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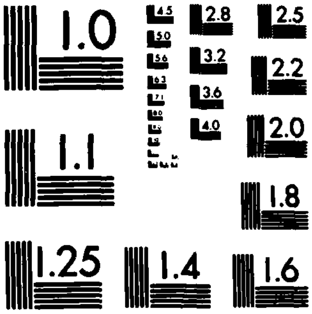

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A reactive shock simulation model used to study the formation and propagation of shocks and detonations in condensed phase materials is described. Two test cases are given: 1) laser initiation of a shock wave propagating through water and 2) the development of a detonation front from a hot spot in liquid nitromethane.

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Appendices

REACTIVE SHOCK PHENOMENA IN CONDENSED MATERIALS: FORMULATION OF THE PROBLEM AND METHOD OF SOLUTION

I. INTRODUCTION

Shock waves are particularly useful dynamic phenomena for generating high temperatures and pressures very quickly. They are used in practical commercial applications such as synthesizing diamonds, in military applications such as igniting explosives, and in basic research applications such as producing a controlled environment for studying elementary chemical reactions rates. In this paper, we describe a numerical reactive shock model developed at NRL which is being used to study the physics controlling the formation and propagation of shocks in condensed phase materials. When coupled to a chemical kinetics reaction scheme, the model describes the detailed chemical processes initiated by shock waves. When coupled to a model for energy release, the code describes detonations.

A review of the theory and equations used in numerical modeling of shocks and detonations in condensed phase explosives has been given by Mader [1]. Mader describes the physics of detonations in common explosives and presents a detailed description of the equations of state of the condensed materials and gaseous products. The model we have developed is different in several ways from the ones he has developed and is based on the Reactive Shock Models described by Oran and Boris [2]. The covective transport equations are solved using a highly accurate finite-difference algorithm, FCT, which has both minimal diffusion and minimal error in the phase propagation [3]. We have added routines for external energy deposition which allow us to simulate particular mechanisms such as laser energy input. The model of the fluid dynamics can be coupled to simple reaction models or to detailed chemical kinetics subprograms in order to study the initiation mechanisms of high energy explosives. Although we describe a one-dimensional model, the basic

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algorithms for the equations of state, energy deposition, and chemical kinetics can be easily incorporated in two- or three-dimensional FCT codes and so the calculations are directly extendable to multi-dimensions. Finally, the methods allow the code to be vectorized, making it possible to run large problems efficiently on vector computers.

In Section II we describe the physics and chemistry in the model and discuss the formulation of the problem. First, we describe the equation of state used in the model for condensed phases. An Arrhenius one-step reaction supplemented with an induction model is assumed to control the conversion of explosive to gas products. Then we describe the equation of state for the products. When both phases coexist, temperature and pressure equilibrium are assumed. In Section III we describe the numerical solution. Finally, typical results are presented in Section IV, where we first describe a calculation in which a laser pulse deposits energy into a thin layer of absorbing material confined between a wall and a liquid. A shock is generated in the liquid and we observe its characteristics as it propagates and decays. We then describe a second example in which a detonation wave develops from a hot spot in liquid nitromethane.

II. FORMULATION OF THE PROBLEM

In principle, a complete, detailed numerical description of the generation and evolution of a reactive shock in a homogeneous material involves the solution of the time-dependent Navier-Stokes equations for the reactive material. We also must incorporate a great deal of information about the chemical and physical properties of the particular material involved. We need to specify the equations of state for reactants and products that go properly to the cold solid and hot gas limits. Heat transfer by conduction is usually too slow to affect the propagation but radiation from the high temperature products to the undecomposed reactive material surface can be quite significant, especially when the products contain solid carbon particles. Thus we need to know the radiative properties of the gases produced and of the material surface. Also, we need to know the chemistry of reactions, or at least the rate of combustion and the energy release. Finally, we might need to describe other effects influencing the propagation process such as species diffusion, carbon deposition and coagulation.

If the material through which the shock propagates is heterogeneous, there are additional complexities. Most commercial explosives, for example, are formed by compressing the explosive powder with a soft binding agent. When such an explosive is subjected to stress, its deformation properties are complicated by the yield of the binding agent. Heat conduction becomes an important mechanism for the growth of the hot spots formed by wave reflections at the complex interfaces between the powder and the binding agent. It would be an enormous task to develop and use a model that would treat each element of an explosive powder or binding material as a separate homogeneous domain with the proper compatibility conditions between one element and another. Usually this problem is dealt with by using a phenomenological composite equation of state whose parameters are derived experimentally from measurements of shock or detonation waves propagating in the actual reactive material.

In this work we consider one-dimensional shocks in homogeneous materials. The effects of bulk viscosity are neglected, therefore omitting the need for deviatoric stress terms (since shear deformations are absent in one dimension). Radiation and heat conduction are assumed insignificant and therefore neglected. Therefore, the propagation of the reactive shock is reduced to solving the set of equations for mass, momentum and energy conservation combined with the proper equation of state and a description of the chemistry:

(1) Mass Conservation

$$\frac{\partial}{\partial t}\left(\rho r^{\alpha-1}\right) + \frac{\partial}{\partial r}\left(\rho u r^{\alpha-1}\right) = 0 \qquad (1)$$

(2) Momentum Conservation

$$\frac{\partial}{\partial t}\left(\rho u r^{\alpha-1}\right) + \frac{\partial}{\partial r}\left(\rho u^2 r^{\alpha-1}\right) + r^{\alpha-1}\frac{\partial p}{\partial r} = 0 \qquad (2)$$

(3) Energy Conservation

$$\frac{\partial}{\partial t}\left(E r^{\alpha-1}\right) + \frac{\partial}{\partial r}\left(E u r^{\alpha-1}\right) + \frac{\partial}{\partial r}\left(r^{\alpha-1} p u\right) = r^{\alpha-1}\rho\Delta\dot{I} \qquad (3)$$

where t denotes the time, r the radius, ρ the density, u the particle velocity and p the pressure. The total energy per unit volume is $E \equiv \rho I + \rho u^2/2$, where I is the specific internal energy (including the stored chemical energy) and $\Delta\dot{I}$ denotes the energy absorbed per unit mass per unit time by the bulk of fluid from an external source. The exponent α is a geometric index: $\alpha = 1,2$ and 3 for planar, cylindrical and shperical geometries, respectively.

