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STRUCTURE, CHEMISTRY, AND INSTABILITY OF DETONATION
IN HOMOGENEOUS, LOW DENSITY FLUIDS - GASES*

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ABSTRACT

The lesson from gas detonation research in the last ten years is that the Chapman-Jouguet description of the detonation process, with its many refinements, is inadequate. The equilibrium properties of the reaction products of detonable gases can be calculated reliably, and the predictions of Chapman-Jouguet theory have been tested directly against experimental observations. Several kinds of experiments have revealed manifestations of the principal area of failure of the steady, one dimensional theory, namely the occurrence of significant transverse motions which, like the detonation itself, are sustained by energy from the exothermic chemical reaction. The characteristic form of the laterally propagating perturbations which accompany this motion is analogous to the Mach stem interaction of two dimensional flow. This particular structural form is seen to be developed most strikingly by fuel - oxygen systems which exhibit branching chain chemical kinetics, and relationships between the reaction course and the Mach stem structure and between the structure and propagation failure limits in gases are indicated. The nonsteady process of initiation of detonation by a

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plane shock wave has also received attention, and one dimensional gas-dynamic computations are able to account for this process fairly well. Nevertheless there are unmistakable indications of the appearance and growth of transverse perturbations in this process as well. Finally, the results of theoretical treatment of the question of stability of steady, one dimensional shock wave flow in the presence of exothermic reaction have indicated certain regimes of instability, and current computational explorations of possible manifestations of such instability include examinations of fluctuations of intensity of plane waves with time and of the kinematics of laterally propagating high frequency sonic disturbances in reactive one dimensional flows.

INTRODUCTION

In discussing gaseous detonations in this Symposium which commemorates the twenty-fifth anniversary of a historic advance in the scientific study of condensed explosives, it may be appropriate to recall briefly the state of understanding of detonations in gases that existed twenty-five years ago. When we do this, we observe that a renaissance in thinking was signaled by the appearance, in the May, 1940 issue of the Russian Journal of Experimental and Theoretical Physics, of a paper, "On the Theory of Detonation in Gaseous Systems", by Ya. B. Zeldovich.¹

In that paper, Zeldovich studied "the conditions of one dimensional steady detonation, effect of heat transfer and resistance, and distribution of temperature, pressure, and so forth, in a strictly steady regime". We recognize this, of course, as the basis of the very familiar Zeldovich-

von Neumann-Döring model of detonation and the "von Neumann spike". Zeldovich continued, however, with a very prophetic statement in the sentence following the one quoted above, "Such computations are required as a starting point of the whole more complicated theory of the propagation of detonation in three dimensions, the theory of periodic states, and so forth".

Elsewhere in the paper, Zeldovich summarized the gas detonation research of the preceding half century, more or less, and foretold that of the past quarter century by the observations, "Up to the most recent times, the hydrodynamic (Chapman-Jouguet) theory of the velocity of detonation, excellently confirmed by test, did not arouse a need for seeking the mechanism of the chemical reaction and an investigation of the conditions at the detonation wave front. If the present work gives rise to new experimental investigations, which penetrate more deeply into the nature of the phenomenon, the object will have been attained".

The present survey does not review all the historical developments comprehensively. Rather it attempts to outline current thinking about the detonation process, and its development from observations and considerations of gaseous detonations. This current picture has emerged largely from the recognition of the important role of nonlaminar flow processes in gaseous detonation, which has occupied a position of prominence since about 1960. In the proceedings of the Discussion on Detonation at the Ninth International Combustion Symposium² at Ithaca in 1962, and in two review articles which appeared in late 1963,^{3,4} the reader may find much of the material included in the present survey, as

well as other related material, presented from other authors' points of view. In various monographs⁵⁻⁸ and in selected recent journal articles, one may find expositions of the more classic topics of gaseous detonations, such as the Chapman-Jouguet-Zeldovich-von Neumann-Döring theoretical model,⁹ and the phenomenology of limits of detonability, spinning detonations, spherical detonation, the transition from subsonic flame to detonation,¹⁰ diameter effects,¹¹ and the rarefaction zone behind the detonation.

