

Cold ignition of combustion-like waves of cryo-chemical reactions in solids

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Abstract. Fronts of weakly exothermal chemical reaction may propagate in solids at very low temperatures ($4\text{ K} \leq T \leq 77\text{ K}$) thanks to a quite unusual mechanism, involving a feedback between the heat produced by the reaction and the disruption of the solid matrix. In this class of phenomena, the reaction may be induced by mechanical constraints, without a large elevation of temperature. On the basis of a simple phenomenological model, we investigate ignition of a propagating front by initially (i) disrupting a localized zone of the solid matrix, or by (ii) introducing a temperature jump, leading to a thermal shock with strong temperature gradients. In particular, we show that reaction can be initiated by disrupting only a very small fraction of the sample. Applications to the problem of initiation of solid explosives by friction or shocks is briefly discussed.

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1 Introduction

Classical combustion at usual temperature involves heat release by exothermal reactions, which accelerates the chemical transformation due to a strong dependence of the chemical reaction rate. Typically, the reaction term has an Arrhenius dependence of the form $\exp(-E_a/RT)$ [1,2]. According to this picture, propagation of combustion fronts should become essentially impossible at very low temperature when the heat generated by the reaction is small, since the reaction rates remains always negligibly small. The propagation of waves of chemical reactions observed in solid phases at very low temperature and for weakly exothermal reactions is therefore a surprising phenomenon, which *can not* be explained by standard combustion theory [3]. It turns out that the mechanism making propagation possible involves brittle disruption of the material, which permits a release of energy, which in turns starts the chemical reaction. While heat is rapidly liberated, the rapid thermal variation induces disruption ahead of the reaction zone, leading to front propagation.

The description of these phenomena therefore requires theoretical models incorporating a coupling between the fields of chemical concentrations or temperature and the mechanical state of the solid. The main physical idea, which was used in the models proposed in [3,4] consists in assuming that (i) chemical activation is happening because of disruption of the solid matrix, and (ii) the

chemical transformations induce effectively a chemical or thermal stress, which in turn induces brittle fracture, allowing the reaction to propagate. The model proposed in [3] assumes that the mechanical state of the system is determined by the temperature field only, by assuming that stress and temperature gradient are simply related, and that a temperature gradient exceeding a certain threshold leads to a rupture and a dispersion of the solid matrix, which in turn allows the reaction to start. The other model introduces an explicit coupling between the chemical (or thermal field) and elastic waves [4]. One of the main physical assumption is that reaction starts whenever the stress exceeds a certain threshold. The existence of these two different mechanisms of propagation is strongly suggested by experimental observations [5]. The models thus proposed introduce critical stresses or temperature gradients, above which reaction starts. These parameters play a crucial role in the chemical reactions at very low temperature we are considering here.

It is tempting to draw an analogy between the purely thermal mode of propagation in cryo-chemistry [3] and the “slow, classical combustion regime”, and between the mode involving gasless, supersonic elastic waves [4] and the “detonation regime” in gaseous combustion. Yet, the models predict that propagation in the models of cryochemical reactions exhibits a number of features, which are very different from what is known in usual combustion. As an example, in the thermal mode, one finds that the front velocity is essentially *independent* of the heat

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diffusivity [6]. In the gasless detonation regime, a jump in *stress*, not pressure is expected.

In this article, we consider the problem of nucleation, or ignition, as it is called in combustion theory, of travelling combustion waves in the thermal model. The description of the formation of a combustion/detonation wave is the simplest genuinely time dependent problem that may be investigated. This problem is very important both for conceptual and for practical reasons. Ignition has been extensively studied in the context of combustion [1], or in phase transitions [7]. A number of theoretical results have been obtained for the problem of ignition of propagating waves in the detonation regime [8]. Here, we present a theoretical analysis of ignition in low temperature, solid phase chemistry, in the thermal regime. The remarkable feature is that combustion waves can be ignited without injecting heat in the system, contrary to what happens in usual combustion. We study how ignition takes place by (i) disruption a small fraction of the sample, and (ii) introducing a temperature jump of very small amplitude. Physically, the unusual nature of the ignition problem is due to the fact that the temperature gradient, not the temperature itself, controls the chemical transformation.

