analytical solutions for the adiabatic oscillations were already set up in (3.7) for a given p_0/μ , p_{ext}/μ , it remains to calculate p_0/μ for an explosive power supply to analytically evaluate the stretch limits. This can be done by integrating (2.14) from $t = 0$ to $t = 0^+$ while setting $\dot{Q} = H\delta(t)$ where $\delta(t)$ is the Dirac delta function. Since $a = A$ and $\dot{a} = 0$ in the integration time period, we have

$$p_0 = p_i + (\gamma - 1) \frac{H}{V_{c0}} \Rightarrow \frac{p_0}{\mu} = \frac{p_i}{\mu} + (\gamma - 1) \frac{H}{\bar{H}}. \quad (3.10)$$

Thus, the pressure rise in the cavity due to an explosive power supply only depends on the heat energy supplied per unit volume. The analytically evaluated limits for both the quasi-static and explosive heat power supply limits coincide with the numerical results.

For energetic crystals. The parameter q defined in §2c which is the heat released per unit volume of crystal, is the equivalent of H/V_{c0} . Considering, for example, the explosives RDX (CH_2NNO_2)₃ and HMX (CH_2NNO_2)₄, we have $q \sim 10$ GPa and thus $p_0 \sim 5$ GPa. A typical binding medium stiffness of $\mu \sim 150$ kPa would then yield a stretch limit of order 30 using (3.7), which implies that a completely explosive release of energy in these crystals would not be possible without fracturing or vaporizing the binding solid. Nonetheless, chemical coupling that can modify the power supply as a function of the cavity motion can lead to initial oscillations at lower stretch values, as will be seen in the next section.

(d) Solid decomposition and chemically coupled results

We will now solve the fully thermo-chemo-mechanically coupled problem described in §2c and investigate the coupling between the mechanical confinement and the reaction chemistry. Other than the activation energy E_a and the Arrhenius constant A_r , for which we examine a broad range of values to understand the constitutive sensitivities, the model parameters are chosen to represent the RDX explosion experiments in [11] and are listed in appendix D. The initial solid volume is prescribed as $V_{s0} = (1 - \varepsilon)V_{c0}$, where ε is a small parameter to characterize the initial volume fraction of gas in the crystal at the start of the reaction so that $V_{g0} = \varepsilon V_{c0}$ and $n_{g0} = \phi V_{g0}/v_s$. We set an initial ignition temperature $T(t = 0) = T_i$ so that $p_i = n_{g0}RT_i/V_{g0} = \phi RT_i/v_s$.

To distinguish different effects, we first show the results obtained for scenarios in which the temperature dependence of the chemical kinetics is negligible (i.e. $E_a \rightarrow 0$), and examine

the influence of the reaction rate, as determined by the Arrhenius constants A_r in figure 6a–c. It can be seen that the mechanical response of the system in figure 6c is very similar to that observed in the thermo-mechanical analysis for the cases of prescribed release of heat energy at different energy supply rates. The fastest rate, where the energy stored in the crystal is released much faster than the timescale of elastic response, resembles an explosive loading followed by adiabatic oscillations, whereas the slow energy release is closer to the quasi-static power supply case where the cavity is steadily growing as the energy is being supplied (note that since $p_i \neq p_{\text{ext}}$ here, even a very slow rate of energy release is not a quasi-static process). The temperature response in figure 6b is non-dimensionalized by the value $\bar{T}$ which is the steady temperature that results in the case of decomposition under rigid confinement (see appendix C) and represents the maximum temperature that can result inside the cavity when none of the energy from the crystal decomposition is expended on mechanical work. The temperature can be seen to drop whenever the cavity is expanding and rise whenever the cavity is collapsing and thus the temperature in the cavity is coupled to the cavity motion.

