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Propagation and ignition of fast gasless detonation waves of phase or chemical transformation in condensed matter

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Abstract. Fast self sustained waves of chemical or phase transformations, observed in several contexts in condensed matter effectively result in "gasless detonation". The phenomenon is modelled by coupling the reaction diffusion equation, describing chemical or phase transformations, and the wave equation, describing elastic perturbations. The coupling considered in this work involves (i) a dependence of the sound velocity on the chemical (phase) field, and (ii) the destruction of the initial chemical equilibrium when the strain exceeds a critical value (strain induced phase transition). Both the case of an initially unstable state (first order kinetics) and metastable state (second order kinetics) are considered. An exhaustive analytic and numerical study of travelling waves reveals the existence of supersonic modes of transformations. The practically important problem of ignition of fast waves by mechanical perturbation is investigated. With the present model, the critical strain necessary to ignite gasless detonation by local perturbations is determined.

PACS. 82.20.Mj Nonequilibrium kinetics – 05.70.Ln Nonequilibrium and irreversible thermodynamics

1 Introduction

Although front propagation accompanying chemical reactions or phase transformations is in many cases controlled by diffusive transfers (of mass or heat), other physical mechanisms of propagation have been identified. A famous example is provided by gaseous detonation [1,2]. Propagation, which in this case results from a coupling between combustion (chemistry) and gas compression (mechanics), is very fast (supersonic), whereas diffusion driven propagation is much slower (subsonic).

In a previous work [3], we proposed that for a number of physical systems, in condensed phases, propagation results from a coupling between chemistry and propagation of elastic waves. Examples of phenomena where a wave of transformation propagates very fast at a velocity of the order of the sound velocity include explosive decomposition of tempered glass under high strain conditions (such as the famous "Prince Rupert drops") [4,5], explosive decomposition of heavy metal azides [6], as well as in semiconductors. It is also a possibility that catastrophic geotechtonic phenomena, such as earthquakes, are due to gasless detonation processes of phase transformations in the earth's crust (for example, explosive decay of a metastable glassy state of rocks to a more stable, polycrystalline phase) [7,8,3]. The hypothesis of phase transformations of rocks induced by a high value of the strain may in fact solve a number of difficulties with the current theory of earthquakes [9]. In this spirit, the explosion of "Prince Rupert's drops" silicate glass matrices may be regarded as a laboratory model of earthquakes. We mention in a somewhat related context the phenomenon of detonation boiling, whereby a front of vapour propagates into overheated fluid, with a fast, albeit subsonic, velocity [10]. Also, some data about the transition between slow and fast heat-mechano-chemical wave modes of, possibly, gasless detonation were discussed in the context of cryochemistry of solids [11]. This physical phenomenon may be very important, as the fast autowave concept may help to explain the mystery of fast chemical evolution of substances in the universe [12].

The standard theory of detonation cannot explain these phenomena. A general model for this class of phenomena was proposed in [3]. The main idea consists in coupling the chemical (or phase) field, c, and the mechanical field, the displacement in the solid, u. We consider systems where a metastable or an unstable state at $c = 0$, coexist with a more stable state at $c = 1$. When the strain field, $(\partial_x u)$ exceeds a certain threshold, $(\partial_x u)_c$, the state of equilibrium at $c = 0$ disappears, therefore inducing a transformation to the stable state $c = 1$. The chemical field influences propagation by modifying the sound velocity in the solid. This model was shown to lead to two kinds of travelling wave solutions: slow (subsonic) waves, driven

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by diffusion, and fast (supersonic) waves, where propagation is induced by the mechanical process. Solutions were explicitly determined in the case where the state $c = 0$ is metastable.

The purpose of this work is to extend the theoretical analysis of the model proposed in [3]. First, it is interesting to know whether the travelling waves found in the case of a metastable kinetics also exist when the $c = 0$ state is unstable, especially since the precise nature of the kinetics of the chemical/phase transformation is not known. Another rather important question is whether these travelling waves are actually observable, in a time dependent problem. This lead us to consider the problem of ignition of a propagating wave, which is an important question for practical applications. In the physical examples we have in mind, waves are produced by a mechanical perturbation. To this end, we study wave ignition by a perturbation of the strain. In order to investigate these issues, we developed a numerical algorithm to integrate the equations of the model.

Section 2 introduces in more details the model equation, introduces the notation, and describes our numerical algorithm. In Section 3, we present our results concerning travelling waves. The analysis of the ignition problem is discussed in Section 4. Finally concluding remarks are presented in Section 5.

2 Theoretical model

Our study is based on the interaction between a chemical (or phase) field, $c(x, t)$ and the displacement field, $u(x, t)$. In the following we restrict ourselves to a 1-dimensional problem. The equations governing the evolution of the system read:

$$\partial_t^2 u - \partial_x (V^2(c)\partial_x u) = 0 \quad (1)$$

$$\partial_t c = f(c) + D\partial_x^2 c + w(c, \partial_x u). \quad (2)$$

Equation (1) is simply the equation of linear elasticity assuming that the stress tensor τ is proportional to the strain, $\partial_x u$: $\tau = E \times \partial_x u$, where E is the Young's modulus [13]. The sound velocity, V, is assumed to depend on c. This is a rather mild assumption, since $V^2 = E/\rho$, and since it is reasonable to expect that E and ρ vary when c varies. We assume in addition that $V^2(c)$ increases monotonically with c:

$$\frac{\mathrm{d}V^2(c)}{\mathrm{d}c} \geq 0. \quad (3)$$

In the physical processes we have in mind, we expect an increase of E and a decrease of ρ when c increases. The importance of this condition was recognized independently by Sornette, in a similar context, using a slightly different approach [9]. In the numerical study, we will use the following form of $V^2(c)$:

$$V^2(c) = V_0^2 + \delta V^2 \tanh(c). \quad (4)$$

On occasions, we have also considered the effect of a viscous term in the elasticity equation (Eq. (1)):

$$\partial_t^2 u - \nu\partial_t\partial_x^2 u - \partial_x(V^2(c)\partial_x u) = 0. \quad (5)$$

As expected, the viscous term introduces some dissipation in the equation of elasticity. Our numerical results, see below, demonstrate that the qualitative behavior of the system is not modified by a small amount of viscosity. We do not consider here plastic deformations, which would presumably lead to a loss of acoustic transparency in the solid, and may stop propagation of fast waves.