Tests of Steady, One Dimensional Theory

Chemically, the detonable gases most studied are mixtures of carbon and/or hydrogen containing fuels with an oxidizer, usually O_2 . Nitrogenous compounds are of lesser prominence, and metals (save boron in B_2H_6)¹² are substantially absent from consideration. The density and the composition of the mixtures, which often include inert diluents, are favorite experimental variables whose effects are determined over wide ranges. Except in carbonaceous systems containing insufficient oxygen,¹³ the reaction products of the more familiar gaseous detonations are also exclusively gaseous molecules whose thermodynamic properties are well known at the low densities normally studied. This means that the Hugoniot equations can be solved numerically for the pertinent states of no reaction and of equilibrium as well as for arbitrary states of intermediate composition, and the predictions of the steady, one dimensional theory can be tested directly.

Of course the detonation velocity is one of the quantities which can be tested, but there are many others as well. Since the mid-1950's, there

have been reported a large variety of experimental observations of detonation waves aimed at determining the condition of the detonation products at the "Chapman-Jouguet plane" and the extent and structure of the reaction zone near the shock front. Some of the quantities which are available for experimental study are indicated in Fig. 1. This pressure vs. specific volume diagram shows computed conditions for selected hypothetical states in the steady, one dimensional detonation of a particular detonable gas, pure ozone. This example, rather than a fuel oxygen mixture, has been chosen for simplicity and to emphasize the fact that the properties represented by this familiar diagram are determined by thermochemistry, not by reaction mechanism.

For the Chapman-Jouguet velocity wave considered in Fig. 1 there are, between the no-reaction and equilibrium states, substantial changes in pressure, density, temperature, and mass flow velocity, and complete replacement of the initial O_3 by the products O_2 and O . Many possibilities are offered for measurement of the course of the reaction provided the requisite time and space resolution can be achieved. Extensive measurements to dissect the wave front structure have been made by x-ray densitometry,¹⁴ spectroscopic temperature determination,¹⁵ photoelectric schlieren densitometry,¹⁶ optical interferometric densitometry,¹⁷ absorption¹⁸ and emission¹⁷ spectrophotometry of individual species concentrations, and pressure profile measurements.¹⁹ While all of these approaches did yield some observations of wave front structure in detonations at low pressures, real quantitative confirmation of the von Neumann spike was never abundantly evident.

The terminal state of the detonation products prior to their gradual expansion in the rarefaction wave is also examinable quantitatively, with less stringent space/time resolution requirements. Figure 1 includes a comparison of several potentially observable quantities between the equilibrium Chapman-Jouguet state and a neighboring state on the weak detonation branch of the equilibrium Hugoniot curve. This comparison illustrates the futility of distinguishing equilibrium states near the minimum velocity Chapman-Jouguet solution on the basis of measured detonation velocity or post-detonation temperature, particularly in the face of the finite perturbation in velocity that arises from wall proximity effects.

The most convincing observations of the conditions reached immediately behind the reaction zone have been quantitative measurements of density (averaged across the width of the tube) by means of x-ray absorption²⁰ and interferometry¹⁷ and the deduction of the flow velocity from the angle of weak disturbances in the flow field detected in schlieren photographs.^{21,22} The densities are found to be significantly (ca. 10%) lower than the computed Chapman-Jouguet density, and the flow velocities are also lower, i.e., the gas is receding from the detonation front at Mach numbers of 1.1 or greater. Also, pressure measurements made at the tube walls^{17,19} and chemical concentrations measured quantitatively by photometry of visible light emission¹⁷ are in agreement with the conclusion that the condition of the detonation products lies in the vicinity of the weak detonation branch of the equilibrium Hugoniot curve. The effects of the occurrence of such "weak" detonations upon the performance of

explosives have not been explored by the investigators working with gases, but they may be important in condensed phase systems.