2 Theoretical model

As explained in the introduction, it is assumed that reaction can proceed only when the solid matrix becomes dispersed. In the model proposed in [3], brittle fracture is postulated to result from a thermal shock: a temperature gradient larger than a critical value, $(\partial_x T)_c$, induces a disruption of the matrix, and chemical reaction may start, therefore leading to heat release for a time τ . The model reads:

$$\partial_t T = D \partial_x^2 T + Q \quad (1)$$

$$\begin{aligned} Q &= 0 & \text{as long as } |\partial_x T| < (\partial_x T)_c \\ &= Q_0 & \text{for a time } \tau \text{ after } |\partial_x T| \text{ has reached } (\partial_x T)_c. \end{aligned} \quad (2)$$

This phenomenological model rests on very simplified assumptions; it cannot be derived at the moment from first principles. However, the model defined by equations (1,2) rests on well-established experimental results. A more precise model must incorporate the fact that solid disruption is induced when a gradient (of stress, temperature,...) exceeds a threshold, as described in our model. As such we expect that the conclusions obtained with our simplified model will be of broader validity.

In this model, one may determine travelling wave solutions, by solving:

$$-v \partial_\xi T = D \partial_\xi^2 T + Q \quad (3)$$

with $\xi \equiv x - vt$. The solution can be easily determined. It is piecewise exponential. By imposing the proper boundary

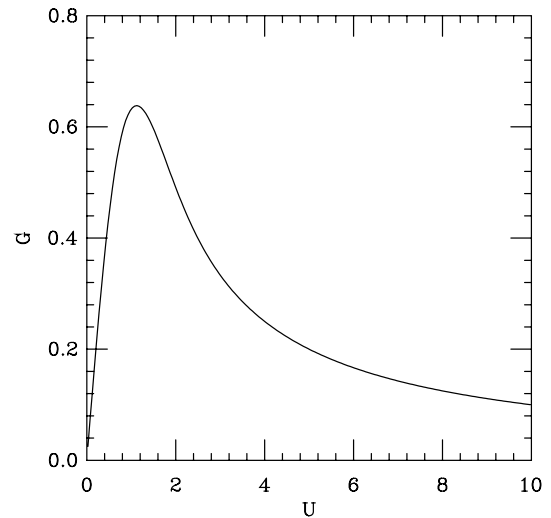


Fig. 1. The curve of existence of the propagating waves. Solutions exist when the (dimensionless) velocity, U is related to the (dimensionless) threshold G , defined by equation (5), by the relation (4), plotted here. For $G \leq 0.64$, two branches of solutions exist. The branch of slow waves ($U \lesssim 1.121$) is not accessible in numerical experiments.

conditions at $\xi \rightarrow \pm\infty$ one obtains [3]:

$$G = \left(1 - \exp(-U^2)\right)/U \quad (4)$$

where:

$$U = v \left(\frac{\tau}{D}\right)^{1/2} \quad \text{and} \quad G = \left(\frac{(\partial_x T)_c}{Q_0}\right) \left(\frac{D}{\tau}\right)^{1/2}. \quad (5)$$

Two solutions exist when $G \leq G_c \approx 0.64$, see Figure 1. In the limit $G \rightarrow 0$, one solution has a low velocity: $v \approx D(\partial_x T)_c/(Q_0\tau)$, and a fast velocity: $v \approx Q_0/(\partial_x T)_c$.

The analytic study of the time dependent problem is completed by a numerical integration of the partial differential equations (1, 2). A standard centered finite difference discretisation is used. The time integration is performed with a Crank Nicholson algorithm [9]. To check the accuracy of the algorithm, we ignited a travelling wave solution, and compared the wave velocity with the exact result equation (4). Because of the intrinsically discontinuous nature of the model, the velocity of the front converges more slowly to its exact value than Δt^2 (we find a convergence in Δt^x , $x \lesssim 1$).