Equation (2) describes the kinetics of phase (chemical) transformation. In the absence of the coupling term, w, equation (2) reduces to a standard reaction diffusion equation. The kinetic function, f, was chosen to correspond to a simple chain branched process: $f(c) = Ac^n(1 - c) - kc$, where $n = 1$ or $n = 2$. In the $n = 1$ case (first order kinetics), the $c = 0$ equilibrium state is unstable, whereas in the $n = 2$ case (second order kinetics), it is metastable. The latter type of kinetics was considered in [3]. By redefining the constants, we write the first order kinetic function ($n = 1$) as:

$$f(c) = Ac(1 - c) \quad (6)$$

and the second order kinetic ($n = 2$) as:

$$f(c) = Ac(c - 0.2)(1 - c). \quad (7)$$

It should be kept in mind that in the problems we are interested in, diffusion is extremely small, so diffusion controlled propagation is very slow. We consider here the two cases of kinetics, $n = 1$ and $n = 2$. In the former case, we expect important analogies with the classical problem of autowave propagation (the so-called KPP problem, [16]).

The term w describes the coupling induced by the strain. On general grounds, it is very reasonable to expect that the thermodynamic state of the system is affected by the applied strain, and that too high a strain induces a phase transition. We assume that this term is 0 as long as the strain, $(\partial_x u)$ is less than the threshold value, $(\partial_x u)_c$, and $w(\partial_x u, c) = W_0(1-c)$ when $(\partial_x u)$ has reached $(\partial_x u)_c$. Once turned on, the w term suppresses the metastable or unstable equilibrium at $c = 0$, therefore inducing a phase transition towards the other stable state at $c = 1$. Let τ_w be the time it takes for the w term to turn off, after it has turned on. The time τ_w is an unknown in the problem. Here, we will restrict ourselves to the case $\tau_w \to \infty$: Once the w term has been turned on, it does not turn off again. The other extreme limit $\tau_w \to 0$ can also be considered [14].

In order to investigate the properties of this model, we have integrated numerically the set of coupled equations (1, 2). The u-equation is hyperpolic, whereas the c-equation is parabolic, which leads to different constraints on the numerical algorithms [15].

It is convenient to rewrite equation (1) in terms of the strain field:

$$\partial_t^2(\partial_x u) - \partial_x^2(V^2(c)(\partial_x u)) = 0 \quad (8)$$

and to integrate it numerically as a set of two first order partial differential equations:

$$\partial_t(\partial_x u) = v \tag{9}$$

and:

$$\partial_t v = \partial_x^2(V^2(c)(\partial_x u)). \tag{10}$$

Space derivatives are discretized by finite differences. The solution of equations (9, 10) is time-stepped with a leap-frog scheme. Stability of the numerical scheme is guaranteed by a current condition ($V\Delta t < \Delta x$). In fact, accuracy considerations forced us to use much smaller time steps. The quality of the integration of the elasticity equation was checked by following the propagation of a localized perturbation in the case where $V^2(c)$ is constant. For the numerical studies presented in this work, we used a large integration domain with zero flux boundary conditions. The integration was stopped well before the elastic waves reached the boundaries and before any reflection occurred.

The c-equation is integrated by using a finite difference discretisation, and by using a standard Crank-Nicholson time stepping. The boundary conditions were of Neumann type (zero flux). Overall, our algorithm is second order both in space and time. Our extensive checks of the algorithm accuracy convinced us that our algorithm is properly working.

3 Travelling wave solutions

In [3], travelling wave solutions were obtained in the case where the $c = 0$ state is metastable. The first step consists in noticing that $c(x) = 0$, $\partial_x u(x) = (\partial_x u)_0$ is a solution, provided $(\partial_x u)_0 < (\partial_x u)_c$. Travelling waves propagating at a velocity v_f satisfy the following equations, in the comoving frame ($\xi = x - v_\mathrm{f} t$):

$$-v_\mathrm{f}\partial_\xi c = f(c) + D\partial_\xi^2 c + w(\partial_\xi u, c) \tag{11}$$

$$\partial_\xi((v_\mathrm{f}^2 - V(c)^2)\partial_\xi u) = 0. \tag{12}$$

For travelling waves with a positive velocity, v_f, with $\partial_x u \to (\partial_x u)_0$ and $c \to 0$ when $x \to \infty$, equation (12) can be integrated once leading to:

$$(v_\mathrm{f}^2 - V(c)^2)(\partial_\xi u) = (v_\mathrm{f}^2 - V(0)^2)(\partial_\xi u)_0. \tag{13}$$

It results from equation (13) that if $v_\mathrm{f}^2 < V(0)^2$, then $(\partial_\xi u) \leq (\partial_\xi u)_0 < (\partial_\xi u)_c$, so the coupling term w never turns on. The mechanical coupling can turn on only if $v_\mathrm{f}^2 > V(0)^2$, that is, if the wave is supersonic.

Solutions can be explicitly constructed when the function $f(c)$ is replaced by a piecewise linear function of c: $f(c) = -Kc$ for $c < c_-$, and $f(c) = -K(c - c_+)$ for $c < c_-$. Such an approximation for the kinetic function (Eq. (7)), is expected to provide qualitatively good results. The main conclusion obtained in [3] can be summarized as follows:

(i) There exists a family of slow travelling waves, where the stress remains always smaller than the threshold value $(\partial_x u)_c$. For these waves, propagation is controlled by diffusion, and not by mechanical effects: $v_\mathrm{f} \propto \sqrt{DK}$.

(ii) There exists a family of fast wave solutions, where the strain $(\partial_x u)$ reaches the critical value, so the w term is turned on. The velocity of these waves is supersonic: $v_\mathrm{f} > V(0)$. It was also found that the velocity of the travelling wave increases when $((\partial_x u)_0 - (\partial_x u)_c) \to 0$. When there exists a value of c_*, such that $v_\mathrm{f} = V(c_*)$, equation (13) shows that a difficulty occurs, since equation (13) suggests a divergence of the strain.