The weak detonation solution of the steady, one dimensional equations predicts a velocity slightly greater than the minimum, or Chapman-Jouguet velocity. This prediction is apparently confirmed^{23,24} by precise experiments, although the small uncertainties in thermodynamic data and in assessing the finite diameter effects cloud the interpretation. In fact, the approximate attainment of the computed Chapman-Jouguet velocity in gaseous detonations can be used as evidence for the substantially complete release of the available chemical energy²⁵ and can even be used successfully to establish thermochemical parameters of major constituents.²⁶

Nonlaminar Flow Effects

The most productive explanation of the failure of gaseous detonations to exhibit the predicted steady, one dimensional structure has been given by White¹⁷ primarily on the basis of his own two dimensional interferometric observations of nonlaminar structure involving significant transverse motions at the wave front. Qualitatively, it can be appreciated that departure from one dimensional motion obscures the detonation front structure to observations which depend for their interpretation upon constancy of properties across a one dimensional wave, and negates the validity of computations which constrain the detonating system to pressure-volume states along a Rayleigh line or on partial reaction Hugoniot curves.

The consequences of the additional motions have been considered quantitatively in terms of an isotropic turbulence model. The resulting first order contributions to the momentum and energy conservation equations

lead, with generalization of the minimum velocity Chapman-Jouguet condition, to solutions with detonation velocities somewhat greater than the one dimensional value. Experimentally, the weak detonation branch of the one dimensional Hugoniot is apparently approached by unsupported detonations whenever the nonlaminar behavior in the detonation front becomes dissipated before appreciable rarefaction of the products has occurred behind the wave. The "strong" branch solutions are of course also accessible for wave velocities greater than the minimum, and densitometric observations indicate that adequately supported or overtly overdriven^{17,20} waves approach these solutions when the nonlaminar motions subside.

Transverse Structure

In the preceding sections we examined the evidence related to the axial structure of detonation in gases, and saw that nonaxial motions play a significant role. We now turn to investigations of the irregularities in the detonation front, that is the transverse structure. Such investigations are, in a sense, an outgrowth of the phenomenological studies of spinning detonation published thirty to forty years ago. Finely resolved observations of detonation fronts using streak²⁷ or even still²⁸ photography of the luminous reaction zone, or streak schlieren photography of transverse density gradients,²⁹⁻³¹ have revealed the presence of high frequency disturbances. The spatial distribution of these disturbances, and the nature of their motions, including their mutual refraction, have been studied very profitably by

means of the inscriptions made in a soot coating on the interior surface of the detonation vessel.^{32,33} The shape of the detonation front is indicated by soot inscription records of the interaction of detonations with plane waves, and also by those instantaneous schlieren³⁴ or interferometric photographs¹⁷ which view an area of the wave simultaneously. The shock front is found to consist of convex segments whose boundaries are not stationary but move across the detonation front as it advances. At the boundaries of these segments, the shock front is broken discontinuously, and additional gasdynamic processes extend from the intersection loci into the reaction zone region behind the primary shock front.

The structure of these shock wave interactions which occur in detonations has been adduced largely by analogy with the familiar behavior of shock waves reflected from an oblique obstacle. This structure is the Mach stem, an unsymmetrical configuration in which the stronger of the two shock wave segments advances across the weaker one, and a third shock wave emanates from the intersection locus and compresses and deflects the flow behind the weaker initial shock to match the pressure and flow direction behind the stronger one, thereby establishing the contact discontinuity between the fluids passing on either side of the intersection locus.

The identification of this two dimensional, triple shock wave interaction at the intersections of the convex segments of gaseous detonation fronts has been made most positively by means of a clever variation of streak schlieren photography in which combinations of slit angles and sweep speeds and directions are arranged to compensate the major wave motions.³⁵

The Mach stem has recently been subjected to direct interferometric examination in isolated form in a detonable gas by a technique introduced by D. R. White.³⁶ This technique generates a temporarily laminar detonation wave by the passage of an ordinary, nonlaminar detonation through a narrow rectangular slot at the throat of a nozzle formed by placing entrance and exit ramps in a square channel. The detonation emerging from this nozzle is overdriven and attenuating as it expands cylindrically, and transverse structure is not detectable interferometrically. When the nozzle is terminated abruptly at the end of the exit ramp, the wave is reflected obliquely from the main channel wall, and a Mach stem is formed which can be observed on its initial traversal across the channel. The structure so generated is shown in the interferogram in Fig. 2, which shows the shock fronts and also the zones of exothermic reaction.