We conclude this section by noting that the slow mode of propagation has never been observed in our numerical experiments. Even when a wave very close to the analytic solution corresponding to the slow mode is initiated, the fast wave quickly takes over. This observation is at odds with the appearance in laboratory experiments of a long transient, where the slow wave could be observed before the fast wave took over [3]. The understanding of this discrepancy will require a detailed investigation of the instability of the slow wave, a problem we will not address here (the stability of the fast mode of propagation has been established in [10]). In the following, we refer only to the fast mode of propagation.

3 Cold ignition by brittle fracture

Brittle fracture plays a crucial role, both in the ignition and in the propagation of fronts of chemical reactions in solid phases at very low temperature. The ignition of reactions in these circumstances may start without any significant input of heat. This situation should be contrasted with the equivalent problem in combustion, in usual conditions, where a large amount of heat must be provided to start the reaction.

To illustrate this point, we first consider the effect of a localized brittle destruction, modelled by turning on the heat production term Q , at time $t = 0$ in the zone of destruction. With this initial condition, we demonstrate that a wave may start if the size of the fractured region, Δ , is larger than a critical size Δ_c . We now proceed to analyse this problem.

3.1 Ignition by a brittle fractured zone in one-dimension

To understand the generation of waves when a localized fractured region is introduced at $t = 0$, we notice that the reaction will generate heat ($Q \neq 0$ for a time τ after the material has been fractured). As a result of this localized (inhomogeneous) heat release, a flux is created, hence the temperature derivative becomes non zero. When the heat released, equal to the product of Q by the size of the fractured region, is large enough, then the temperature gradient may reach the critical value, $(\partial_x T)_c$, and a chemical wave may start.

The qualitative argument above may be made more rigorous by using the explicit solution of the heat equation with a source term in $d = 1$ space dimension:

$$T(x, t) = \int_0^t \frac{dt'}{(4\pi D(t-t'))^{1/2}} \times \int_{-\Delta/2}^{\Delta/2} Q(x', t') \exp\left(-\frac{(x-x')^2}{4D(t-t')}\right) dx'. \quad (6)$$

The localized character of the source term is explicitly taken into account in the equation above. The fact that the highest value of the heat flux is reached at the boundary of the fractured zone is physically reasonable, and can be justified by a precise analysis. As long as the threshold value $(\partial_x T)_c$ has not been reached before, the temperature derivative at $x = \Delta/2$ is simply:

$$\partial_x T(\Delta/2, t) = -Q_0 \int_0^t \frac{dt'}{\sqrt{4\pi D t'}} \left(1 - \exp\left(-\frac{\Delta^2}{4D t'}\right)\right). \quad (7)$$

This integral can be reduced, after the change of variables $t' = \theta \Delta^2 / 4D$, to:

$$\partial_x T(\Delta/2, t) = -\frac{Q_0 \Delta}{\sqrt{16\pi D}} \int_0^{4Dt/\Delta^2} \frac{d\theta}{\sqrt{\theta}} \left(1 - \exp\left(-\frac{1}{\theta}\right)\right). \quad (8)$$

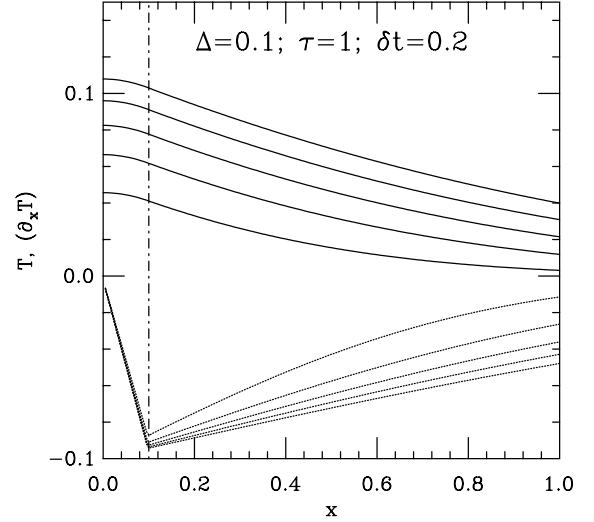


Fig. 2. The evolution of temperature (full line) and of the temperature derivative (dashed line) after a brittle fracture has been initiated at time $t = 0$, in a region of size Δ . The evolution for $t \leq \tau$ is shown. The maximum value of $|\partial_x T|$ is reached at the boundary of the fractured region (marked by the vertical dashed line). A wave starts when the maximum of $|\partial_x T|$ reaches $(\partial_x T)_c$ after a time τ . The parameters used in the simulation are $D = 1$, $Q_0 = 1$, $\tau = 1$. The time step is 2.5×10^{-3} , the lattice spacing is 5×10^{-3} .