Temperature spike. Interestingly, our analysis shows that for sufficiently fast solid decomposition the temperature will spike up to values close to the limiting value ($\bar{T}$). This happens in the short timescales before mechanical motion begins and small amounts of gas are confined to a small volume. The rate of temperature rise in this initial spike will depend on the reaction rate and the initial gas volume in the cavity, but any spike will necessarily have to be significantly faster than the timescale of elastic oscillation (additional details can be found in appendix C). For the RDX decomposition considered here $\bar{t} \approx 38 \mu\text{s}$ and $\bar{T} \approx 7150 \text{ K}$, and thus the temperature can increase to high values rapidly. We note that rapid temperature spikes to such values have previously been reported in shock loaded polymer bonded explosives [70]. In the case of the fastest reaction rate (smallest A_r^{-1}) that resembles an explosive loading, the temperature oscillations are close to adiabatic. For the numerical results in figure 6b, the initial temperature at ignition was set as $T_i = 0.2\bar{T}$ (which sets p_i through (2.9)), but it is seen that irrespective of the initial temperature, the temperature spikes to the value of $\bar{T}$ for sufficiently fast kinetics.

To study the system response in the fully chemically coupled case allowing for thermal coupling of chemical kinetics ($E_a \neq 0$), we find it useful to span the parameter space of chemical kinetics parameters E_a, A_r , by defining a thermo-chemical coupling parameter ξ_T as

$$\xi_T = \ln \left(\frac{k(T_{\text{max}})}{k(T_{\text{min}})} \right) = \frac{E_a}{R} \left(\frac{1}{T_{\text{min}}} - \frac{1}{T_{\text{max}}} \right) > 0, \quad (3.11)$$

which quantifies the ratio of the fastest to slowest reaction rates during the cavity motion where T_{max} and T_{min} are the maximum and minimum temperatures attained respectively. The larger the parameter, the stronger the coupling between the mechanics and chemical kinetics. Larger values of E_a and $\bar{T}$, which are properties of the explosive and smaller value of T_{min} , can lead to larger values of the coupling parameter. Lower confining modulus of the binder can lead to larger stretches and lower T_{min} , which would increase the coupling of the chemical kinetics and the mechanics; however, too low a modulus would lead to high stretches that would fracture the material and allow the gaseous products to escape, which would reduce the coupling (such fracturing is seen in the second-stage explosion in experiments of [11]).

For the results in figure 6d–f, we choose reaction rates that are fast compared with the elastic timescale. Thus, we achieve the short time-scale temperature spike to value $\bar{T}$ by setting $k(\bar{T}) = 1/\bar{t}$ (which corresponds to $A_r^{-1} = \bar{t}$ in the case of $E_a \rightarrow 0$). To simplify the long time-scale integration we set $T_i = \bar{T}$ to avoid the initial short time-scale integration. This sets $T_{\text{max}} = \bar{T}$ in (3.11), and we span the space of the parameter ξ_T . However, since T_{min} cannot be known *a priori*, we set $T_{\text{min}} = 0.6\bar{T}$ and the response is plotted for three increasing values of the coupling parameter $\xi_T = (0, 1.5, 1.8)$. The corresponding values of the activation energy and reaction rate are $E_a = (0, 2.25, 2.7)R\bar{T}$ and $A_r \approx (1, 9.49, 14.88)/\bar{t}$. The dimensional value of E_a for the latter two cases evaluates to $133.8 \text{ kJ mol}^{-1}$ and $160.5 \text{ kJ mol}^{-1}$, respectively, which are similar to experimentally reported values for RDX and HMX [62,68].