Strehlow³⁷ has applied the Rankine-Hugoniot equations to the oblique plane shock fronts in this interaction and demonstrated their consistency with the flow matching conditions across the initial portion of the contact discontinuity which separates unreacted gas behind the Mach stem from the unreacted gas behind the reflected shock. The general behavior of Mach stems in reactive media, for such cases as that in which there is no macroscopic region of unreacted material surrounding the three shock intersection locus, has not yet been examined at all thoroughly, either experimentally or theoretically.

Plane Wave Initiation

We have seen that by suitably constraining the system one can realize detonations which are temporarily free of detectable transverse perturbations.

Another instance of such a constrained system is the initiation of detonation by a plane shock front transmitted from an inert material. In gases, this is done by reflection of a plane, unreactive shock wave at the flat closed end of a shock tube. Strehlow and co-workers³⁸ have studied the nonsteady wave motions of such detonation initiation by streak schlieren and combined streak schlieren interferometric techniques. An example of the record produced by the combined technique is shown in the top part of Fig. 3. Just as in the case of plane shock initiation of liquid nitromethane,³⁹ the shocked explosive reacts first at the piston face, after some delay, and this explosive reaction generates compression waves which coalesce to a shock closely followed by reaction. This wave overtakes the original, externally supplied shock, momentarily overdriving it, establishing a contact surface, and ultimately producing a conventional detonation. Depending upon conditions, the nonsteady wave which overtakes the external shock may have the Chapman-Jouguet velocity for the gas mixture heated and compressed by the external shock, or it may be an accelerating, nonsteady wave whose velocity is only about half of the Chapman-Jouguet velocity. The behavior of this nonsteady wave development can be accounted for quite well by one dimensional, time dependent computations using the method of characteristics,⁴⁰ and the optical observations failed to indicate any departure from plane, one dimensional behavior in this initiation process.

Nevertheless, when smoke inscription plates were made in the same apparatus, finely structured patterns qualitatively like those seen in gaseous detonations after long, unsupported runs were observed.⁴¹ This

structure was not evident right at the end wall of the tube, but developed some distance away. In the case shown in Fig. 3, the structure developed between the end wall and the position at which the nonsteady detonation overtook the external shock, and a boundary with a discontinuous change in the slope of the diagonal structure pattern occurred where the two waves met. The size of the structure pattern then changed gradually as the overdriven detonation attenuated to a steady, unsupported velocity.

Structure in Other Detonation Situations

Overdriven detonations are conveniently achieved in gases by shock tube methods. Such detonations have been found to exhibit final state properties described satisfactorily by the strong detonation branch solution of the Rankine-Hugoniot equations. Examination of overdriven detonations for transverse structure^{17,33} has shown that the structure is present in a form qualitatively similar to that found in supported, lower (Chapman-Jouguet) velocity waves. The scale of the structure is found to be progressively finer in more and more overdriven waves, and the finer structure is correspondingly more difficult to resolve, but there is no evidence of a limit for the occurrence of transverse structure, at least within the regime of shock strengths in which the reaction remains exothermic.

Gaseous detonations have also been studied in spherical and cylindrical geometries, by soot inscription^{42,43} and visible light emission⁴⁴ techniques, and regularly spaced transverse structure has been found.

Another observation which is relevant to the generality of transverse structure in detonation is a hitherto unpublished one made in our laboratory

on the occurrence of transverse structure in dilute gas mixtures which are outside the limits of detonability. When a 1% acetylene, 1.5% oxygen, 97.5% argon mixture at about 50 torr initial pressure in a 10 cm diameter shock tube was shocked weakly at a velocity near its computed Chapman-Jouguet velocity (ca. 0.9 mm/ μ sec) no evidence of transverse structure was obtained. But at a threshold velocity of about 1.2 mm/ μ sec, single spin was evident in photographic and smoked foil records, and at higher velocities, up to ca. 1.5 mm/ μ sec, progressively higher modes of transverse structure were observed by the smoked foil technique.