We show in this section that similar conclusions can be drawn in the case where $c = 0$ is an unstable state. We will then study the problem numerically, and demonstrate that the travelling wave solutions are indeed observable.

3.1 Analysis when c = 0 is an unstable fixed point

Mathematically, the problem of propagation of a front into an unstable phase is significantly different from the problem of propagation into a metastable phase, even when the coupling w with the mechanical field does not turn on. Instead of a discrete set of travelling wave solutions when $c = 0$ is metastable, a continuum of solution is found: For any $v_\mathrm{f} > v_\mathrm{f}^\mathrm{m}$, one may find a steady front. However, when the initial condition is such that c decays faster than exponentially at $x \to \infty$ the solution tends asymptotically to the slowest travelling wave [16–18].

We show here that in the presence of a non trivial coupling with the velocity field, there exists a continuum of supersonic travelling wave solutions, provided that the front velocity is larger than some finite value.

As in [3], we use a piecewise linear approximation of the function f:

$$\begin{aligned} f(c) &= Kc && \text{for } c < 1/2 \\ f(c) &= K(1-c) && \text{for } c \geq 1/2. \end{aligned} \tag{14}$$

Subsonic travelling waves solutions can be easily found. Introducing $\alpha_\pm = \frac{1}{2D}(-v_\mathrm{f} \pm \sqrt{v_\mathrm{f}^2 - 4KD})$ and $\beta_\pm = \frac{1}{2D}(-v_\mathrm{f} \pm \sqrt{v_\mathrm{f}^2 + 4KD})$ ($\alpha_\pm < 0$, $\beta_+ > 0$, $\beta_- < 0$), the function:

$$\begin{aligned} c(\xi) &= \frac{1}{2(\alpha_+ - \alpha_-)}\Big((\alpha_+ + \beta_+)\exp(\alpha_-\xi) \\ &\qquad -(\alpha_- + \beta_+)\exp(\alpha_+\xi)\Big) && \text{for } \xi > 0 \\ c(\xi) &= 1 - \frac{1}{2}\exp(\beta_+\xi) && \text{for } \xi < 0 \end{aligned} \tag{15}$$

is a solution. This solution satisfies the physical constraint that c should always be positive provided $v_\mathrm{f} \geq 2\sqrt{KD}$. There exists therefore a continuous family of solutions: any velocity larger than $v_\mathrm{f}^\mathrm{m} = \sqrt{KD}$ is possible. However, for a large class of initial conditions, the initial value problem leads to a front propagating at the smallest available velocity: $v_\mathrm{f}^\mathrm{m} = 2\sqrt{KD}$.

Fast waves, where the coupling term w turns on, can also be found. We begin by rewriting equation (13) as:

$$(\partial_\xi u) = \frac{(v_\mathrm{f}^2 - V(0)^2)}{(v_\mathrm{f}^2 - V(c)^2)}(\partial_\xi u)_0. \tag{16}$$

When $v_\mathrm{f}^2 > V(0)^2$, the strain increases when c increases, and may possibly reach $(\partial_\xi u)_c$. Let c_s the value of c, where the strain reaches the critical value $(\partial_\xi u)_c$. The solution of equation 11 may be determined by dividing up the domain into three regions:

(i) $\xi > \xi_\mathrm{s}$, where $c < c_\mathrm{s}$, $\partial_\xi u < (\partial_\xi u)_c$ so $w = 0$;
(ii) $0 < \xi < \xi_\mathrm{s}$, where $c_\mathrm{s} < c < 1/2$, and $\partial_\xi u > (\partial_\xi u)_c$ so $w \neq 0$,
(iii) $\xi \leq 0$, where $c \geq 1/2$, and $w \neq 0$.

Explicitly, one finds for $\xi \leq 0$ (region (iii)):

$$c(\xi) = (1 + W/K) - (1/2 + W/K)\exp(\beta_+\xi); \tag{17}$$

for $0 < \xi \leq \xi_\mathrm{s}$ (region (ii)):

$$c(\xi) = -W/K + \frac{(1/2 + W/K)}{(\alpha_- - \alpha_+)}\Big((\alpha_- + \beta_+)\exp(\alpha_+\xi) - (\alpha_+ + \beta_+)\exp(\alpha_-\xi)\Big); \tag{18}$$

and for $\xi_\mathrm{s} < \xi$ (region (i)):

$$c(\xi) = \Big(\big(\frac{\alpha_-}{\alpha_+ - \alpha_-}\big)\frac{W}{KD_+} + \big(\frac{\alpha_+ + \beta_+}{\alpha_- - \alpha_+}\big)\big(\frac{1}{2} + \frac{W}{K}\big)\Big)\exp(\alpha_+\xi) + \Big(\big(\frac{-\alpha_+}{\alpha_+ - \alpha_-}\big)\frac{W}{KD_-} + \big(\frac{\alpha_+ + \beta_+}{\alpha_+ - \alpha_-}\big)\big(\frac{1}{2} + \frac{W}{K}\big)\Big)\exp(\alpha_-\xi) \tag{19}$$

where $D_\pm = \exp(\alpha_\pm\xi_\mathrm{s})$, and the condition that $c(\xi_\mathrm{s}) = c_\mathrm{s}$ imposes that:

$$c_\mathrm{s} = -\frac{W}{K} + \left(\frac{1}{2} + \frac{W}{K}\right)\left(\frac{\alpha_- + \beta_+}{\alpha_- - \alpha_+}D_+ + \frac{\alpha_+ + \beta_+}{\alpha_+ - \alpha_-}D_-\right). \tag{20}$$

In the case we are considering, where D is small and $v_\mathrm{f}/KD \gg 1$, $\beta_+ \simeq K/v_\mathrm{f}$, $\alpha_- \simeq -v_\mathrm{f}/D$ and $\alpha_+ \simeq -K/v_\mathrm{f}$. In addition, D_+ is *a priori* much larger than D_-, which allows to simplify equation (20) to:

$$\xi_\mathrm{s} = \frac{v_\mathrm{f}}{K}\ln\Big(\frac{1/2 + W/K}{c_\mathrm{s} + W/K}\Big)\cdot \tag{21}$$