The above relations are supplemented by both a mechanical equation of state and a caloric equation of state, written symbolically as

$$p = p(\rho, I, w)$$

$$T = T(\rho, I, w),$$

where T is the temperature and w is the explosive mass fraction. We use an equilibrium equation of state for the condensed explosive and for the gaseous products. Thus we assume that the different intermolecular and intramolecular degrees of freedom of a molecule are in equilibrium at every instant in time. In other words, if the translational energy increases, the rotational, vibrational and electronic degrees of freedom absorb enough of the new energy to reach the same temperature instantaneously. Although this assumption is not strictly correct [4], it is a good approximation for most purposes and it enables us to avoid the complexities involved in a model which takes the relaxation of the molecular degrees of freedom into consideration.

The equation of state for the condensed explosive is usually derived experimentally by determining the states behind explosion-generated shocks in the explosive material. Since the pressure generated behind the detonation wave in the condensed phase is of the order of 100 Kbars, the ideal gas assumption is not valid for the gaseous products. As a consquence, we cannot assume that the different gases constituting the products can be treated as independent, noninteracting species. A theoretial description of the products then has to consider the forces between molecules of different species as well as those between identical ones, thus adding more complications to finding an equation of state for the mixture of products. The BKW [5], LJD [6], and WCA [7] equations of state are all attempts to describe mixtures of gasses at very high pressures.

Finally, we need to know the rate of decomposition of the material in terms of the instantaneous state parameters such as temperature, and either pressure or density. Specifically, we need an expression for the evolution of the composition with time.

II.1. Equations of State of the Condensed Phase

The first equations of state developed for condensed phases were derived by determining the isothermal compressibility using a method developed by Bridgman [8]. The states off the isotherm are then calculated from thermodynamic relations. However, practical considerations limit isothermal or static compression experiments to pressures which are much lower than those encountered in shock compressed condensed phase materials, especially those occuring in detonations.

In response to this problem, Walsh and Christian [9] developed a technique for deriving an equation of state by determining the locus of single-shocked states, i.e. the Hugoniot curve. States off the Hugoniot can be then evaluated using thermodynamic relations. The Walsh and Christian method involves measuring the relation between the shock velocity (produced by an explosion) and the free surface velocity in the explosive material, and then using the fact that the free surface velocity is almost exactly double the particle velocity behind the shock wave. This assumption is valid to 1% for pressures up to 500 Kbar. The relation between the shock velocity, u_s, and the particle velocity, u_p, has been found to be very nearly a linear fit [10]

$$u_s = c_o + s_o u_p \tag{4}$$

where c_o is the sound speed in the undisturbed material. Once c_o and s_o are measured, the pressure of the condensed phase, denoted from now on by a subscript c, is given by

$$p_c = p_H + \frac{\gamma}{v_c} \{I_c - I_H\} \tag{5}$$

where

$$p_H = p_o + \frac{\rho_o c_o^2 \eta}{(1-s_o \eta)^2} \tag{6}$$

is the Hugoniot pressure corresponding to a compression,

$$\eta \equiv \frac{v_o - v_c}{v_o} = 1 - \frac{\rho_o}{\rho_c} .$$

In the above relations, the subscript "o" denotes the state of the undisturbed material, while v is the specific volume and γ is the Gruneisen gamma. The Hugoniot internal energy, I_H, is obtained from

$$I_H = I_o + \frac{1}{2} (p_H + p_o) v_o \eta. \tag{7}$$

The temperature T_c is given by

$$T_c = T_H + \frac{I_c - I_H}{C_v} \tag{8}$$

where T_H is obtained from

$$\ln T_H \equiv F_s + G_s(\ln v_c) + H_s(\ln v_c)^2 + I_s(\ln v_c)^3 + J_s(\ln v_c)^4. \tag{9}$$

The coefficients F_s, G_s, H_s, I_s and J_s of the expansion are derived from a least squares fit to the Hugoniot temperature T_H in terms of the logarithm of the volume. The details of the derivation of the condensed phase equation of state are given in the Appendix A1.

Equations (4) to (9) are used when $v_c < v_o$, i.e. for compressed states. When $v_c > v_o$,

$$p_c = \frac{\gamma}{v_c} \{I_c - (I_o - \frac{p_o v_o}{\gamma} - \frac{C_v \eta}{3\alpha})\} \tag{10}$$

and

$$T_c = T_o + \frac{I_c - I_o}{C_v} \tag{11}$$

where C_v is the specific heat at constant volume and α is the coefficient of linear expansion.

II.2. Equation of State of the Gas Products and the Rate of Reaction

The equation of state of the gas products expresses the pressure and temperature in terms of the specific volume, the internal energy, and the composition of the products. If the detailed chemistry of the reaction zone is sought, the reaction zone composition could, in principal, be obtained theoretically by first determining and then solving an appropriate set of chemical kinetic and thermodynamic equations. On the other hand, if we assume an infinitely fast rate of reaction, the reaction zone reduces to a discontinuity propagating through the explosive. The composition of the products immediately behind the wave front can then be obtained by simultaneously solving the chemical equilibrium relations and the jump conditions. The gas products then expand or contract isentropically (maintaining chemical equilibrium at every point) according to the upstream boundary conditions.

Since very little is known about the mechanism of decomposition of condensed explosives, our preliminary model adopts the following assumptions:

a) The condensed explosive is converted to gas products in chemical equilibrium according to the global finite raction rate:

$$\frac{dw}{dt} = - wZ^* e^{-E^*/RT} \tag{12}$$

b) To avoid solving the chemical equilibrium relations for the composition every time the equation of state of the products is needed, we assume that the states of the gas products are close to those encountered in a steady Taylor-type detonation wave. In this type of wave, the condensed explosive reaches the Chapman-Jouguet (CJ) equilibrium state instantaneously after crossing the wave front and then expands isentropically to the undisturbed pressure. The equilibrium isentrope is therefore a good reference, the same way the Hugoniot was a reference for the compressed condensed explosive. Then we can use an average Gruneisen gamma to evaluate the pressure and temperature of states off the isentrope. The details of the derivation of the gas products equation of state are given in Appendix A2.

