Nonlinear wave mechanisms of very fast chemical and phase transformations in solids. applications to cosmic chemistry processes near to 0 K, to explosive-like decays of metastable solid phases and to catastrophic geotectonic phenomena

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ABSTRACT

In the Universe, chemical reactions occur at very low temperature, very close to 0 K. According to the standard Arrhenius mechanism, these reactions should occur with vanishingly small efficiency. However, cold planets of the solar system, such as Pluto, are covered by a crust composed of ammonia and methane, produced on earth only at very high temperature and pressure, in the presence of catalysts. This observation is incompatible with the predictions of Arrhenius kinetics. Here, we propose a general mechanism to explain the abundance of chemical reactions at very low temperature in the Universe. We postulate that the feedback between mechanical stress and chemical reaction provides, through fracture propagation, the energy necessary to overcome the activation barrier in the absence of thermal fluctuations. The notion described in this work can also be applied to other fields such as explosive-like solid phase transformations and catastrophical geotectonics phenomena (earthquakes).

Keywords: Nonlinear Waves;
Coupling between Chemistry and Mechanics;
Combustion at Very Low Temperature;
Geochemistry; Cosmochemistry; Geotectonics

1. NONLINEAR PROPAGATION OF FRACTURE IN FROZEN REAGENTS MATRIX: A MECHANISM OF FAST CHEMICAL EVOLUTION OF MATTER IN UNIVERSE

Chemical evolution in solid phase occurs in the Universe, whose temperature is very close to 0 K, at rates much faster than expected based on standard Arrhenius considerations. This fact has remained difficult to explain for many years: how to reconcile the abundance of certain chemical species, whose synthesis on earth cannot proceed without very high temperature and pressure conditions, with the classical picture of chemical reactions occurring as a result of thermal fluctuations overcoming an activation barrier?

A similar situation has been reported in the case of cryo-chemical reactions in which the solid reagents were previously exposed by gamma- or photo-irradiation (see [1,2] and references therein). The chemical reaction has been observed to lead to travelling wave, propagating at very low temperatures in laboratory experiments (4 K in liquid helium, and at 77 K in liquid nitrogen) at velocities which can not be explained by traditional Arrhenius combustion theory.

Explaining these phenomena is the theoretical challenge that we are addressing in this short review. The observed phenomena of very fast chemical reactions at extremely low temperatures can be explained quantitatively as resulting from a coupling between chemical transformation and local brittle fracture propagating over the frozen sample of reagents, with the following mechanism. Consider a chemical reaction starting on the surface. The heat released during the reaction induces strong strain in the solid matrix, which may lead to brittle fracture close to the region where the reaction started. The brittle fracture in turn facilitates the reaction in the neighbourhood of the region where the reaction started. As a result, reaction propagates, due to the coupling between mechanical and chemical processes. This sort of phenomenon has been observed for several classes of reaction (hydrocarbon chlorination, olefin hydrobromi-

nation, polymerization and copolymerization); it results from an efficient way of transferring mechanical energy from the solid matrix into chemical transformation. The theory developed here thus rests on the assumption that a mechanical energy accumulated in solid matrix can be transformed into a chemical energy even at extremely low temperatures, therefore leading to rates of chemical transformation larger than predicted by classical Arrhenius factors, by many orders of magnitude. This energy transformation is a result of self-sustained brittle disruption (fracture in form of dispersed solid substance) of solid matrix, resulting in propagation of nonlinear "tribo-chemical" waves.

The first simplest theoretical model of nonlinear transformation waves in solid-phase cryochemical reactions was proposed in [1,2] and developed in [3]. The model considered was based on the physical notion that brittle fracture is induced by thermal strain, induced by the heat released during the chemical reaction investigated the role of various parameters describing heat-transfer parameters, sample sizes, as well as the effects of threshold of "cold ignition", inducing trans- formation waves in the frozen reagent matrix. In [1,2] and references therein, we study the consequences of the postulated mechanism by investigating the properties of the wave solutions in different conditions: under uniform pressure of reagent sample (in compliance with our theory, wave velocity decreased when increasing the solid matrix strength), waves in thin films (existing of wave modes under exclusion of heat factor), method of wave initiation (shock by needle-brittle fracture ignites the wave, unlike plastic deformation).