The integral above converges when its upper bound goes to infinity: $\int_0^\infty d\theta/\sqrt{\theta}(1 - \exp(-1/\theta)) = 2\sqrt{\pi}$. It follows that for small values of Δ , $\partial_x T(\Delta/2, \tau) \approx Q_0 \Delta / (2D)$, provided $\tau \gg \Delta^2 / (4D)$. As expected, the absolute value of the temperature derivative $\partial_x T(\Delta/2, t)$ is a monotonically increasing function of Δ (the larger the region where heat is released, the higher the flux). For a given value of $(\partial_x T)_c$, there exists a critical value Δ_c defined implicitly by:

$$(\partial_x T)_c = \frac{Q_0 \Delta_c}{\sqrt{16\pi D}} \int_0^{4D\tau/\Delta_c^2} \frac{d\theta}{\sqrt{\theta}} \left(1 - \exp\left(-\frac{1}{\theta}\right)\right) \quad (9)$$

such that for $\Delta < \Delta_c$, the critical value $(\partial_x T)_c$ is not reached while the Q term is on, and for $\Delta > \Delta_c$, the critical value $(\partial_x T)_c$ is reached at a time $t < \tau$. In the former case, the solution will relax for $t > \tau$ towards the value at $x \rightarrow \infty$, and propagation of a wave does not start. In the other case ($\Delta > \Delta_c$), the source term gets turned on for $t > \tau$ in the initially unfractured region, resulting in a propagating wave. Provided $\Delta_c / (D\tau)^{1/2} \ll 1$, equation (9) reduces to:

$$\Delta_c \approx 2 \frac{(\partial_x T)_c}{Q_0} D = 2(D\tau)^{1/2} G \quad (10)$$

where G was defined in equation (5). Equation (9) predicts that ignition by a brittle fractured zone becomes impossible when $G \geq 1/\sqrt{\pi} \approx 0.564$ (the critical length becomes infinite).

The predictions for the critical size have been tested numerically in the small G regime. We explicitly checked that the maximum derivative is located at the edge of the fractured zone, see Figure 2. The value of Δ necessary to

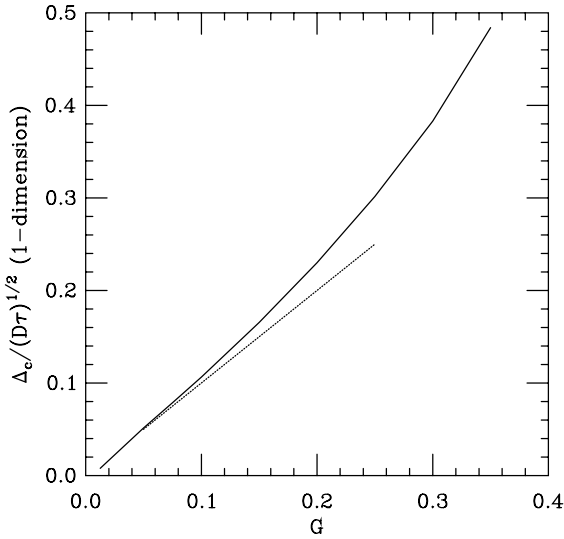


Fig. 3. Dependence of the critical size of the fractured zone necessary to ignite a wave, Δ_c , as a function of $(\partial_x T)_c$, in 1-dimension. For small G , the curve is well represented by the prediction equation (5) (dashed line). The physical parameters in this figure are $\tau = 1$, $Q_0 = 1$ and $D = 1$.

start propagation is plotted in Figure 3 as a function of $(\partial_x T)_c$, or equivalently, G (since all the other parameters are set to 1: $Q_0 = 1$, $D = 1$, $\tau = 1$). A linear dependence of Δ as a function of G is observed for small values of G , in complete agreement with the analysis above. The numerical errors become large for $G \lesssim 0.4$. Since, as we will explain in Section 3.3, the experiments we are aware of correspond to small values of G , our numerical study covers the physically important range of parameters.