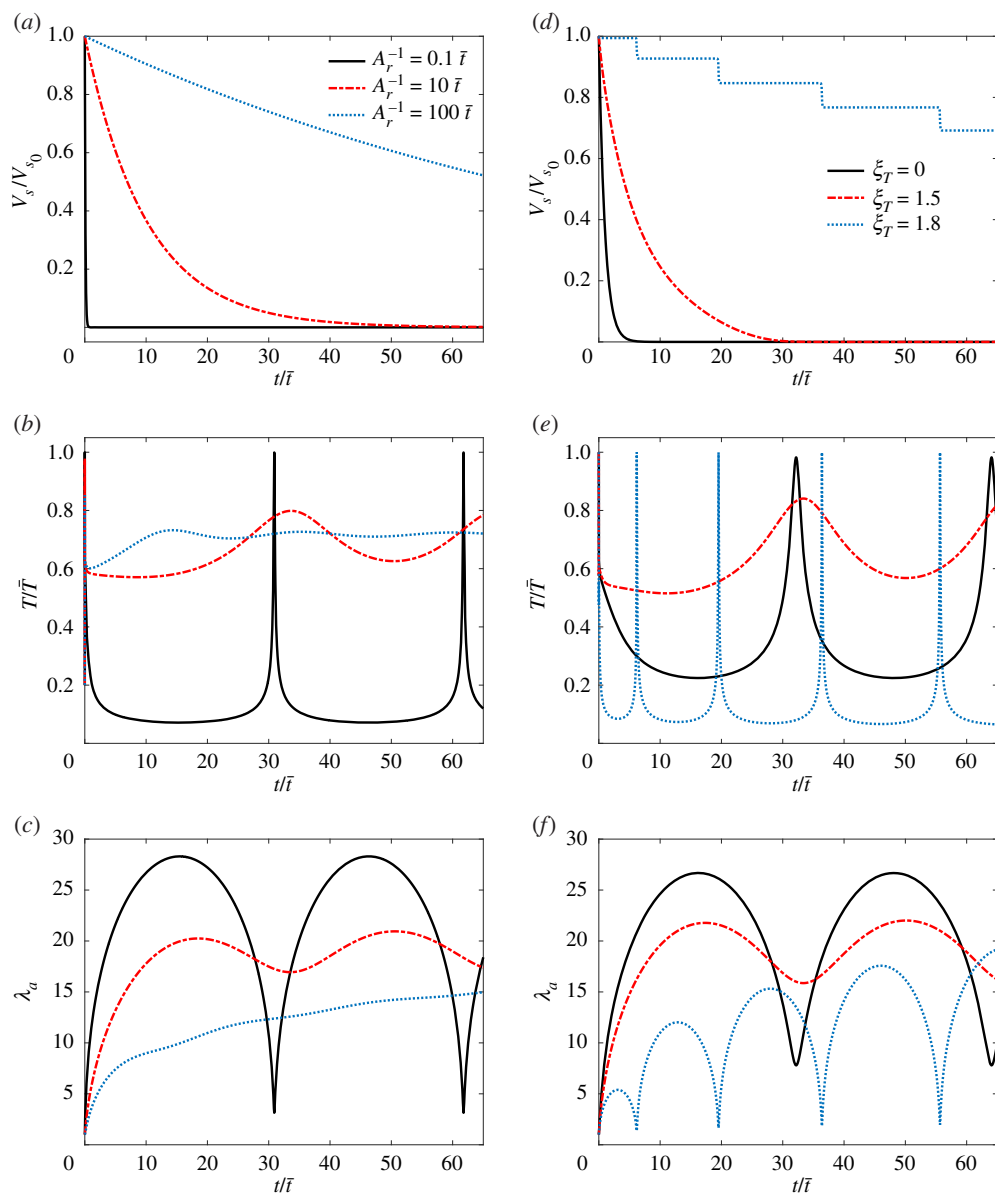


Figure 6. Response of the system in the case of solid decomposition reaction occurring inside the cavity. (a)–(c) Response when activation energy $E_a \rightarrow 0$, which decouples the chemical kinetics from the cavity motion. (d)–(f) Response for the fully coupled problem where $k(\bar{T}) = 1/\bar{T}$. (Online version in colour.)