The development of the thermal theoretical model has been recently complemented by taking in account a more accurate description of the mechanical stress [4]. It has been shown that travelling wave velocities in the cryo-chemical systems can reach values with magnitudes significantly faster than what can be achieved in standard chemical reactions (deflagration theory in combustion, [5]). The result was experimentally confirmed (see [6] and cited publications).

To analyze the practical implications of the scientific concept put forward, we investigated further the properties of propagating nonlinear transformation waves of monomer cryo-polymerization with reinforced inert component [7]. The results of the experiments with the model systems suggest new technological developments, in particular concerning polymer composites production under cryo-conditions (4.2-77 K), using the notion of nonlinear travelling waves described here, with cosmic and solar radiation for activation of the frozen monomer matrix.

2. NONLINEAR FRACTURE TRAVELING WAVES MECHANISMS OF EXPLOSIVE-LIKE METASTABLE SOLID PHASE STATES TRANSFORMATIONS

We hypothesize that the mechanism identified in the cryo-chemical context provides the proper framework to explain the fast cryochemical reactions of cosmic substances occurring in the Universe. This mechanism seems particularly appropriate to explain the formation, from the frozen mixture of elements, of compounds such as ammonia and methane that are found in appreciable amounts in crusts of the cold planets of the Solar system.

A model of nonlinear traveling wave [8,9] was developed to describe the very fast decay of metastable solid phases (as a rule, amorphous states), for example, in physics and technology of semiconductors [10], or in the physical contexts of explosives sensibility to friction and shock [11], or of "Tempered Glasses" destruction [12]. The explosions of "Prince Ruppert Drops" (also known as "Batav Tears") provide a particularly interesting and impressive example of the class of phenomena studied here [13].

The model developed in [8,9] describes "gasless detonation" in solid fractures, and shares several important concepts with the models presented in [1-3]. However, whereas fractures in [1,3] are caused by too strong a thermal stress (temperature gradient above a threshold), they are induced in [8,9] by a change of the solid matrix density during the phase transformation. In addition, a more precise description of the coupling to the mechanical stress leads to the conclusion that the propagation is supersonic, thus providing a natural explanation for the extremely fast decays of metastable phases.

The theoretical description proposed here is based on a reaction-diffusion equation, describing phase transformations, and on the wave equation, describing elastic perturbations. The simple picture we are proposing is that the phase transformation and the mechanical properties of the matrix are coupled. On general grounds, it is reasonable to expect that the phase transformation induces a change of the matrix properties; we postulate that the sound velocity depends on the state of the phase transformation. In the same spirit, we postulate that too high a strain effectively initiates the decay of metastable phase. This can be rationalized by arguing that when the strain exceeds a critical value, the matrix is destroyed, which in turn facilitates the phase transformation. The feedback (coupling) considered in this works thus involves 1) A dependence of the sound velocity on the phase field, and 2) The induction of phase transformation.

An exhaustive analytic and numerical study of travelling waves of fracture reveals the existence of supersonic wave modes of decay of metastable phases in solids.

With the physical ideas explained above, we introduce, in 1-dimension the concentration field, C, which describes the phase transformation (C = 0 in the metastable state, and C = 1 in the transformed state), and the mechanical field (u, describing the deformation, the stress being proportional to $\partial_x u$). The evolution equations are written as:

$$\partial_t^2 u - \partial_x \left(V^2 \partial_x u \right) = 0 \qquad (1)$$

$$\partial_t c = f(c) + D \partial_x^2 c + w(\partial_x u) \qquad (2)$$

Eq.1 is simply the equation that describes mechanical perturbation in the solid matrix, whereas **Eq.2** is a simple reaction-diffusion equation that describes phase transformation. The unperturbed state is defined (arbitrarily) by the variable $c = 0$, whereas the fully transformed state is given by $c = 1$. The kinetic term $f(c)$ is nonlinear, describing a chain branch reaction ($f(c) = 0$ in the initial phase, $C = 0$). Whether the state is unstable or metastable does not affect the main predictions of the model. The coupling between the chemical and the mechanical fields is provided by the term $w(\partial_x u)$ in **Eq.1**, which physically expresses that the phase transformation is initiated by stress. More precisely, we assume that $w(\partial_x u)$ is zero, and turns on when the stress exceeds a certain limit $(\partial_x u)_c$ and remains at a value W_0 for a time τ after this threshold has been reached. The velocity of sound is also assumed to increase monotonically as the phase transformation proceeds $-V = V(C)$.