Thus spin and its higher mode transverse wave analogs are seen to be widely occurring finite amplitude manifestations of structural instability of plane, exothermically reacting shock waves in gases, and not to be characteristic of proximity to a Chapman-Jouguet, sonic flow condition or of the waves being externally supported or unsupported.

Theoretical Examination of Stability

The observation of the widespread occurrence of transverse perturbations in the detonation front has led to theoretical examination of the stability, or the lack of it, of the classical plane detonation wave. From Rayleigh's writings about the enhancement of sound by heat addition⁴⁵ we have the very simple principle that sonic disturbances in an exothermically reacting medium are amplified when the reaction rate is enhanced, relative to the rate in the undisturbed medium, in phase with the pressure crests and retarded, relatively, in phase with the troughs.

In discussing problems in the development of the steady, one dimensional wave theory twenty-five years ago, Zeldovich¹ noted, "On the other

hand, when small disturbances are imposed the velocity of the chemical reaction is likewise subject to variation. It is, at present, impossible to predict the result of the computation of the stability with respect to small disturbances, which may depend upon the special properties of the chemical kinetics (autocatalysis, heat of activation)".

Shchelkin⁴⁶ has proposed a basis for assessing the stability of the plane, one dimensional detonation wave model which involves the difference in properties between the shock front and the equilibrium condition and the activation energy for the reaction. His semiquantitative argument has not actually been usable as a neutral stability criterion, but rather has served only to indicate the expectation of instability in substantially all detonating gas systems of interest. Shchelkin and co-workers⁴⁷ have also proposed a quantitative relationship between the frequency of finite amplitude transverse perturbations in detonations and the induction period for the exothermic reaction, again emphasizing the dependence of these quantities on the temperature through the activation energy.

The detailed consideration of the stability of the plane, steady detonation front to sonic perturbations has been carried out by Erpenbeck.⁴⁸ The formalism which he developed from a complicated linearization of the full flow equations permits one to consider the exponential rate of growth of harmonic displacements of the shock front position of any particular transverse wavelength. Stability is recognized by the absence of positive growth rates for any transverse wavelength. Thus the complete question of stability for any particular chemical reaction system and

shock strength requires examination of the entire spectrum from zero to infinite transverse wavelength. The necessary computation for each point is quite formidable and requires high speed computing machinery even for an ideal gas chemical system described by many simplifying assumptions.

Nevertheless, stability of overdriven detonations in such a system has been examined^{49,50} for a range of interesting values of the exothermicity and the activation energy. Shock waves without exothermic reaction are found to be stable.⁵¹ With an exothermic reaction present, analysis for wavelengths greater than a few tenths of the unperturbed reaction zone half-thickness indicates that waves approaching the Chapman-Jouguet velocity are unstable with respect to all wavelengths when the exothermicity and activation energy are sizable. For sufficiently overdriven waves, the very long wavelengths and the very short ones do not grow, but there appears to remain a range of wavelengths near one reaction zone half-length to which the detonation is unstable for arbitrarily large overdrive. With lower activation energy, and thus reduced dependence of the chemical energy release rate upon the state of the gas, the Chapman-Jouguet wave may be stable to very long or very short wavelengths, but the wavelengths in a broad band near the reaction zone half-thickness remain unstable. Reducing the exothermicity to very low levels, which are somewhat dependent upon the activation energy but are not large even for zero activation energy,⁵⁰ does cause disappearance of the instability for wavelengths near the reaction zone half-length. On the other hand, even arbitrarily small amounts of exothermicity are not free of instability

at some range of shock strength, provided the activation energy exceeds some modest minimum.

This last finding has come from a consideration of the limiting form of the stability criterion for very short wavelengths.⁵² This asymptotic stability analysis yields a form which is computationally much more tractable to apply to a specific chemical system than the general finite wavelength criterion. Thus the determination of the existence of instability, in the short wavelength regime, is now practical for any detonation system for which the steady wave properties can be specified.