3.2 Ignition by a brittle fractured zone in higher dimension

In this subsection, we consider the problem of ignition by a brittle fractured zone in higher space dimension. In practice, the case $d = 2$ is appropriate for thin films of frozen reagents, whereas the case $d = 3$ applies for wave ignition in three-dimensional ampoules.

Technically, the calculation of the previous subsection may be extended in $d = 2$ dimensions: starting at $t = 0$ from a disk of diameter Δ , where a fracture is applied, one may compute the normal derivative on the circle of radius $\Delta/2$ at time t as:

$$\begin{aligned} \partial_n T(\Delta/2, t) &= \frac{Q_0 \Delta}{2\pi D} \int_0^{2\pi} d\theta \int_0^{1/2} z dz \\ &\times \frac{(1/2 - z \cos \theta)}{(1/4 + z^2 - z \cos \theta)} \exp\left(-\frac{\Delta^2}{4Dt}(1/4 + z^2 - z \cos \theta)\right). \end{aligned} \quad (11)$$

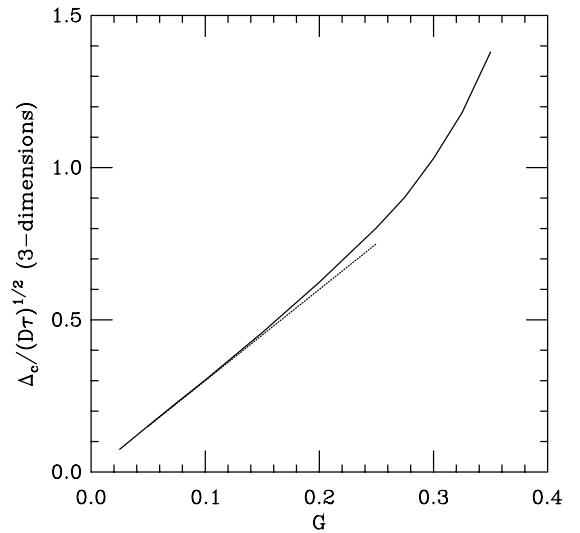
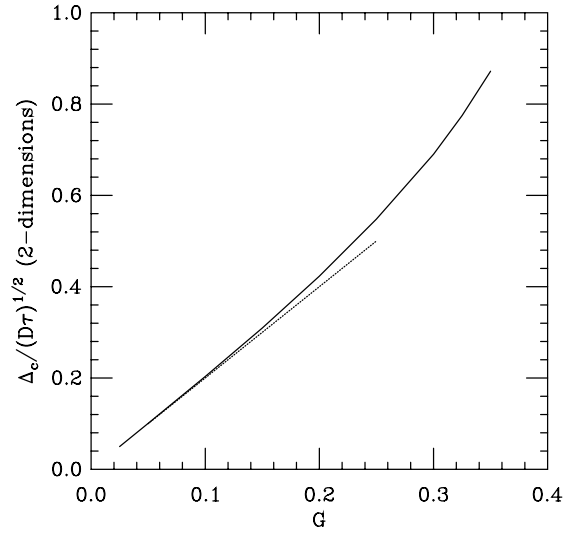


Fig. 4. Dependence of the critical size of the fractured zone necessary to ignite a wave, Δ_c , as a function of $(\partial_x T)_c$, in 2-dimension (a), and in 3-dimensions (b). The curve is well represented by the prediction equation (14). The dashed line shows the prediction equation (14). The physical parameters in this figure are $\tau = 1$, $Q_0 = 1$ and $D = 1$.