The pressure of the gas products, denoted by a subscript g, is given by

$$p_g = p_i + \frac{\gamma_i'}{v_g}(I_g - I_i) \tag{13}$$

The pressure, p_i, and internal energy, I_i, on the isentrope are determined from

$$\ln p_i \equiv A + B(\ln v_g) + C(\ln v_g)^2 + D(\ln v_g)^3 + E(\ln v_g)^4 \tag{14}$$

and

$$\ln(I_i+Z) \equiv K + L(\ln p_i) + M(\ln p_i)^2 + N(\ln p_i)^3 + O(\ln p_i)^4. \tag{15}$$

The coefficients of the expansions in Eq. (14) and Eq. (15) are derived from a least squares fit to the equilibrium isentrope. In the above, γ_i' is the Gruneisen gamma evaluated at the state "i" on the isentrope, and Z is a constant which adjusts the standard state energy to be consistent with that of the condensed explosive. Finally,

$$T_g = T_i + \frac{I_g - I_i}{C_v'} \tag{16}$$

where

$$\ln T_i = Q + R(\ln v_g) + S(\ln v_g)^2 + T(\ln v_g)^3 + U(\ln v_g)^4, \tag{17}$$

where C'_v is the average specific heat of the products.

II.3. Equation of State for Mixtures of Condensed Explosive and Gas Products

Since the internal energies of both the condensed explosive and gas products are measured from the same reference energy, there is no need for a heat release term explicity in the energy equation. Instead, the heat released by the chemical decomposition appears as an increase in temperature and pressure. In other words, for the same values of v and I, the equation of state of the products yields a much higher temperature and pressure than the equation of state for the condensed explosive. In between the two extremes, $w = 1$, representing the pure condensed explosive, and $w = 0$, representing the gaseous products, the temperature and pressure increases continuously as w decreases.

The finite rate of burning expressed in Eq. (12) yields a reaction zone of finite thickness in which $0 < w < 1$ and which contains a mixture of condensed explosive and gas products. We assume that in those regions containing such a mixture the condensed phase is composed of a large collection of small fragments uniformly distributed over the region. Moreover, we neglect all transient effects between the condensed and gas phases and assume temperature and pressure equilibrium, $T_c = T_g$ and $P_c = P_g$. Since the volumes and internal energies of the two phases are additive, determining the equation of state of the mixture,

$$T = T(v,I,w)$$

$$p = p(v,I,w),$$

reduces to finding the values of I_c, I_g, v_c and v_g that satisfy

$$T_c(v_c,I_c) = T_g(v_g,I_g) \tag{18a}$$

$$p_c(v_c,I_c) = p_g(v_g,I_g) \tag{18b}$$

$$I = wI_c + (1-w)I_g \tag{18c}$$

$$v = wv_c + (1-w)v_g \quad . \tag{18d}$$

Equations (18) are four equations in four unknowns v_c, v_g, I_c and I_g. They can be reduced to a single nonlinear equation expressing the difference in pressure ($p_c - p_g$) in terms of v_c (or v_g). To obtain this reduction, we first enforce the temperature equilibrium

$$c_c = T_g = T.$$

Then we rewrite Eqs. (8) and (16) as

$$I_c = I_r(v_c) + C_v(T - T_r(v_c))$$

$$I_g = I_i(v_g) + C_v'(T - T_i(v_g))$$

and multiply the first by w and the second by (1-w). After using Eq. (18c) we solve for T:

$$T = \frac{I + w(C_v T_r - I_r) + (1 - w)(C_v' T_i - I_i)}{wC_v + (1 - w)\, C_v'} \quad . \qquad (19)$$

In Eq. (19), the subscript r denotes the reference state of the condensed material. As explained in Appendix A1, r denotes H when $\eta > 0$, and c' ($v_{c'} \equiv v_c$, $p_{c'} \equiv 0$) when $\eta < 0$.

Next, we solve for the pressure difference ($p_c - p_g$). Now that the equilibrium temperature is known for a given choice of v_c (or v_g), substituting for ($I_c - I_r$) by $C_v(T-T_r)$ in Eq. (21) and for ($I_g - I_i$) by $C_v'(T-T_i)$ in Eq. (27), we get

$$p_c - p_g = [p_r(v_c) - p_i(v_g)] + \frac{\gamma C_v}{v_c}[T - T_r(v_c)] - \frac{\gamma_i' C_v'}{v_g}[T - T_i(v_g)] \quad . \qquad (20)$$

Equation (2) is solved by iterating on v_c (or v_g).

II.4. Induction Model

Since an Arrhenius one-step reaction alone cannot represent an extended period with no apparant temperature or pressure change, the reaction rate given in Eq. (12) must be supplemented with a model for such an induction time. Thus if it is required, an induction time can elapse before the reaction rate of Eq. (12) an thus the energy release and conversion to products is switched on. If the steady state induction time (at constant temperature, T^o, and pressure, p^o) is denoted by $\tau^o(T^o,p^o)$, the quasi-steady induction time for varying temperature and pressure, τ, is determined from the solution of the integral equation

$$\int_o^{\tau} \frac{dt}{\tau^o(T(t),p(t))} = 1 \ .$$

In our algorithm, τ is obtained from the solution of $f(\tau) = 1$, where

$$\frac{df}{dt} = \frac{1}{\tau^o(T,p)} \tag{21}$$

and $f(0) = 0$. Moreover, τ^o may be determined emperically or using detailed chemical kinetics calculations. Here we will assume it takes a simple Arrenius form:

$$\tau^o = A^{\ddagger} e^{E^{\ddagger}/RT^o} .$$

III. NUMERICAL SOLUTION

We must solve the set of conservation equations (1) to (3), the rate of reaction, Eq. (12), and the induction time lapse, Eq. (21). These are supplemented by the equations of state for the range $0 \leq w \leq 1$. First we write Eqs. (12) and (21) in the same transport form as Eqs. (1) to (3). This is accomplished by transporting ρw and ρf instead of w and f, namely

$$\frac{\partial}{\partial t}(\rho w r^{\alpha-1}) + \frac{\partial}{\partial r}(\rho w u r^{\alpha-1}) = \rho r^{\alpha-1} w Z^* e^{-E^*/RT} \tag{22}$$

and

$$\frac{\partial}{\partial t}(\rho f r^{\alpha-1}) + \frac{\partial}{\partial r}(\rho f u r^{\alpha-1}) = \frac{\rho r^{\alpha-1}}{\tau^{o}(p,T)} . \tag{23}$$

Equations (12) and (22) are equivalent, as are Eqs. (21) and (23). The integration step starts by evaluating the time step δt using the Courant condition

$$\delta t \leq \min \left(\frac{\delta x}{|u|+c}\right)$$

where c is the sound speed. This guarantees the stability of the numerical solution of Eqs. (1)-(3) and (22)-(23). The expressions for the sound speed in the condensed phase, gas phase, and the mixture of both phases are given in Appendix A3.