Multiphase explosive bursts. It can be seen in figure 6d–f that the larger the ξ_T , the larger the coupling between the chemical kinetics and mechanics, when compared with the uncoupled chemical kinetics results ($\xi_T = 0$). The temperature is coupled to the cavity motion similar to the $E_a \rightarrow 0$ case, however the reaction rate is now affected by the temperature oscillation. When the coupling parameter value is high, the reaction can almost ‘switch off’ and ‘switch on’ as the cavity elastically expands and collapses, respectively (causing the temperature to drop and rise), leading to multi-phase explosion behaviour where the chemical energy is released in bursts. The mechanical oscillations also start off at lower stretches and become increasingly

violent with every explosion and will eventually approach the limits predicted earlier for the explosive power supply once all the crystal has been consumed. The time between the explosion phases is of the order of 100 μs , we note that two phase explosions separated by similar timescales have been reported in explosions of polymer-encased RDX and HMX using drop hammer initiation [12].

The mechanics and chemistry can thus interact to give rise to interesting multi-phase phenomena that might be consequential in understanding the explosion behaviour of energetic materials. Since the characteristic time, $\bar{t}$, scales with the size of the cavity and depends on the mechanical behaviour of the confining material, the results developed in this manuscript can also potentially be used to investigate potential multi-explosion phenomena at larger length scales. We also note that investigation of a number of kinetics models and a wide space of reaction parameters always yielded coupled multi-explosion behaviour only at timescales shorter than the explosive limit mechanical oscillation time period. While this time period is of the order of 1 ms for the explosion experiments in [11] where multi-stage explosion behaviour was reported, the second-stage explosion reported therein happens over a time-span of 100 ms, which suggests that their observation is more likely from other experimental artifacts, or a secondary gas phase reaction, as speculated therein, rather than from coupled chemo-mechanics of the solid decomposition.

4. Conclusion

In this work, the emergence of multiphase energetic bursts in violent confined explosions is explained and demonstrated by the development of a thermo-chemo-mechanically coupled model that is solved both analytically and numerically to investigate the dynamic response of cavities in incompressible solids with thermo-chemical processes occurring inside them. The strong coupling between reaction chemistry and mechanics was demonstrated, whereby the reaction can ‘switch off’ and ‘switch on’ due to the cavity dynamics leading to multi-phase explosion behaviour that has been observed in earlier experiments. Additionally, this framework explains the previously reported short time-scale temperature spikes that emerge before motion of the cavity occurs. A thermo-mechanical version of the model where the cavity is supplied with a prescribed heat power supply as a function of time is first used to investigate fundamental problems such as a prescribed supply of heat energy at different rates. The dimensionless response of the mechanical motion and evolution of thermodynamic parameters inside the cavity was established and the mechanical stretch limits and oscillation time periods were analysed. Analytical solutions for the stretch limits were developed for special cases including explosive and quasi-static power supply of a given amount of heat energy to the cavity. These results can aid in estimating the mechanical limits and understanding the response of the system, for generic chemical reactions and other scenarios where a cavity is supplied with heat power. Future studies should extend the current framework to account for heat and mass transfer, more complex chemical kinetics, material compressibility, asphericity [71], surface tension and inelastic behaviour of the confining solid.

Data accessibility. Code is available as Supplementary Material.

The data are provided in the electronic supplementary material [72].

Authors' contributions. S.C.: conceptualization, formal analysis, investigation, methodology, software, visualization, writing—original draft, writing—review and editing; J.L.: conceptualization, data curation, formal analysis, investigation, visualization, writing—review and editing; T.C.: conceptualization, funding acquisition, methodology, project administration, supervision, writing—review and editing.

All authors gave final approval for publication and agreed to be held accountable for the work performed therein.

Competing interests. We declare we have no competing interests.