In the limit $\Delta^2/(4Dt) \ll 1$, the expression above reduces to:

$$\partial_n T(r = \Delta/2, t) = \frac{Q_0 \Delta}{4D} \quad (12)$$

leading to the following estimate for the critical nucleus:

$$\Delta_c = \frac{4D(\partial_x T)_c}{Q_0} = 4(D\tau)^{1/2} G. \quad (13)$$

This can be explicitly checked numerically. The critical radius, computed in 2-dimensions as a function of G is shown in Figure 4a. The condition $\Delta^2/(4Dt) \ll 1$ is satisfied for small values of G ; in this regime, the relation equation (13) is well satisfied.

In fact, the critical radius may be computed in any dimension in the $\Delta^2/(4Dt) \ll 1$ limit. One finds:

$$\Delta_c = \frac{2dD(\partial_x T)_c}{Q_0} = 2d(D\tau)^{1/2}G. \quad (14)$$

This result can be justified by simply integrating equation (1) over the sphere of radius $\Delta/2$:

$$\frac{d}{dt} \int T d^d x = Q Vol_d(\Delta/2) - D Area_d(\Delta/2)(\partial_n T) \quad (15)$$

where $Vol_d(\Delta/2)$ and $Area_d(\Delta/2)$ are respectively the volume and the area if the sphere of radius $\Delta/2$ in d -dimensions. The two quantities are related by:

$$\begin{aligned} Vol_d(R) &= \int_0^R Area_d(R') dR' \\ &= Area_d(1) \int_0^R R'^{d-1} dR' = \frac{R Area_d(R)}{d}. \end{aligned} \quad (16)$$

In the limit $\Delta^2/4D\tau \gg 1$, as we will justify, the left hand side of equation (15) is negligible compared to any of the two terms on the right hand side. This can be seen by using the Green's function representation of the temperature generated by a heat source term, Q , localized in a sphere of radius $\Delta/2$, to obtain:

$$\begin{aligned} \frac{d}{dt} \int d^d x T(x, t) &= \frac{t^{-d/2}}{(4\pi D)^{d/2}} \int_{|x| < \Delta/2} dx \int_{|x'| < \Delta/2} dx' \\ &\quad \times \exp\left(-\frac{(x-x')^2}{4\pi Dt}\right) \\ &\approx \frac{1}{(4\pi Dt)^{d/2}} \left(\frac{\Delta}{2}\right)^{2d} Q. \end{aligned} \quad (17)$$

This term is effectively smaller than $Q Vol_d(\Delta/2)$ provided $\Delta^2/Dt \ll 1$. Equation (15) thus implies that

$$\partial_n T(\Delta/2) = \frac{\Delta Q}{2dD} \quad (18)$$

which in turn leads to equation (14).

This result has been checked numerically. Figure 4b shows the dependence of the critical radius on the the dimensionless combination G . As it was the case in 1 and 2 dimensions, in the small $\Delta/(D\tau)^{1/2}$ limit, or equivalently, in the small G limit, the linear relation (14) is well satisfied.

The conclusion from this section is that the critical size of the fractured zone leading to wave nucleation increases essentially linearly with space dimension. Qualitatively, this effect results from the dependence of the heat loss term across a sphere as a function of the space dimension: as d increases, the heat losses across the sphere become more important. As a consequence, a larger amount of injected heat, hence a larger critical size, is required to ignite wave propagation.

3.3 Physical estimates

The available experimental data allow us to estimate the value of Δ_c in real systems. In the case of the chlorination of butylchloride, in liquid nitrogen ($T \approx 77$ K), $\tau \approx 0.1$ s, $Q_0\tau \approx 60$ K, and $(\partial_x T)_c \approx 300$ K/cm [3,5]. The heat diffusivity D is of the order $D \approx 10^{-2}$ cm²/s (or less), so $G \approx 0.15$, and $\Delta_c \approx 5 \times 10^{-3}$ cm. Effectively, in the experiments, the critical length is very small. We thus obtain the physically very important result: in order to initiate propagation of a travelling wave of cryochemical transformation, it is enough to rupture locally a very small piece of the solid matrix of reagents, of size of the order of 10 μ m. Preliminary experimental results do show that a scratch by a thin needle is enough to initiate wave propagation of cryochemical waves [11]. It would be interesting to measure systematically the critical size of the fracture zone as a function of the other parameters in the system. We note that this result is very suggestive of what may happen in the (plausibly) related problem of initiation of explosion in solid explosive by shock or friction.