Of course, the above stability analysis only applies to infinitesimal perturbations, and does not determine the ultimate form or spectrum of finite amplitude disturbances. It does, however, cover the limiting case of infinitely long wavelength, i.e., the case of one dimensional unsteadiness in time.⁴⁹ This class of instabilities is subject to numerical examination by already developed methods for treating one dimensional time dependent flows. Two types of computational procedures have recently been applied to cases in which the detonation is predicted to be stable to infinitesimal one dimensional perturbations at one shock strength and unstable at another. One of these computational investigations has considered the detonating fluid as an inviscid, ideal gas, containing discontinuous shock fronts, by the method of characteristics.⁵³ The other has treated a viscous fluid with shocks of finite thickness by direct numerical integration of the Navier-Stokes equations in Lagrangian finite difference form.⁵⁴ The results of computations by these two methods for an ideal gas system with substantial exothermicity and activation energy are in agreement

with each other and with the infinitesimal amplitude stability predictions. For a strong enough piston supported shock wave, the wave structure approached the steady structure of classical theory after some numerically unavoidable initial transients. However, for a less strongly driven wave, one for which longitudinal instability is predicted by the formal analysis, quasi-periodic fluctuations in the properties of the detonation front developed after a short time. These occurred, for the particular case tested, at intervals of about nine times the unperturbed half-reaction time, and the amplitude of the fluctuations, as measured by the shock front pressure, was a substantial fraction of the steady wave amplitude.

It has also been possible to make some progress in considering the growth of transverse instabilities in idealized computational systems. Strehlow and Fernandes⁵⁵ have explored the propagation of transverse acoustic waves in exothermically reactive shocks in the short wavelength limit by means of the equations for ray propagation in a variable flow velocity, variable sound velocity medium. They have focused attention on the position in the one dimensional reaction zone at which the propagation ray is parallel to the shock front, such that the disturbance will propagate large lateral distances, and have considered the amplification of such a disturbance. In subsequent work, Barthel and Strehlow⁵⁶ have examined the kinematics of disturbances in the region between the shock front and the lateral propagation position in the reaction zone. They find that, for an idealized but reasonable model, sound waves are trapped in this region and become convoluted, in time contacting the shock front repeatedly with regular periodicity. The qualitative correspondence of

this periodicity with that exhibited by the finite amplitude, Mach stem disturbances observed in real gaseous detonations is encouraging in indicating the utility of further consideration of this aspect of the general problem of the manifestations of instability.

Marginally Propagating Detonations

As we have seen, the structure of detonation waves has two aspects, one being the sequence of physico-chemical states experienced by the detonating medium and the other the geometric configuration of boundaries or transition zones between these states. Likewise, stability has two somewhat different aspects, one having to do with the failure of detonations to exhibit steady, laminar flow and the other with the ability or inability of detonation to propagate indefinitely long times or distances under particular experimental circumstances. It is in this area of limits of propagation that perhaps the least quantitative progress has been achieved in recent gaseous detonation research. Zeldovich approached propagation limits theoretically by considering heat and momentum losses to confining walls within the steady, laminar flow model,¹ and has since concluded⁵ that this is not an adequate approach to the problem.

Progress has been made, however, in characterizing the behavior of marginally propagating detonations. This progress has served to make evident the considerable complexity of the question of propagation failure. There does not appear to be any clearly definable boundary between stable and unstable detonation propagation, but rather there are ranges of conditions in which transitional behavior can be recognized.

The best recognized characteristic feature of marginally propagating detonation waves in gases is the occurrence of spin, which is now identified simply as the coarsest mode of transverse shock wave disturbance compatible with the geometry of the detonating system. In a round tube this is, to a good approximation, the fundamental circumferential mode of acoustic vibration of the column of burned gas.^{57,58} The geometric structure of the front of spinning detonations has recently been elucidated,^{59,60} and the major features are indicated in Fig. 4.