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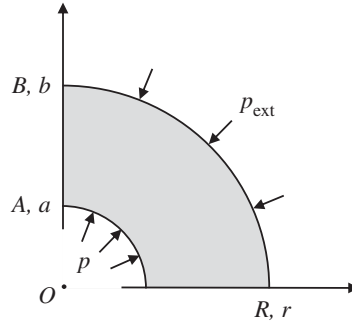


Figure 7. Schematic illustration of the problem setting of deformation of a solid medium with a cavity, loaded by an internal pressure p on the cavity wall and an external pressure p_{ext} on the outer surface. Typically $p_{\text{ext}} = p_{\text{atm}}$ where p_{atm} is the atmospheric pressure.

Appendix A. Dynamics of confining solid

(a) Kinematic relations

The confining solid is modelled as an infinite incompressible body with a spherical cavity that undergoes spherically symmetric deformation by application of internal and external pressures p and p_{ext} , respectively, as illustrated in figure 7. The radial coordinate in the initial and deformed configurations is defined by R and r , respectively. The corresponding inner and outer radii of the body in the undeformed and deformed configurations are A , B and a , b , respectively. We consider an infinite body and thus $B/A \rightarrow \infty$. Limiting our attention to incompressible materials, the deformation gradient can be written in spherical basis as

$$[\mathbf{F}] = \begin{bmatrix} \lambda_r & 0 & 0 \\ 0 & \lambda_\theta & 0 \\ 0 & 0 & \lambda_\phi \end{bmatrix} = \begin{bmatrix} R^2/r^2 & 0 & 0 \\ 0 & r/R & 0 \\ 0 & 0 & r/R \end{bmatrix}, \quad (\text{A } 1)$$

where λ_i ($i = r, \theta, \phi$) are the principal stretches associated with $\mathbf{F}$ and $\lambda = \lambda_\theta = \lambda_\phi = r/R$ is the circumferential stretch.

Additionally, for any spherical sub-region incompressibility implies

$$r^3 - a^3 = R^3 - A^3, \quad (\text{A } 2)$$

which for the entire body reads $b^3 - a^3 = B^3 - A^3$. The circumferential stretch can then be written in terms of the circumferential stretch at the cavity wall, λ_a , as

$$\lambda(R, t) = \frac{r(R, t)}{R} = \left(1 + (\lambda_a^3(t) - 1) \left(\frac{A}{R} \right)^3 \right)^{1/3}; \quad \lambda_a(t) = \frac{a(t)}{A}. \quad (\text{A } 3)$$

The circumferential stretch at the outer radius of the body, λ_b , is thus given as

$$\lambda_b(t) = \lambda(B, t) = \frac{b(t)}{B} = \left(1 + (\lambda_a^3(t) - 1) \left(\frac{A}{B} \right)^3 \right)^{1/3} \rightarrow 1. \quad (\text{A } 4)$$

The radial velocity and acceleration are derived from (A 2) as

$$\dot{r} = \frac{a^2 \dot{a}}{r^2} \quad \text{and} \quad \ddot{r} = \frac{2a \dot{a}^2 + a^2 \ddot{a} - 2r \dot{r}^2}{r^2}. \quad (\text{A } 5)$$

Thus, the motion of the entire body is described by the motion of the inner cavity wall due to incompressibility. In what follows, we relate the motion of the cavity wall to the mechanical loading on the solid.

(b) Equation of motion of cavity

The total kinetic energy in the confining solid can be evaluated by integrating over the body as

$$T_E = \frac{\rho}{2} \int_{\mathcal{R}} \dot{r}^2 dV = 2\pi\rho \int_a^\infty \left(\frac{a^2 \dot{a}}{r^2} \right)^2 r^2 dr = 2\pi\rho a^3 \dot{a}^2, \quad (\text{A } 6)$$

where ρ is the constant mass density of the confining solid. It is then straightforward to derive the rate of change of total kinetic energy stored in the solid in (2.3). To describe the elastic energy stored in the solid, we consider a strain energy density of the form $\psi = \hat{\psi}(\mathbf{F})$, which for the case of spherically symmetric deformation in (A 1) can be written as

$$\hat{\psi}(\mathbf{F}) = \bar{\psi}(\lambda_r, \lambda_\theta, \lambda_\phi) = \bar{\psi}(\lambda^{-2}, \lambda, \lambda) = \tilde{\psi}(\lambda). \quad (\text{A } 7)$$