The solution of Eqs. (1)-(3) and (22)-(23) is obtained by operator splitting the fluid dynamic step, the chemical reaction step, and the energy deposition step. The fluid dynamic step is solved using JPBFCT (a modified version of ETBFCT [3]), a fourth order flux-corrected transport algorithm. Equations (1), (2), and the fluid dynamic components of Eqs. (3), (22) and (23), the left hand sides, are transported using JPBFCT to advance ρ, u, I, w, and f. The explosive mass fraction w is then limited between 0 and 1 using

$$w = \max\{0, \min(1,w)\} \tag{24}$$

and the equation of state is used to get p and T.

Next, the program checks if the induction time has elapsed (f > 1) and if so, switches on the chemical reaction. The fraction of induction time, f, is advanced and if switched on, the mass fraction, w, is also advanced, by solving the ordinary differential equations:

$$\frac{\partial}{\partial t}(\rho f r^{\alpha-1}) = \frac{\rho r^{\alpha-1}}{\tau^o(T,p)} \tag{25a}$$

and

$$\frac{\partial}{\partial t}(\rho w r^{\alpha-1}) = \rho w r^{\alpha-1} Z^* e^{-E^*/RT}, \tag{25b}$$

the right hand sides of Eqs. (22) and (23). The solution for f is given by the explicit formula

$$f^{new} = f^{old} + \frac{\delta t}{\tau^{o}(T,p)} \tag{26a}$$

and the new value of w comes from the implicit formula

$$w^{new} = w^{old}/(1+Z^{*}e^{-E^{*}/RT}\delta t), \tag{26b}$$

The equation of state is then used again to determine p and T, after the burning process.

Finally, if energy is deposited from an external source, it is added to the specific internal energy I, and the equation of state is used again to obtain p and T in preparation for a new integration time step.

IV. TYPICAL RESULTS

IV.1. Laser-Induced Shock Wave Structure

The calculation presented below was performed to assess the ability of long duration laser pulses to create a shock wave structure with a reasonably wide plateau behind the shock. Since the plateau would provide an environment with constant pressure and temperature in which optical probes measurements would be relatively easy to analyze, it is a potentially important feature of an experiment. In an upcoming report we will discuss those properties of the material and laser pulse which control the evolution of the plateau. In this section we describe one test calculation in some detail.

Consider a 30μm layer of plexiglass confined on one side by a rigid wall and on the other by a semi-infinite slab of water. A 20 ns half-width laser pulse is deposited into the plexiglass in such a way that the energy deposited per unit volume decays linearly with the depth into the plexiglass and vanishes at the edge where the plexiglass meets the water.

The computational grid spacing in each material is uniform, but varies with the material. The initial cell size in the plexiglass zone is taken as 1.5 μm. The initial cell size in the water zone is then determined such that the ratio of the cell sizes is nearly equal to the ratio of the local sound speeds. Thus the Courant time-step is nearly equal in both regions. The number of cells in each zone is fixed. The interface of the last cell in the plexiglass zone moves with the local particle velocity. As a result the cells in the plexiglass zone expands while those in the water contract. However, each region maintains uniform grid spacing at all times. The power of the laser pulse is assumed to be triangular in shape with a 40 ns base width. The initial temperature and pressure are $300^{\circ}K$ and 1 atm, respectively. The parameters used in the different equations of state are given in Table I.

The calculated pressure at different times is illustrated in Fig. (1). The position of the interface between the plexiglass an water is denoted by a dot on each of the shown profiles. As the input power increases for the first 20 ns, the pressure near the wall increases continuously. When the power begins to decrease, the pressure at the wall starts to drop and a propagating wave develops (26 ns). The calculation predicts a 10-20 ns plateau behind the shock wave with a peak pressure which is essentially constant for a time longer than the duration of the laser pulse (44 ns). Later in the calculation, the details of the initial energy deposition process are essentially forgotten. Then the wave continously approaches the classical blast wave profile which would result if a fixed amount of energy is deposited instantaneously in an infinitismally thin layer of water. Such a blast wave calculation is illustrated in Fig. (2). Here we notice that the shock wave pressure decays faster than in Fig. (1).

The plateau results from the interaction betwen the way the laser energy is deposited and the way it is transported to the water. In Fig. (1), we notice that during the power rise-time of the laser pulse and up to 22 ns, the pressure profile decays away from the wall. During this period, the pressure builds up in the plexiglass faster than the material can expand. While the pressure is building up within the plexigless, compression pressure waves emanate from this region and propagate into the water. As a result, the pressure profile follows the trend of the energy deposition curve.

TABLE I.

Plexiglass	Water
ρ_o = 1.18 gm/cc	ρ_o = 1.0 gm/cc
c_o = 0.243 cm/μs	c_o = .01483 cm/μs
s_o = 1.5785	s_o = 1.97
α = 10^{-4} $^{\circ}K^{-1}$	α = 6×10^{-5} $^{\circ}K^{-1}$
γ = 2.157	γ = 1.65
C_v = 0.35 cal/gm $^{\circ}$K	C_v = 1.0 cal/gm $^{\circ}$K