The solution thus explicitly determined depends on two parameters: v_f and c_s. The two parameters are related by the relation:

$$(\partial_\xi u)_c = \frac{(v_\mathrm{f}^2 - V(0)^2)}{(v_\mathrm{f}^2 - V(c_\mathrm{s})^2)}(\partial_\xi u)_0 \tag{22}$$

therefore demonstrating the existence of a 1 parameter family of solution. The additional physical constraint that c should be always positive restricts the range of possible solution. In the case we are interested in $v_\mathrm{f} \gg (KD)^{1/2}$, an analysis of equation (19) shows that the value of c remains always positive provided

$$v_\mathrm{f} \geq \Big(\frac{DW}{c_\mathrm{s}}\Big)^{1/2}. \tag{23}$$

This relation is to be compared with the analysis of [3] in the case where $c = 0$ is metastable (see Eq. (11) of [3]), where an equality was found instead of the inequality, (Eq. (23)). Combining equations (4, 22) and (23) (replacing the inequality by an equality), one finds:

$$v_\mathrm{f}^2 = V(0)^2 + \frac{(\partial_\xi u)_c}{(\partial_\xi u)_c - (\partial_\xi u)_0}\delta V^2\tanh(c_\mathrm{s}) \geq \Big(\frac{DW}{c_\mathrm{s}}\Big). \tag{24}$$

The inequality in equation (24) shows that c_s must be larger than a given quantity, hence, v_f must be larger than a minimum velocity. Similarly to the purely diffusive case, one finds that the solutions for c are possible provided the velocity v_f is large enough. In the limit $((\partial_\xi u)_c - (\partial_\xi u)_0) \to 0$, $c_\mathrm{s} \gtrsim ((\partial_\xi u)_c - (\partial_\xi u)_0)^{-1/2}$ which implies in turn that the smallest possible value of v_f is larger than $((\partial_\xi u)_c - (\partial_\xi u)_0)^{-1/4}$.

At this point, we have shown the existence of a family of travelling wave solutions depending on one parameter. From this point of view, the situation for fast waves is completely similar to the situation for slow, diffusive waves.

Although there is no theorem proving that for initial conditions decaying fast enough when $\xi \to \infty$ the solution of the full time dependent problem behaves when $t \to \infty$ as a front moving with the lowest possible velocity, heuristic arguments suggest that it should be the case in our problem. If it is indeed the case, then the behavior of the time dependent solution, and the observed velocities of the travelling waves should be identical to what happens for the metastable case. For lack of a genuine proof, we will rest on numerical simulations to demonstrate this fact.

The difficulty about the possible divergence of the strain when the waves are not fast enough ($v_\mathrm{f}^2 < V(1)^2$), obvious from equation (16), shows that the strain profile cannot be stationary. This is true when $c = 0$ is either stable or metastable. However, the c profile, which is not sensitive to the details of the strain profile, may be stationary. The results of numerical simulations presented in the following subsection allow us to address this problem.

4 Numerical study of travelling waves

In a system initially at rest ($c = 0, (\partial_\xi u) = (\partial_\xi u)_0 = 1$) we introduce at $t = 0$ a mechanical perturbation near $x = 0$. Postponing the discussion of the ignition problem to the next section, we simply state that fast supersonic waves may be ignited when the mechanical perturbation is strong enough.

Figure 1 shows travelling wave solution when the kinetics is of second order ($c = 0$ is metastable) when $(\partial_x u)_c = 1.075$, Figure 1a, and when $(\partial_x u)_c = 1.00625$, Figure 1b. The dashed curves show the c profile, and the full lines show the strain profiles. The solution is moving right, two consecutive solutions are separated by $\Delta T = 6.25$. The velocities of the c-front were in both cases found to be supersonic, as expected: $v_\mathrm{f} = 5.33$ in

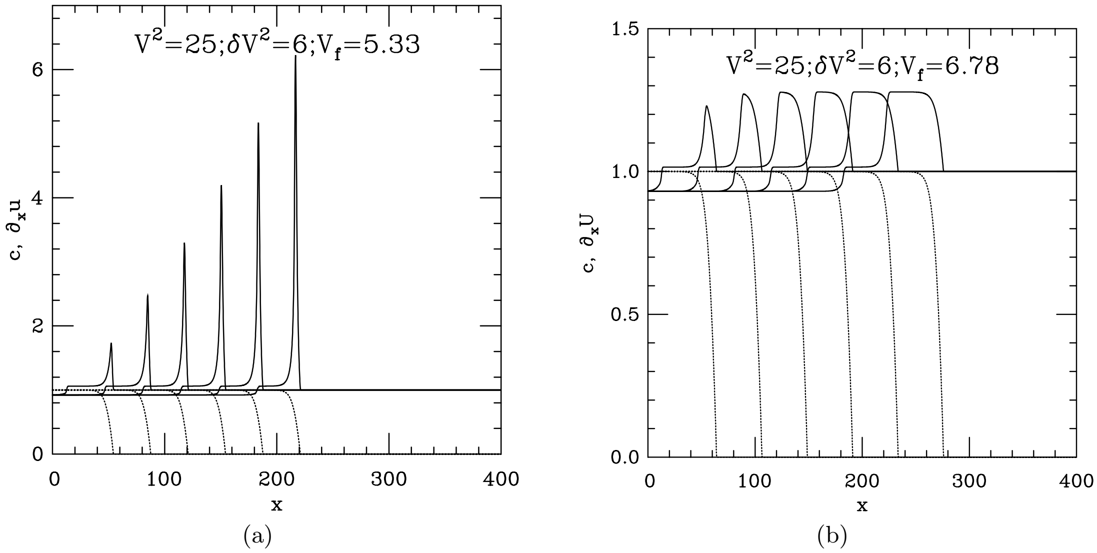


Fig. 1. Propagation of a front in the case of second order kinetics. The dashed lines correspond to the c profile, the full lines to the strain profile. The solution propagates from left to right; two consecutive solutions are separated by $\Delta T = 6.25$. Fast waves are shown, propagating at a supersonic velocity: $v_\mathrm{f} = 5.33$ ($(\partial_x u)_c = 1.075$) (a) and $v_\mathrm{f} = 6.78$ (b) ($(\partial_x u)_c = 1.00625$); the sound velocity is $V(0) = 5$. In Figure 1a, the wave velocity is smaller than $V(1) = 5.44$; and the strain develops a spike of strain, whose amplitude grows roughly linearly with time. A small amount of viscosity does not change qualitatively the picture. In Figure 1b, the wave velocity is larger than $V(c = 1)$, and the strain profile reaches a steady shape in the region of the front. The parameters used in the simulation are $\Delta x = 0.1$, $\Delta t = 0.0025$, $D = 1.$, $u = 0.2$, $A = 1$.