Using (A 2), (A 3), (A 4), the total elastic energy stored in the solid U_E and its rate of change $\dot{U}_E$ can be written as

$$U_E = 4\pi \int_A^\infty \psi R^2 dR = 4\pi A^3 (1 - \lambda_a^3) \int_{\lambda_a}^1 \frac{\psi \lambda^2}{(1 - \lambda^3)^2} d\lambda \quad (\text{A } 8)$$

and

$$\dot{U}_E = P_m \dot{V}_c \quad \text{where } P_m = \int_{\lambda_a}^1 \frac{\tilde{\psi}'(\lambda)}{1 - \lambda^3} d\lambda. \quad (\text{A } 9)$$

Using (2.3), (A 9) and (2.1) in (2.2), we can write the following equation that relates the cavity motion to the loading on the solid:

$$P(t) = \rho \left(\frac{3}{2} \dot{a}^2 + a\ddot{a} \right) + P_m(\lambda_a(t)), \quad (\text{A } 10)$$

where the pressure arising from the elastic material resistance, P_m , is defined in (A 9). Alternative derivations of the above equation of motion can be found in [42,43,51].

Choice of constitutive model. We employ the neo-Hookean free energy function for isotropic materials

$$\hat{\psi} = \frac{\mu}{2} (\text{tr}(\mathbf{F}^T \mathbf{F}) - 3) \quad \text{and} \quad \tilde{\psi} = \frac{\mu}{2} (2\lambda^2 + \lambda^{-4} - 3), \quad (\text{A } 11)$$

where μ is the shear modulus. For the above constitutive choice, it is straightforward to arrive at (2.5), (2.6) and (2.7) using (A 8), (A 9) and (A 10) (see also [69]).

Appendix B. Pressure evolution in solid decomposition reaction

Consider the interior of the cavity consisting of the mixture of the solid crystal and gaseous products. Since we neglect heat transfer in the solid, the interior of the cavity is a closed thermodynamic system whose rate of change of internal energy U_c can be written as follows:

$$\dot{U}_c = u_s \dot{n}_s + u_g \dot{n}_g + \dot{U}_g, \quad U_g = \frac{pV_g}{\gamma - 1}, \quad (\text{B } 1)$$

where u_s, u_g are the chemical internal energies per unit mole of the solid crystal and gaseous products, respectively, and U_g is the kinetic internal energy of the gas. Using $\dot{n}_g = -\phi \dot{n}_s$ from (2.15) in (B 1), we can write

$$\dot{U}_c = -\dot{Q} + \dot{U}_g, \quad \dot{Q} = (\phi u_g - u_s) \dot{n}_s = -q_r \dot{n}_s, \quad (\text{B } 2)$$

where $\dot{Q}$ is the energy release rate from the solid decomposition reaction and q_r is the energy released per unit mole consumption of the solid crystal. We can write the first law of

thermodynamics for our closed system as

$$\dot{U}_c + \dot{W}_c = 0 \quad \text{and} \quad \dot{W}_c = p\dot{V}_c. \quad (\text{B } 3)$$

Using (B1)–(B3) and (2.17), we can write the evolution equation for the pressure as

$$\dot{p} = (\gamma - 1) \frac{\dot{Q}}{V_g} - \gamma p \frac{\dot{V}_c}{V_g} + p \frac{\dot{V}_s}{V_g} \quad \text{where } \dot{Q} = -q_r \dot{n}_s = -\frac{q_r}{v_s} \dot{V}_s = -q \dot{V}_s. \quad (\text{B } 4)$$