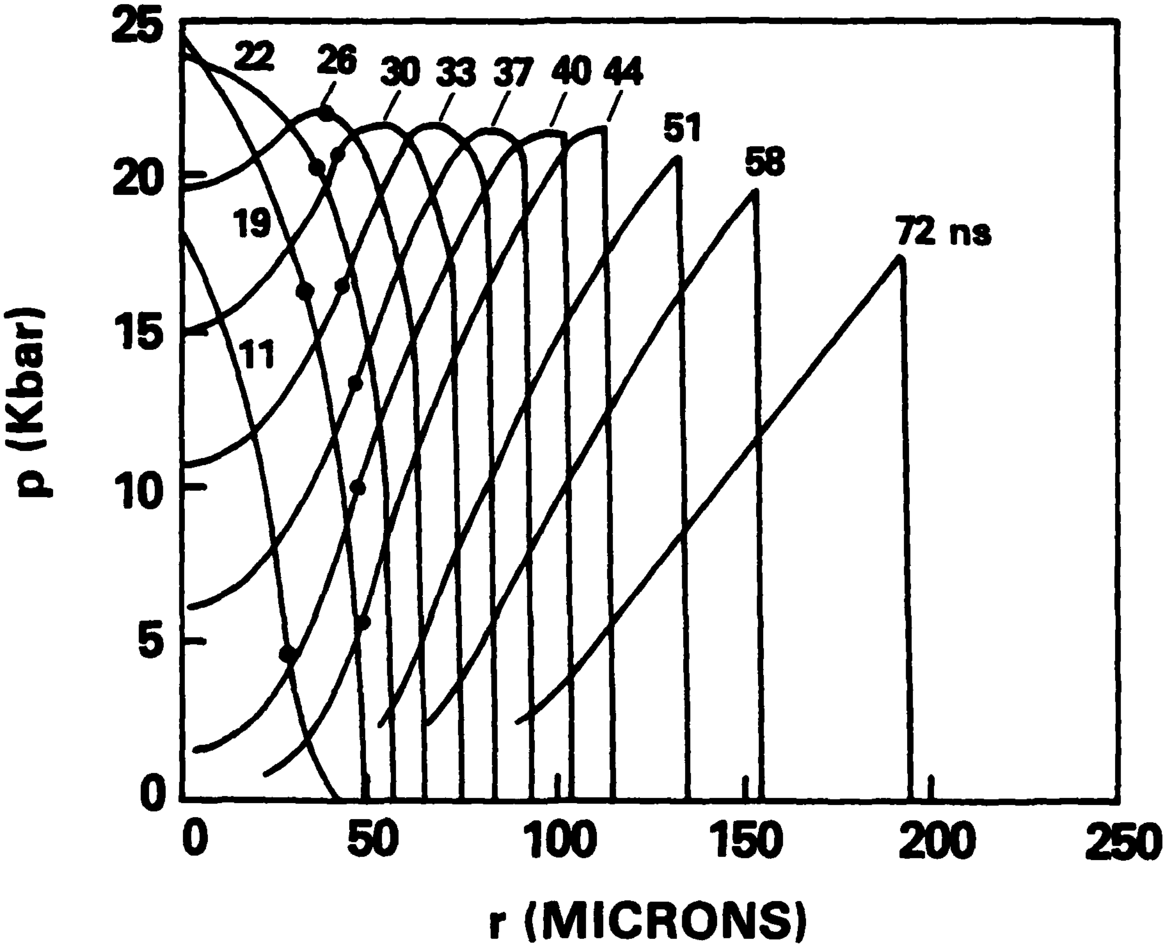

Figure 1 Calculated pressure profiles for a 20 ns half-width laser pulse deposited in 30 microns of plexiglass in contact with water. The dot on each curve denotes the position of the interface between plexiglass and water.

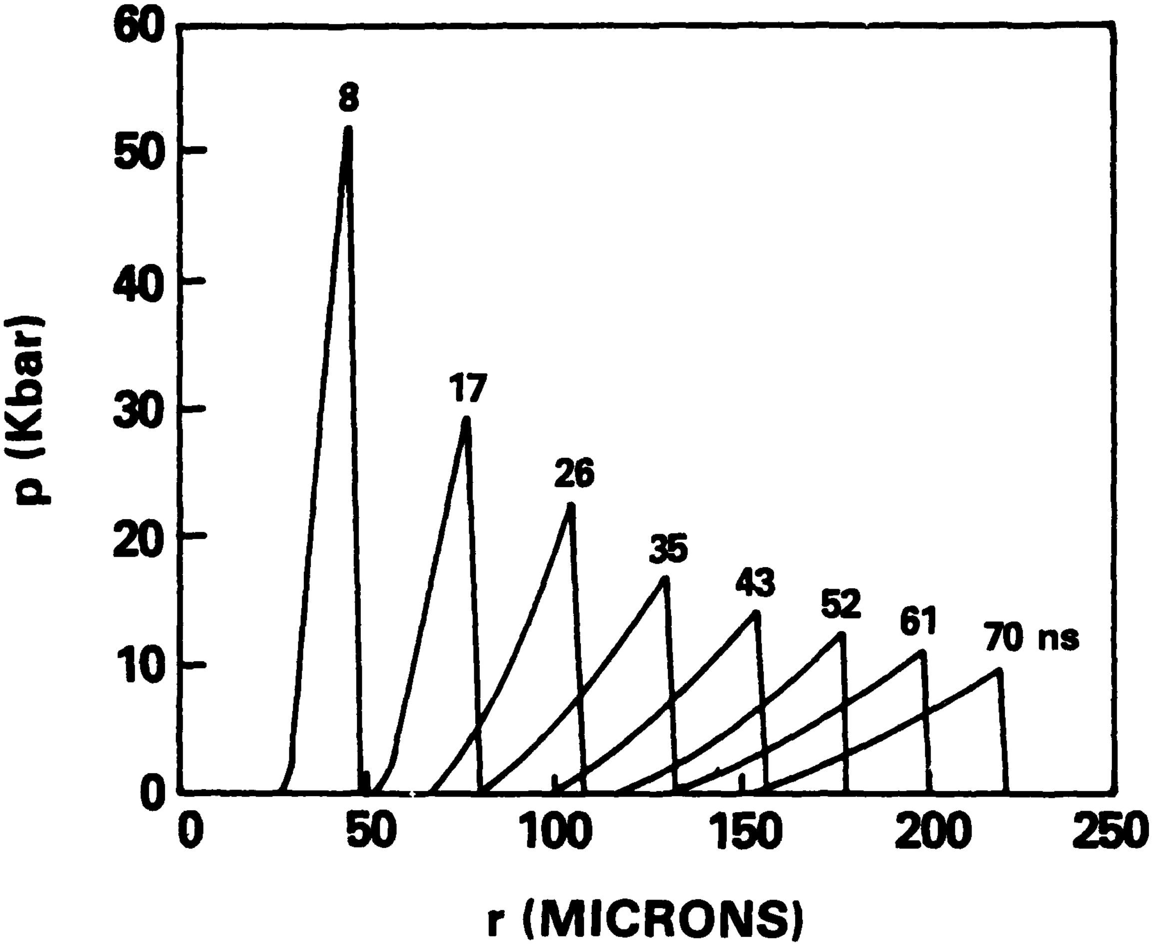

Figure 2 Classical blast wave solution in water for the same amount of energy deposition as in Fig. 1.