The physical picture is that the stress field induces the phase transformation, through the coupling term $w(\partial_x u)$. This phase transformation in turn leads to mechanical perturbation, which propagate ahead of the zone undergoing phase transformation. The phase transformation studied here depends crucially on the coupling with mechanical perturbations, which propagate at the speed of sound. This leads to fronts of phase transformation that propagate at velocities much larger than what is typically obtained in standard reaction-diffusion cases. A full analysis of steadily propagating fronts [8,9] confirms that front propagation occurs at a supersonic velocity, thus demonstrating our claim that the model leads to much higher front propagation velocity than expected on theory of standard combustion (reaction-diffusion) they. As a consequence, in contrast to the prediction of reaction-diffusion theory, the front velocity does not depend crucially on the diffusion coefficient D: the analysis [8,9] was carried out for values of D very close to zero (diffusion mobility in solid states has a very small value), and the velocity was found to be of the order of the sound velocity.

The physical picture presented here is reasonable on simple physical grounds, and provides a general description of some interesting phenomena observed in nature. It would be clearly very important to check the tenets postulated here. At a dynamical level, one needs to follow the evolution of a wave of transformation propagating at a velocity of the order of the sound velocity in a solid (~1000 m/s). A temporal resolution of the order of 1 ms would be necessary to resolve the evolution of the wave in systems such as described in [13]. The available fast cameras enable a time resolution of ~0.01 ms, which still makes the detection of the travelling waves very challenging, even with the best equipment currently available. In the same spirit, it would be interesting to carry out systematic studies of the materials involved in these reactions under very high strain conditions, very close to conditions leading to rupture. Experiments necessary to substantiate the hypotheses presented here thus require state-of-the-art techniques, which should become available in the coming years.

3. APPLICATION OF THE TRAVELLING WAVE CONCEPT TO CATASTROPHIC GEOTECTONIC PHENOMENA AND EARTHQUAKES

We make the hypothesis that the mechanism [8,9] of explosive-like metastable solid phases decays presented above may be applied to describe theoretically the processes of initiation and dynamics of propagation of geotectonic phenomena and earthquakes.

The underlying postulate to apply the theory developed here to geotectonic phenomena in earthquakes is based on the first observation that numerous metastable phases have been identified in rocks in the earth crust. Many transitions have been found between them, induced by pressure or temperature changes. It is thus entirely plausible that changing the state of strain may lead to a transformation of the rock, analogous to the phase (or chemical) transformations postulated above. The dynamics of these phase transformations remains very difficult to study, in view of the extreme conditions where these transformations occur. Our work thus proposes a few simple feedbacks between mechanical and phase transformations, known to happen simultaneously during earthquakes. A bifurcation approach to modeling of the geological phenomena is proposed in the present work.

An understanding of the mechanisms of initiation ("ignition") and propagation of earthquakes has potentially very important consequences for society in general. Results of the model developed in [8,9] are in general

agreement with some works of geophysicists [14,15] in which a phase transformation concept was used to explain certain aspects of earthquakes. The theory however remains to be tested in more detail on real systems. Laboratory experiments devoted to the explosive decomposition of "Prince Ruppert drops" should provide a good testing ground. We mention in this context that the existence of an explosive decay of the "Prince Ruppert drops", with supersonic velocities ("gasless detonation") had been established in [13]. Moreover, the decomposition of amorphous silicate glasses is expected to provide important hint concerning the decomposition of rocks, thus providing a connection to the physics of earthquakes.

In conclusion of the short review we argue that the proposed models are fundamentally new objects in the theory of nonlinear traveling wave processes. The models presented here require improvements at several levels, and confrontation to experimental study. They provide a reasonable first step to understand a broad class of phenomena, which certainly deserve increased attention.

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