Appendix C. Pressure and temperature evolution under rigid confinement

Under rigid confinement, we have $\dot{V}_c = 0$ so that $\dot{V}_g = -\dot{V}_s$ and the pressure evolution equation (2.19) using (2.18) reduces to

$$\dot{p} = (\bar{p} - p) \frac{\dot{V}_g}{V_g} = (p - \bar{p}) \frac{\dot{V}_s}{V_g} \quad \text{where } \bar{p} = (\gamma - 1)q. \quad (\text{C } 1)$$

Irrespective of the initial pressure, the behaviour of the above evolution equation is such that the pressure will evolve to the value $\bar{p}$ and remain steady after as the reaction continues. The rate at which this steady pressure is achieved depends on $|\dot{V}_s|/V_g$ and thus in the case $V_{g0} \rightarrow 0$, this pressure will be achieved immediately. Note that $\bar{p}$ is the same as p_0 evaluated for explosive power supply to a cavity when $p_i = 0$ and $H/V_{c0} = q$ in (3.10).

Assuming $V_{s0} \rightarrow V_{c0}$, the volume of gas will be exactly equal to the volume of solid consumed under rigid confinement and the number of moles of solid consumed will thus be V_g/v_s . The number of moles of gas is thus $n_g = \phi V_g/v_s$. The temperature at any point in time is then linearly related to the pressure, including the steady value

$$T = \frac{pV_g}{n_g R} = \frac{pv_s}{\phi R} \Rightarrow \bar{T} = \frac{\bar{p}v_s}{\phi R} = (\gamma - 1) \frac{qv_s}{\phi R}. \quad (\text{C } 2)$$

Thus, irrespective of the initial temperature, the temperature will evolve to a steady value of $\bar{T}$. Note that when $V_{g0} \neq 0$, the analysis above still holds when the mechanical confinement is not exactly rigid, as long as $\dot{V}_c/\dot{V}_s \rightarrow 0$. Thus for sufficiently fast reaction rates, in the very short times when $\dot{V}_c$ is infinitesimal, the temperature and pressure will briefly spike up to the values of $\bar{T}$ and $\bar{p}$ before dropping as the mechanical motion commences.

Appendix D. Parameters for chemically coupled results

For the RDX decomposition reaction $\phi \approx 10$ [57]. The heat energy released per unit volume consumption of RDX is estimated as follows:

$$q = 1.6 \times 4184 \times 10^3 \text{ J kg}^{-1} \times 1820 \text{ kg m}^{-3}, \quad (\text{D } 1)$$

where 1.6 is the TNT relative effectiveness factor of RDX, 4184 kJ kg^{−1} is the energy released per unit mass consumption of TNT (2,4,6-trinitrotoluene) and 1820 kg m^{−3} is the mass density of RDX. The molar mass of RDX is 222 g and thus its molar volume $v_s = 0.222 \text{ kg mol}^{-1}/1820 \text{ kg m}^{-3} = 1.22 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$. Thus the values of $\bar{T}$ and $\bar{p}$ turn out to be

$$\bar{p} = (\gamma - 1)q = 4.87 \text{ GPa} \quad \text{and} \quad \bar{T} = \frac{\bar{p}v_s}{\phi R} \approx 7150 \text{ K}. \quad (\text{D } 2)$$

We set the initial gas volume fraction $\varepsilon = 10^{-10}$ and the initial cavity/crystal radius to $A = 0.5 \text{ mm}$ (thus any potential vaporization of confining solid is ignored here). The confining medium is taken to be PDMS (Polydimethylsiloxane) rubber (Sylgard 184, Dow Corning) with base to cross linker ratio of 10 : 1 with mass density $\rho = 965 \text{ kg m}^{-3}$ and Young's modulus $E = 3\mu = 500 \text{ kPa}$. Thus, $\bar{t}$ evaluates to 38.05 μs . The external pressure is set to atmospheric pressure so that $p_{\text{ext}} = 100 \text{ kPa}$.

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