When the power begins to drop, the pressure in the plexiglass drops even faster due to material expansion. A rarefaction wave is created near the wall and propagates into the water, while the compression waves downstream steepen up to form a shock. The rarefaction and the compression waves combine to create a zone of relatively uniform pressure right behind the shock. During this period the peak pressure remains nearly constant for a period of time. Eventually at 40 ns in Fig. (1), the rarefaction wave catch up with the shock resulting in a plateau immediately behind it, and later (51 ns) the plateau disappears. As the shock wave propagates downstream, the rarefaction waves cause the profile to change from convex to concave, and approach the classical blast wave profile.

Finally, Fig. (3) illustrates the calculated pressure waves for the same conditions of Fig. (1), except that all cell sizes are twice as large. This serves as a test of the convergence of the numerical solution. A close comparison between the two figures reveals that the pressure waves corresponding to the same time are nearly coincident. Those of Fig. (3) are slightly lower in value near large pressure gradients due to the larger numerical diffusion associated with larger cell sizes.

IV.2. Evolution of a Detonation Wave from a Hot Spot

The next calculation shows that heating a high energy explosive uniformly does not necessarily lead to homogeneous ignition. Ignition may start at hot spots caused by the inhomogenieties of either the material or the heating mechanism. The reaction would then propagate, consuming the material between hot spots before any significant reaction occurs in the background material which is at slightly lower temperature.

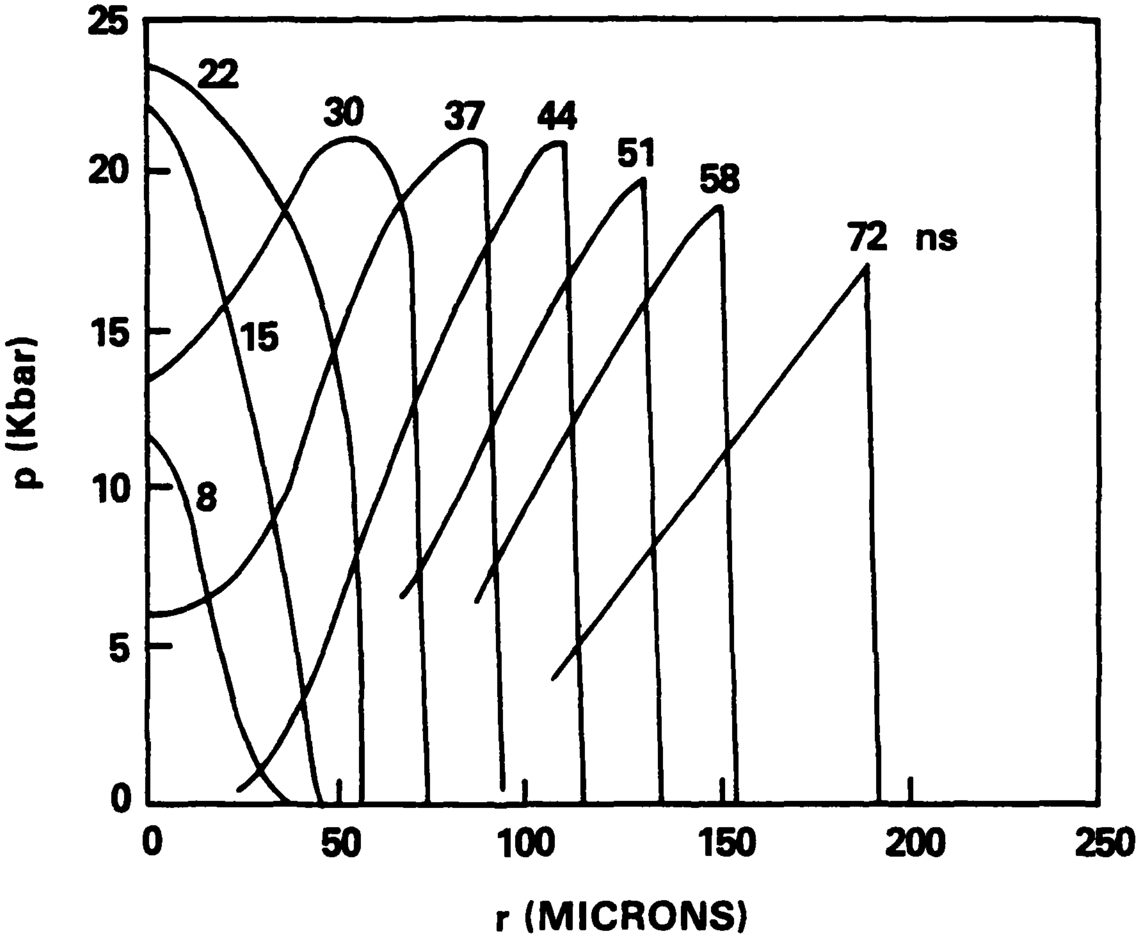

Figure 3 Calculated pressure profiles for the same physical conditions as in Fig. 1, but for computational cell sizes twice as large.

Here we model a sample of liquid nitromethane which is 1.2 cm long. It is assumed that the sample is initially at 1000°K. This is beyond its ignition temperature so that, in principle, it should start reacting. The pressure is initially 1 atm yielding a background density of 0.692 gm/cc. The hot spot is modelled by superimposing a Gaussian temperature profile 200° K higher than ambient and 0.1 cm wide on the background temperature at the center of the sample. This symmetry allows us to perform the calculations for half the sample only, and the center of the Gaussian is formally equivalent to a rigid wall.

The computational grid is uniformly spaced with a fixed cell size of 0.01 cm. The parameters of the eqution of state and the rate of reaction for liquid nitromethane are given in Table II. We notice that $A^{\ddagger} = 0$. In this case, it is assumed that the parameters of the one-step Arrhenius reaction are adjusted to crudely incorporate any induction time.

The calculation predicts the formation of a detonation wave within 0.4 μs. As illustrated in Fig. (4), the detonation pressure builds up quickly towards a steady wave pressure of 65 Kbars that propagates at 0.54 cm/μs (Mach number = 3.72). At 1.28 μs, the detonation wave initiated at the hot spot has almost consumed the whole sample before any significant reaction occurs at the background temperature. Without the presence of the hot spot, the material would have exploded 31.2 μs, much later than it has here.

ACKNOWLEDGMENTS

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TABLE II.