Figure 1a, $v_\mathrm{f} = 6.78$ in Figure 1b, both larger than $V(0) = 5$. However, in Figure 1a, the front velocity is smaller than $V(c = 1)$ ($\delta V^2 = 6$, so $V(c = 1) = 5.44$), whereas in Figure 1b, it is larger. The striking consequence is that in Figure 1a, the very narrow peak in the strain profile grows seemingly without limit, whereas in Figure 1b, the strain profile evolves towards a steady profile in the front region. We checked that in agreement with equation (13), $(v_\mathrm{f}^2 - V(c)^2)(\partial_x u)$ is constant in the front region. In the conditions of Figure 1a, a small amount of viscosity does not prevent the formation and growth of an ever growing peak of strain. Figure 1a demonstrates that the growth of the maximum of strain is roughly linear in time.

The difference of behavior between Figure 1a ($v_\mathrm{f} < V(1)$) and Figure 1b ($v_\mathrm{f} > V(1)$) can be understood qualitatively. Behind the front, strain perturbations propagate with a velocity $V(1)$. Hence, when $v_\mathrm{f} > V(1)$, the strain perturbation is made of a front propagating ahead of the perturbation, with a velocity v_f, and a front behind it, moving at a velocity $V(1)$. As a result, the size of the region where the strain is perturbed grows linearly in time, as observed numerically (Fig. 1b). In the other case, when $v_\mathrm{f} < V(1)$, the front at the rear of the perturbation would propagate at $V(1)$, and would run into the slower front ahead. As a result, the strain is concentrated over a narrow region, as observed (Fig. 1a).

This points out to a limitation of our model: when $(\partial_x u)_c - (\partial_x u)_0$ is too large, the wave velocity is too small, and the strain $\partial_x u$ seems to grow for ever (in spite of this difficulty, the c-front is observed to move steadily). Nonlinear aspects of elasticity theory, such as plasticity, must be taken into account to solve this problem. On the other hand, when $(\partial_x u)_c - (\partial_x u)_0$ is not too large, the model is consistent in the sense that the generated strain remains finite.

Qualitatively very similar results were observed in the case where the kinetics is of first order ($c = 0$ is unstable). The solutions in physical space are essentially indistinguishable from the solutions shown in Figure 1 in the second order kinetics case. A spike of strain grows linearly with time when the velocity is too small.

In all cases, the wave velocity decreases when $(\partial_x u)_c - (\partial_x u)_0$ increases. The dependence of the front velocity v_f as a function of the threshold $(\partial_x u)_c - (\partial_x u)_0$ is shown in Figures 2a, b, in the case of a second order kinetics (Fig. 2a) and in the case of a first order kinetics (Fig. 2b). The two curves are strikingly similar, and show a divergence of the wave velocity when $(\partial_x u)_c - (\partial_x u)_0 \to 0$, as expected. Figure 2c shows the velocity v_f as a function of $((\partial_x u)_c - (\partial_x u)_0)^{-1/4}$, in the case of the second order kinetics. The dependence of the velocity is as much as one can tell linear for large values of $((\partial_x u)_c - (\partial_x u)_0)^{-1/4}$, in agreement with the analytic estimates. Again, the curve obtained in the case of a first order kinetics would be completely similar.

Figure 2d shows the dependence of the front velocity as a function of W_0. Not surprisingly, v_f is an increasing function of W_0. Based on equations (4,22) and (23), one expects that the wave velocity will behave as $W^{1/4}$ when $W \to \infty$. This is consistent with our numerical results.