4 Ignition by a temperature jump

We consider a temperature step: $T = \delta T$ for $x \leq 0$ and $T = 0$ for $x > 0$. Right at the step location, very large temperature gradients induce brittle fracture, and if the temperature jump is high enough, we demonstrate that a wave may start propagating. Importantly, the critical temperature jump can be very small: in the limit $(\partial_x T)_c \rightarrow 0$, the critical temperature jump goes to zero, and as such, is much smaller than the temperature jump in a stationary travelling wave front.

In many combustion problems, a large temperature perturbation is needed to ignite a reaction. For the type of cryo-chemical reactions considered here, we show that a temperature step of *very small amplitude* (much smaller than the adiabatic temperature of the reacted medium after combustion) is enough to ignite a propagating wave.

A temperature jump leads to a very strong temperature gradient, therefore generating a region with brittle destruction. The sharp temperature jump should be regarded here as a model for the ignition of propagation by a strong temperature gradient, as it was indeed done in experiments. Intuitively, one expects that the higher the amplitude of the jump, the larger the fractured region. As we have seen in the previous subsection, when the size of the domain with brittle destruction is large enough, propagation of waves may start. Ignition is therefore expected to take place when the temperature jump is larger than a certain threshold, δT . In this subsection, an analytic estimate of the critical temperature jump is provided, as well as a numerical determination.

With a temperature jump as an initial condition, the temperature derivative at $t = 0$ a δ -function: $\partial_x T(x, t = 0) = (\delta T)\delta(x - 0)$. The temperature derivative evolves according to:

$$\partial_t(\partial_x T) = D\partial_x^2(\partial_x T) + \partial_x Q \quad (19)$$

which again has the explicit solution:

$$\begin{aligned} \partial_x T(x, t) = & -\frac{(\delta T)}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \\ & - \int_0^t \frac{dt'}{(4\sqrt{\pi}(D(t-t'))^{3/2})} \int_{-\Delta/2}^{\Delta/2} Q(x', t')(x-x') \\ & \times \exp\left(\frac{-(x-x')^2}{4D(t-t')}\right) dx'. \quad (20) \end{aligned}$$

The evolution of the sharply peaked temperature gradient profile is very fast. In a time of order $\frac{1}{4\pi D}(\delta T/(\partial_x T)_c)^2$, the temperature derivative is everywhere less than $(\partial_x T)_c$. When $(\partial_x T)_c \rightarrow 0$, this time is much shorter than τ , the time where the source term Q acts. This statement has been checked numerically. We therefore separate the evolution into a first phase, where the infinitely peaked temperature derivative decreases to values less than $(\partial_x T)_c$, followed by a second phase where the temperature gradient builds up, due to the source term Q . This second phase is very similar to the problem already considered in the previous subsection.

To describe the first phase, we therefore neglect the second term on the right-hand-side of equation (20). The solution reaches $|\partial_x T| = (\partial_x T)_c$ at values of x , defined by:

$$x^2 = 4Dt \left(\ln \frac{\delta T}{(\partial_x T)_c} - \frac{1}{2} \ln 4\pi Dt \right). \quad (21)$$

At $t \geq \frac{1}{4\pi D}(\frac{\delta T}{(\partial_x T)_c})^2$, the solution is everywhere less than the $(\partial_x T)_c$, so equation (21) does not have physical solutions. The maximum value of $|x|$, solution of equation (21) is:

$$x_m = \frac{1}{(2\pi e)^{1/2}} \left(\frac{\delta T}{(\partial_x T)_c} \right). \quad (22)$$