Liquid Nitromethane

ρ_o = 1.128 gm/c

c_o = 0.1647 cm/μs

s_o = 1.637

α = $3 \times 10^{-4}\ {}^{o}K^{-1}$

γ = 0.6805

C_v = 0.414 cal/gm°K

C_v' = 0.556 cal/gm°K

Z = 0.1

Z^* = $4.0 \times 10^{8}\ \mu s^{-1}$

E^* = 5.36×10^{4} cal/mol

F_s = +5.41171

G_s = -2.72959

H_s = -3.21986

I_s = -3.90757

J_s = +2.39028

A = -3.11585

B = -2.35968

C = $+2.10663 \times 10^{-1}$

D = $+3.80357 \times 10^{-3}$

E = -3.53455×10^{-3}

K = -1.39937

L = $+4.79350 \times 10^{-1}$

M = $+6.06708 \times 10^{-2}$

N = $+4.10673 \times 10^{-3}$

O = $+1.13327 \times 10^{-4}$

Q = +7.79645

R = -5.33007×10^{-1}

S = $+7.09020 \times 10^{-2}$

T = $+2.06150 \times 10^{-2}$

U = -5.66140×10^{-3}

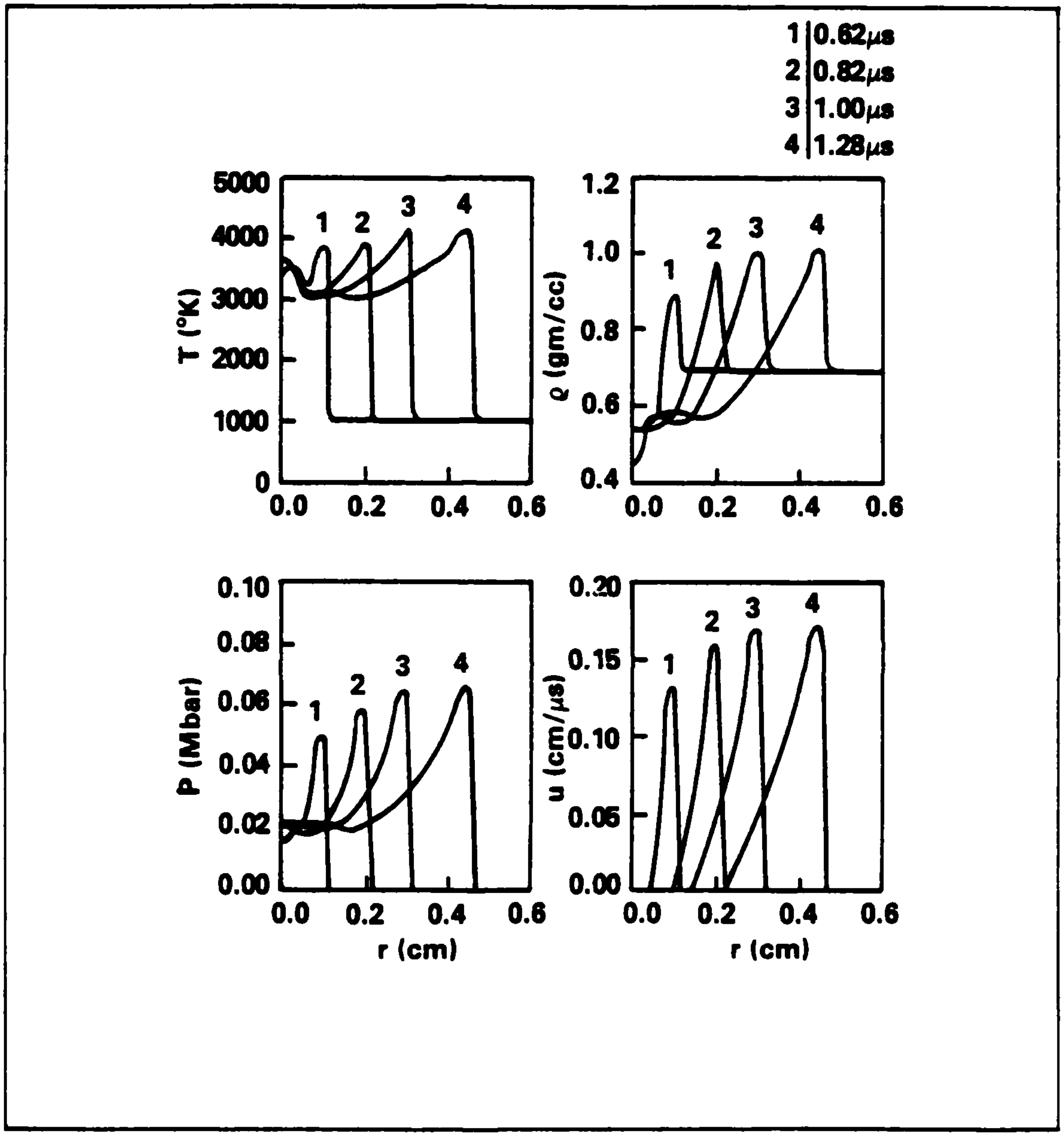

Figure 4 Formation and evolution of a detonation front from a 1200 K hot spot in liquid nitromethane at 1000 K.

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APPENDICES

A1. Equation of State of the Condensed Phase

Here we adopt the Walsh and Christian method [9] for deriving the equation of state of a condensed explosive. This method begins by fitting the measured shock velocity, u_s, and measured particle velocity, u_p, to the linear relation,

$$u_s = c_o + s_o u_p \quad .$$

Then combining the above equation with statements of conservation of mass

$$(u_s - u_p)\rho_H = u_s \rho_o$$

and conservation of momentum

$$p_H - p_o = \rho_o u_s u_p$$

across the shock, we get

$$p_H - p_o = \frac{\rho_o c_o{}^2 (1 - \frac{\rho_o}{\rho_H})}{[1 - s_o(1 - \frac{\rho_o}{\rho_H})]^2} \quad , \tag{A1.1}$$

where the subscript "o" denotes the state of the undisturbed material, and the subscript "H" denotes a point on the Hugoniot. Denoting the volumetric compression by η,

$$\eta \equiv \frac{v_o - v_H}{v_o} = 1 - \frac{\rho_o}{\rho_H} \tag{A1.2}$$

where v is the specific volume, Eq. (A1.1) reduces to

$$p_H = p_o + \frac{\rho_o c_o^2 \eta}{(1-s_o \eta)^2} \quad . \tag{A1.3}$$

Finally, from energy conservation across the shock front, the internal energy, I_H, can be written as

$$I_H - I_o = \frac{1}{2}(p_H + p_o)(v_o - v_H) = \frac{1}{2}(p_H + p_o)\, v_o \eta . \tag{A1.4}$$