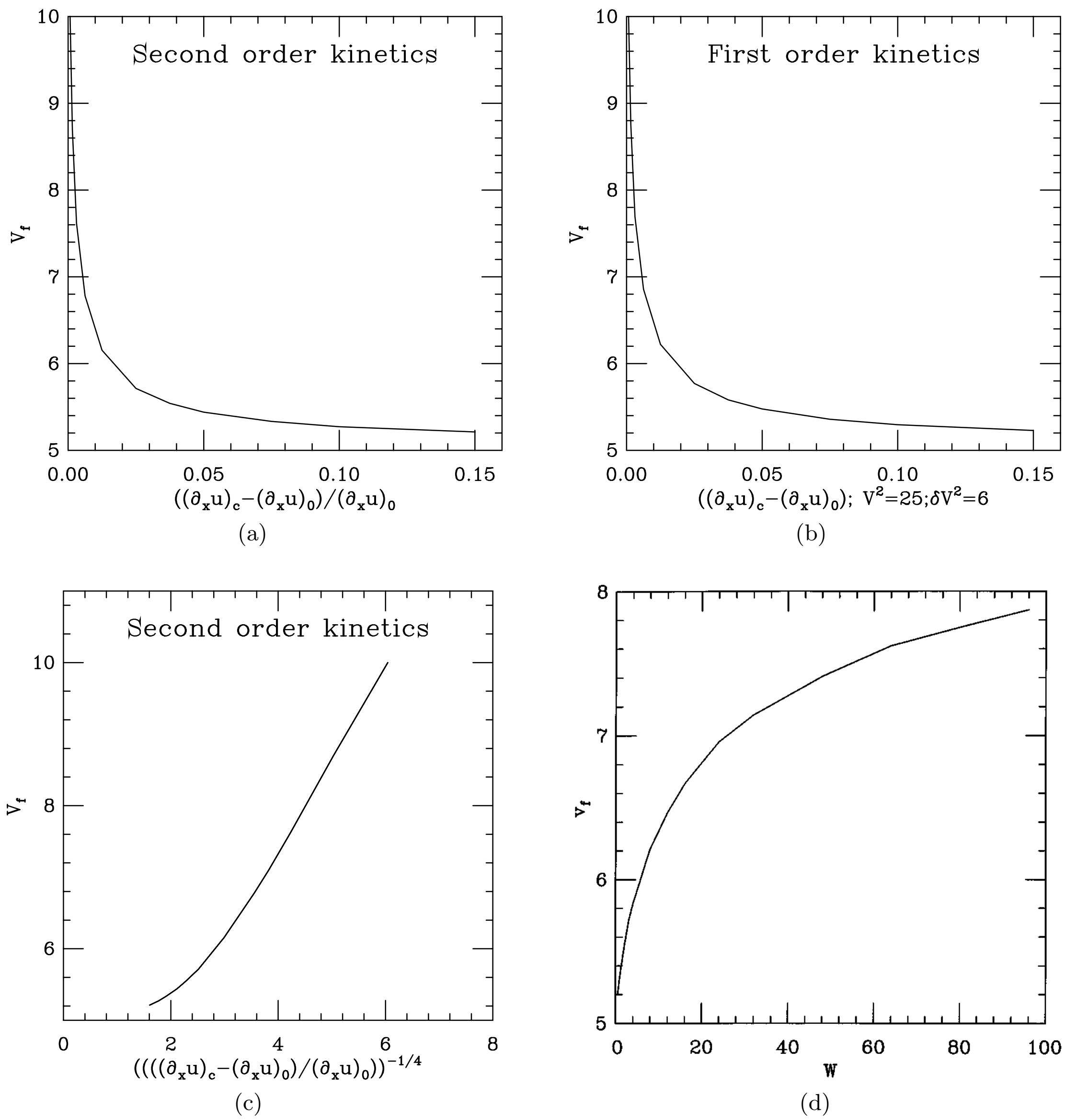


Fig. 2. Dependence of the velocity of propagation of fronts as a function of the parameters. Figures 2a-c show the dependence of v_{f} as a function of $(\partial_x u)_c$, and Figure 2d show the dependence of v_{f} as a function of W. Figure 2a (respectively 2b) shows v_{f} as a function of $(\partial_x u)_c$ for a second order (respectively first order) kinetics. In both cases, the velocity tends to $V(0)$ when $(\partial_x u)_c - (\partial_x u)_0$ is large, and to ∞ when $(\partial_x u)_c - (\partial_x u)_0 \to 0$. Figure 2c shows the data of Figure 2a as a function of $((\partial_x u)_c - (\partial_x u)_0)^{-1/4}$, in agreement with the prediction that the velocity diverges with a $-1/4$ power. Figure 2d shows the dependence of v_{f} as a function of W_0. The slow increase of v_{f} when W increases is consistent with a $W^{1/4}$ behavior.

5 Ignition of fast waves

The phenomena we are interested in, as explained in the introduction, involve in a crucial way mechanical perturbations. This suggests to consider the following problem: starting from a uniform state, at rest, initially in the metastable/unstable phase ($c = 0$) with a uniform strain $(\partial_x u)_0$, one introduces at $t = 0$ a mechanical perturbation localized near $x = 0$: $\partial_x u = (\partial_x u)_0 + \delta u F(x)$, where $F = 0$, except in a neighborhood of $x = 0$ ($\max F(x) = 1$). The problem is to understand the response of the system to this perturbation.

The evolution of the system can be qualitatively understood by considering first the case where $\delta V^2 \to 0$ ($V^2(c) = V^2(0)$). The wave equation (1) for $(\partial_x u)$ can then be easily solved:

$$(\partial_x u)(x,t) = \frac{1}{2}\Big((\partial_x u)(x - V(0)t, 0) + (\partial_x u)(x + V(0)t, 0)\Big) \qquad (25)$$

where $(\partial_x u)(x,0)$ is the initial condition: $(\partial_x u)(x,0) = (\partial_x u)_0 + \delta u F(x)$. In deriving equation (25), it is assumed that at $t = 0$, $\partial_t u(x, t = 0) = 0$. After a transient, the solution at time $t > 0$ will be made of two localized perturbations of amplitude $\delta u/2$ (half the amplitude of the initial condition), located around $x = \pm V(0)t$. This leads to the three different possibilities:

Regime A: If $\delta u \le ((\partial_x u)_c - (\partial_x u)_0)$, the value of the strain is always smaller than the threshold value $(\partial_x u)_c$. As a consequence, the w term never turns on. As such, the chemical/phase transformation is unaffected by the mechanical perturbation, which is simply radiated away.

Regime B: If $((\partial_x u)_c - (\partial_x u)_0) < \delta u \le 2((\partial_x u)_c - (\partial_x u)_0)$, then, the mechanical perturbation is initially strong enough to turn on the w term. As a result, the chemical wave starts. However, the initial strain perturbation eventually decays as it is radiated away from the $x = 0$ region, and after a while, the amplitude of the strain is everywhere lower than the excitation threshold, $(\partial_x u)_c$. This implies that the strain wave is not strong enough to maintain the mechanical coupling; as a result, only the diffusive mode of propagation is possible, after a transient.

Regime C: If $2((\partial_x u)_c - (\partial_x u)_0) < \delta u$ the amplitude of the strain at $x = \pm V(0)t$ is always larger than the threshold value $(\partial_x u)_c$, so the chemical/phase transformation is triggered by the mechanical wave; fast waves are excited.

Effectively, a non zero δV^2 in the mechanical equation adds a source of strain, due to the coupling with c. As an example, a slow front driven by diffusion will generate a strain signal, which will propagate ahead of the front. The problem of strain radiation by a chemical front has been considered, in a somewhat related context in [19]. The result of this radiation is that in the case B above, the amplitude of the strain pulse propagating ahead of the front is affected, and as a consequence, the threshold for the ignition of fast wave. An accurate determination of the radiated strain by a front is therefore necessary to estimate the ignition threshold for fast waves. Obviously, in the regime A, $\delta u < ((\partial_x u)_c - (\partial_x u)_0))$, the conclusion that the chemical/phase transformation does not start is unaffected by the radiation of strain waves.