Other studies^{61,62} of marginally propagating detonation over quite long runs have revealed the occurrence of periodic large separations of the shock front and the chemical reaction zone, with accompanying changes in the shock front strength and velocity. This behavior has not been strictly analogous to the computationally investigated behavior of one dimensional, time dependent detonation flow because the observed "galloping" behavior in gases has invariably been accompanied by transverse perturbations as well. In fact, the analogy between the behavior of such unsteadily propagating detonations in their re-initiation cycle and the much studied initial transition from deflagration to detonation in gases is striking.⁶³

Chemical Kinetics in Detonation

The final area to be considered in this survey is the chemical kinetics of exothermic reactions under detonation wave conditions. As was indicated earlier, the detonable gases with which the most experience exists are mixtures of fuels, mostly hydrogenous, with oxygen. The outstanding

characteristic of the kinetics of combustion of such mixtures is the acceleration of the reaction during its early stages by a branching chain mechanism. In such a process, the reaction rate is proportional to the amount of one of the reaction products that has accumulated. Mathematically, the reaction rate increases as $e^{\alpha t}$, where t is time and α is a positive proportionality coefficient which is a function of the temperature, density, and composition of the system. Thus a very minute initial rate of reaction may be increased by a very large factor, while α remains constant, before macroscopic reaction with appreciable temperature rise and consumption of reactants is evident. The finite period of time required for the appearance of macroscopic reaction, the so-called induction time, is a very well developed feature of the reaction zone structure of the familiar gas detonations.

Condensed explosives, on the other hand, are generally supposed, on the basis of low temperature thermal decomposition and thermal explosion limit experiments, to exhibit first order decomposition kinetics with a rate coefficient related to the temperature by an Arrhenius factor, $e^{-E_{act}/RT}$. Such a reaction accelerates during its course only as the temperature rises due to macroscopic reaction. While long induction periods do occur in low temperature experiments on a time scale determined by conductive heat losses, realistic activation energies are such that at the high temperatures encountered in the shock fronts of detonation, reaction is initially quite rapid and acceleration factors greater than about 10^2 are not possible between shock front and equilibrium conditions. Thus sharply terminated induction zones are not characteristic of thermally accelerating reaction under detonation conditions.

This distinction is drawn because much emphasis has been given by some authors⁴³ to the role of the induction period in determining the form and periodicity of the transverse structure of gaseous detonations. It should not be overlooked, however, that Erpenbeck's⁵⁰ analysis for thermally accelerating reaction mechanisms has shown that for reasonable exothermicity, acceleration is not necessary for transverse instability. Moreover, the decomposition of ozone, which is known to occur by a thermally accelerated mechanism and not by a branching chain, also exhibits instabilities, both in unsupported⁶⁴ and overdriven detonations.^{65,66}

The finite amplitude form of the instabilities in the ozone decomposition detonation or other detonations without branching chain kinetics has not been well characterized, however, and this area of incomplete knowledge of gaseous detonations may harbor important clues to two questions. The first is the possibility that gaseous explosives without branching chain kinetics may exhibit recognizably different detailed forms of transverse instability and propagation limit behavior. The second, related question concerns the possibility that condensed explosives, if they do react by thermally accelerating mechanisms, might be more closely akin to gaseous detonation systems with thermal acceleration than to the branching chain systems.

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Figure Captions

- Fig. 1 Computed pressure - volume diagram for steady, one dimensional detonation of pure ozone at 1 atm initial pressure, with chart comparing experimentally observable properties at no reaction, equilibrium Chapman-Jouguet, and weak equilibrium detonation conditions. D , detonation velocity; T , temperature; p , pressure; ρ , density; U_p , particle velocity, M , Mach number of equilibrium flow, with respect to shock front.
- Fig. 2 Instantaneous interferogram of reactive Mach stem generated in otherwise laminar wave in detonable gas by nozzle technique. (Fig. 1 of Ref. 36.)
- Fig. 3 Streak schlieren interferogram and smoked plate inscription record of reflected shock initiation event in rectangular shock tube. (Similar experiment to that represented in Fig. 1 of Ref. 55 or Figs. 1 and 2 of Ref. 41.)
- Fig. 4 Annotated photograph of three dimensional, colored model of spinning detonation wave front.

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