It is reached at time $t = \frac{1}{4\pi e D}(\frac{\delta T}{(\partial_x T)_c})^2$. Effectively a region of size $w = 2x_m$ undergoes brittle destruction. The subsequent evolution can be described by the considerations of the previous subsection: provided the width is larger than a critical width, of order $2D(\partial_x T)_c/Q_0$ when $(\partial_x T)_c$ is small enough, a wave is initiated, otherwise, the excited region cannot start a new wave. This leads to a critical temperature jump:

$$\delta T_c = \left(\frac{\pi e}{2}\right)^{1/2} (\partial_x T)_c^2 \left(\frac{Q_0}{D}\right). \quad (23)$$

The numerical problem turns out to be difficult, since one has to follow a solution with a singular initial condition, evolving over a very fast time scale. A precise numerical solution therefore requires very small time steps, and a very fine mesh. Our numerical results were always somewhat sensitive to the time/space discretisation. By comparing various discretisations, we estimate the error bars on the numerical results presented here to be less than $\sim 10\%$.

The numerical results for the critical value of the temperature jump, δT_c as a function of the $(\partial_x T)_c$ is shown

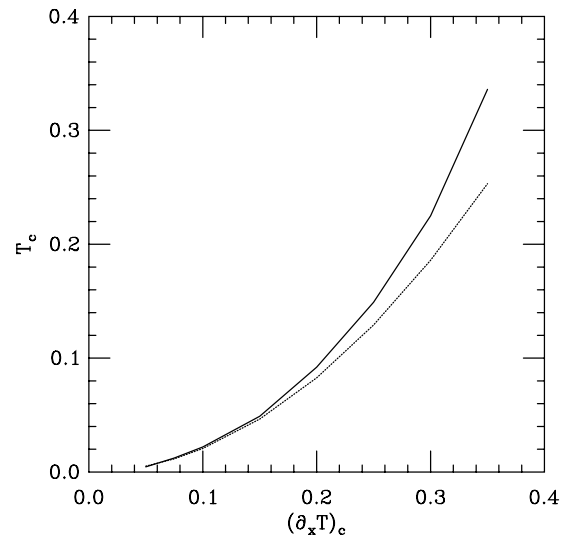


Fig. 5. Dependence of the critical amplitude of a temperature jump, δT to start wave propagation (solid line). The numerically determined values of δT_c are in good agreement with the prediction of equation (23) when $(\partial_x T)_c \rightarrow 0$ (dashed line). The physical parameters in this figure are $\tau = 1$, $Q_0 = 1$ and $D = 1$.

in Figure 5. The data is completely consistent with the quadratic behavior in equation (23); the numerical prefactor determined is very close to the value $(\frac{\pi e}{2})^{1/2}$.

5 Conclusions

In this article, we have considered the problem of ignition in a model introduced earlier to describe front propagation in weakly exothermal cryochemistry in solid phases. Our results provide an explanation for a number of experimental phenomena, described in [3]. We emphasize, in particular, the following facts:

- i) Waves of chemical transformation can be excited *without heating*, and only by local disruption (as achieved experimentally by turning of a metal bar frozen in the sample). Remarkably, we find with realistic parameters that the critical size is very small, of the order of $\sim 10 \mu\text{m}$.
- ii) Waves are ignited as a result of a rapid variation of temperature (in experiments a pulse of electric discharge emitted with a microheater frozen in the sample), or equivalently by large temperature gradients. On the contrary, a very slow temperature variation or small temperature gradient does not lead to ignition.

The estimates for the critical size, presented in Section 3.3, lead to very small values. This may be related to the well known very large sensitivity of crystalline explosives to friction and shocks. So far, models based on thermal considerations have failed to provide an explanation for this important observation. Our approach suggests a new way to address the problem. Some experimental evidence that this hypothesis is correct can be found in the work [14] on the dynamics of decay of heavy metals azides.

The importance of the problem of ignition by a mechanical perturbation extends far beyond the specific problem of cryochemistry we have considered in this article. Our result on cold ignition may be used in a number of contexts, such as geotectonic phenomena (it has been recently proposed that phase transition coupled to mechanical perturbations may be important in understanding geotectonic phenomena, involved in earthquakes dynamics [12]), as well as to the catastrophic decay of metastable phases in solids [13].

Obviously, the possible applications of the presented results are only hypothetical schemes. They call for more experimental and theoretical investigations.

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