To estimate the amount of strain radiated by a front, it is convenient to expand the solution of equation (1) in power of $\delta V^2/V(0)^2$ considered as a small parameter:

$$(\partial_x u) = (\partial_x u)^0 + (\partial_x u)^1 + ... \tag{26}$$

where $(\partial_x u)^n = \mathcal{O}(\delta V^{2n}/V(0)^{2n})$. Substituting in equation (1) one finds the two first orders:

$$\partial_t^2(\partial_x u)^0 - \partial_x^2(V(0)^2\partial_x u)^0 = 0 \tag{27}$$

$$\partial_t^2(\partial_x u)^1 - \partial_x^2(V(0)^2\partial_x u)^1 - \partial_x^2\big((\delta V^2(c))(\partial_x u)^0\big) = 0 \tag{28}$$

where $\delta V^2(c) \equiv (V^2(c) - V^2(0))$. This initial condition is $(\partial_x u)^0 = (\partial_x u)(x, t = 0)$ and $(\partial_x u)^1 = 0$. The solution of equation (27) is simply given by equation (25). Once $(\partial_x u)^0$ is known, equation (28) can be solved in closed form:

$$(\partial_x u)^1 = -\frac{1}{2V(0)} \times \int_0^t \mathrm{d}t' \Big[\partial_x(\delta V^2(c)(\partial_x u)^0)(x - V(0)(t-t'), t') - \partial_x(\delta V^2(c)(\partial_x u)^0)(x + V(0)(t-t'), t')\Big]. \tag{29}$$

In the regime B when $\delta V^2 = 0$, a subsonic wave of chemical/phase transformation is ignited. A front of strain is radiated ahead of the chemical front, propagating at a velocity v_f. The distance between the chemical and the strain front grows like $(V(0) - v_\mathrm{f})t$. To estimate the amplitude of the strain perturbation, we simply perform the integral equation (29) near the point reached by the radiated strain wave at time t. Specifically, $\int_0^t \mathrm{d}t'\partial_x(\delta V^2(c)(\partial_x u)^0)(x - V(0)(t-t'), t')$ is rewritten as is written as $\frac{1}{(V(0)-v_\mathrm{f})}\int \mathrm{d}\xi \partial_x(\delta V^2(c)(\partial_x u)^0)(\xi, 0)$ by using the fact that, in the integrand, the function $\delta V^2(c)(x, t) = \delta V^2(c)(x - v_\mathrm{f}t, 0)$ (steadily propagating chemical front), and by using the change of variable $t' = t - x/(V(0) - v_\mathrm{f})$. The amplitude of the radiated strain wave is then simply:

$$u_1 = \frac{(V^2(c=1) - V^2(c=0))}{V(0)(V(0) - v_\mathrm{f})}(\partial_x u)_0. \tag{30}$$

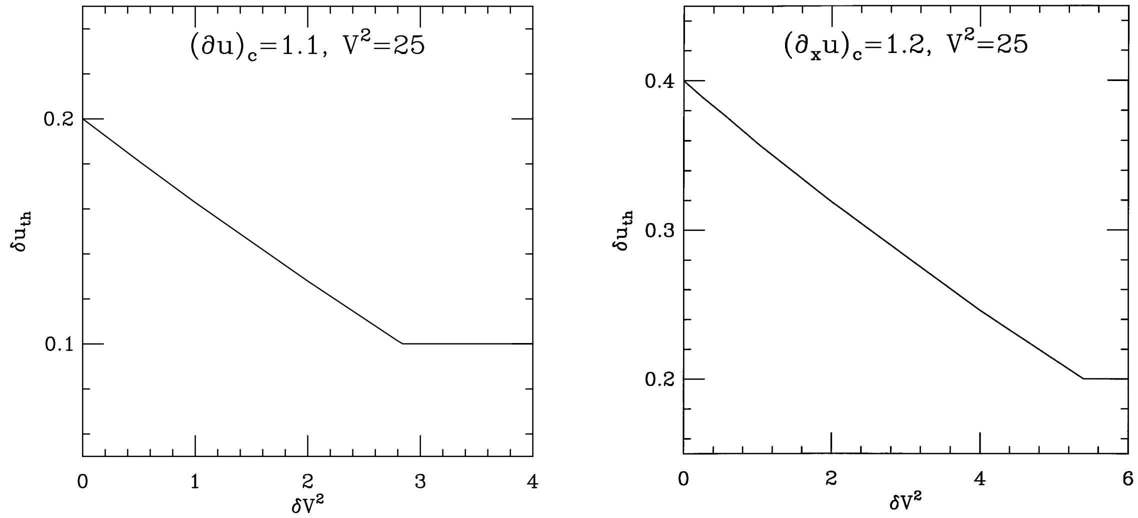
The strain wave generated by a subsonic chemical wave has been computed by numerical simulation of the equations (1, 2), and shown to be in very good agreement with the prediction of equation (30).

The strain generated by the subsonic front enhances the initial strain pulse, $(\partial_x u)^0$. As a result, the slow, subsonic chemical wave becomes supersonic if the amplitude of the initial strain wave, $\delta u/2$ plus the amplitude generated by the slow front, u^1, becomes larger than $(\partial_x u)_c - (\partial_x u)_0$. This implies that the threshold of ignition of fast waves is

$$\delta u_\mathrm{th} \approx \inf\Big(2((\partial_x u)_c - (\partial_x u)_0 - u_1), ((\partial_x u)_c - (\partial_x u)_0)\Big). \tag{31}$$

In equation (31), we explicitly use the fact that the ignition threshold for fast waves cannot be less that the ignition threshold for slow waves, $(\partial_x u)_c - (\partial_x u)_0$. This opens the possibility that when $(\partial_x u)_c - (\partial_x u)_0$ is small enough, a mechanical perturbation can only excite fast waves. Equation (31) comes from an expansion in powers of δV^2, and effectively assumes that the radiated strain waves remain small.

The prediction of equation (31) has been tested by solving directly the partial differential equations equation (1, 2). The problem is complicated by the fact that the ignition threshold depends in fact on the precise shape of the function F. As an example, the measured ignition threshold, defined as the amplitude δu_th above which a fast wave is generated, was in fact found to depend on the overall size over which the function F is localized (in other words, on the function F_Δ, defined as $F_\Delta(x) = F(x/\Delta)$).



(a) (b)

Fig. 3. The ignition threshold of fast waves as a function of ∂_V^2 for $(\partial_x u)_c = 1.1$ (a) and $(\partial_x u)_c = 1.2$ (b); $(V(0)^2 = 25$, $(\partial_x u)_0 = 1)$. The ignition threshold decreases roughly linearly when δV^2 increases, until it reaches $(\partial_x u)_c - (\partial_x u)_0$, as expected from equation (31).

This dependence can be understood by carefully investigating the transient regime shortly after the mechanical perturbation has been applied. In view of this dependence, it would be more correct to interpret equation (31) as an upper bound for the ignition threshold: the details of the transients may lead to a lower ignition threshold, but any perturbation with an amplitude higher than $\delta u_{\rm th}$ will necessarily lead to the nucleation of a fast wave.

Still, equation (30) predicts qualitatively the correct behavior of the ignition threshold (for a given shape of the function F) on the other parameters of the problem, such as $V(0)^2$, δV^2 and $(\partial_x u)_c$ ($(\partial_x u)_0$ being fixed). As an example, we show, Figure 3, the dependence of the ignition threshold on δV^2, at several values of $(\partial_x u)_c$: $(\partial_x u)_c = 1.1$ (Fig. 3a) and $(\partial_x u)_c = 1.2$ (Fig. 3b). As predicted by equation (31), the ignition threshold $\delta u_{\rm th}$ is equal to $2((\partial_x u)_c - (\partial_x u)_0)$ when $\delta V^2 \to 0$. The ignition threshold decreases roughly linearly when δV^2 increases, until it reaches the constant value $\delta u_{\rm th} = ((\partial_x u)_c - (\partial_x u)_0)$ at large values of δV^2. The fact that the ignition threshold is not strictly linear as a function of δV^2 is not unexpected, since equation (31) comes from the lowest order in a perturbation expansion in δV^2. In the same spirit, Figure 4 shows the dependence of the ignition threshold as a function of the the value of the threshold $(\partial_x u)_c$, at fixed δV^2 ($\delta V^2 = 2$ in Fig. 4a and $\delta V^2 = 4$ in Fig. 4b). When $((\partial_x u)_c - (\partial_x u)_0)$ is small enough, the ignition threshold is equal to $((\partial_x u)_c - (\partial_x u)_0)$. At larger values, a change of slope from 1 to ≈ 2 is observed in the curves, as expected from equation (31). As before, although deviations from the predicted behavior are observed, the qualitative results are well captured by equation (31).

The estimates presented in this section suggest that the ignition threshold for fast waves should be essentially independent of the parameter W; this is fully consistent with our numerical results.

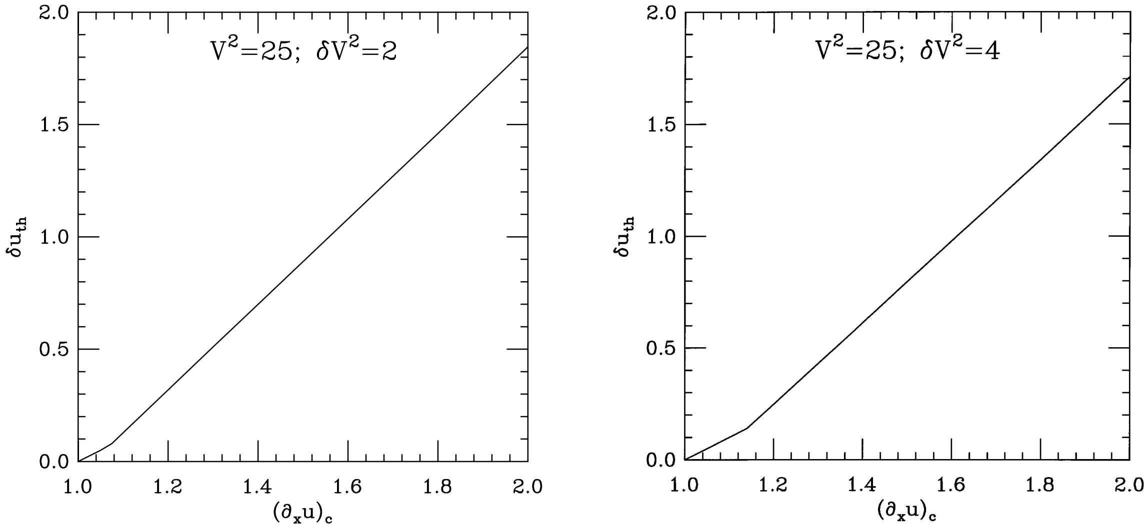
6 Conclusions

In this article, we have explored a number of properties of the model proposed in [3] in order to describe a number of fast chemical or phase transformation. We have first extended the results concerning the existence of travelling waves with second order kinetics to first order kinetics. Our numerical results have demonstrated that fast travelling waves spontaneously appear for a large class of initial conditions. Finally, we have considered the problem of ignition of fast waves by mechanical perturbations, and computed the ignition threshold of supersonic waves.

Our results concerning the growth of a strain spike for otherwise steadily propagating c-fronts suggest that our model, in its present version, is incomplete, and that nonlinear elasticity effects, such as plasticity, should also be included. We believe that this problem can be easily fixed.

Although we have not explicitly obtained analytical stability results for the fast fronts, our numerical results suggest that fronts are stable in 1-dimension. Results concerning the stability of fronts in higher dimension, or in the presence of impurities would be of interest for more physical applications.

The proposal that propagation may be induced by a coupling between phase transformation and mechanics, as described by the model equations (1,2) remains to be explored experimentally. The key question consists in proving that during the decomposition of a metastable phase, eventually leading to explosion, a phase/chemical transformation occurs and couples to elastic waves.



(a) (b)

Fig. 4. The ignition threshold of fast waves as a function of $(\partial_x u)_c$ for $\delta V^2 = 2$. (a) and $\delta V^2 = 4$. (b); $(V(0)^2 = 25$, $(\partial_x u)_0 = 1.)$. The ignition threshold is equal first to $(\partial_x u)_c - (\partial_x u)_0$, and then increases roughly like $2((\partial_x u)_c - (\partial_x u)_0)$, as expected from equation (31). Roughly linearly when δV^2 increases, until it reaches $(\partial_x u)_c - (\partial_x u)_0$.

We believe that it deserves a careful experimental investigation.

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