By using the fact that temperature has a relatively small effect on compressibility, Walsh and Christian [9] were able to determine the variation of the temperature along the Hugoniot by assuming that C_v and $(\partial p/\partial T)_v$ are constants:

$$T_H = T_o\, e^{b(v_o - v_H)} + \frac{e^{-bv_H}}{C_v} \int_{v_o}^{v_H} e^{bv} f(v) dv \tag{A1.5}$$

where C_v is the specific heat at constant volume. In Eq. (A1.5),

$$f(v_H) \equiv \frac{1}{2} \frac{dp_H}{dv_H}(v_o - v_H) + \frac{1}{2} p_H$$

while

$$b \equiv \frac{(\partial p/\partial T)_v}{C_v} \quad .$$

By performing the integration in Eq. (A1.5), we obtain the temperature along the Hugoniot. Since in a typical calculation, Eq. (A1.5) has to be evaluated each time the temperature is needed, Mader [1] fit the $T_H - v_H$ curve using a fourth degree polynomial in log of the volume:

$$\ell n\ T_H = F_s + G_s(\ell n\ v_H) + H_s(\ell n\ v_H)^2 + I_s(\ell n\ v_H)^3 + J_s(\ell n\ v_H)^4. \quad \text{(A1.6)}$$

Equations (A1.1) to (A1.5) are quite general and are equally valid for solids and liquids. For some solids, however, a kink in Eq. (4) occurs at the point where there is a change of phase to liquid. In this case, another set of coefficients, c_1 and s_1, are required in addition to c_o and s_o.

In reactive-shock phenomena, the states attained after compression are expected to fall near the Rankine-Hugoniot locus, making this line a good reference state. Thus with the use of the Gruneisen* γ, defined as $\gamma \equiv v(\partial p/\partial I)_v$, we can reach any state off the Hugoniot from point H which has the same specific volume as this state. This is illustrated schematically in Fig. (A1.a). Denoting the condensed explosive by the subscript "c", we have for constant γ,

$$p_c - p_H(v_c) = \frac{\gamma}{v_c}\,[I_c - I_H(v_c)]. \quad \text{(A1.7)}$$

Similarly, since $C_v \equiv (\frac{\partial I}{\partial T})_v$, for a constant C_v

$$T_c - T_H(v_c) = \frac{I_c - I_H(v_c)}{C_v} \quad \text{(A1.8)}$$

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*For an ideal gas Gruneisen gamma, $\gamma \equiv v(\frac{\partial p}{\partial I})_v = (\frac{\partial \ln T}{\partial \ln v})_s$ (s denotes the entropy) is related to the adiabatic index $\gamma_{is} \equiv (\frac{\partial \ln p}{\partial \ln v})_s$ by $\gamma = \gamma_{is} - 1$.

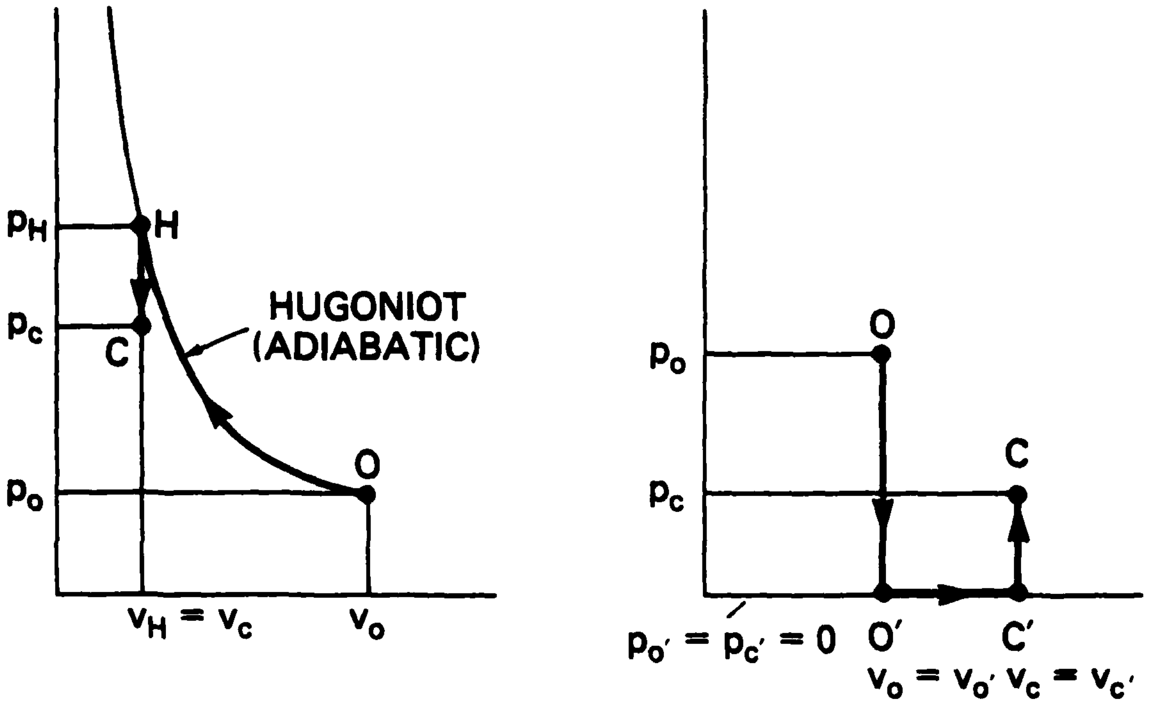

Figure A1 (a) Path used in deriving the equation of state of a compressed condensed explosive beginning from its undisturbed state.
(b) Path used in deriving the equation of state of an expanded condensed explosive beginning from its undisturbed state.

where $p_H(v_c)$, $I_H(v_c)$, and $T_H(v_c)$ are evaluated using Eqs. (A1.3), (A1.4), and (A1.6) when $v_H = v_c$.

Equations (A1.1) to (A1.8) are used to determine the state of a compressed condensed explosive. For an expanded explosive, however, a different method is used to obtain the state properties. This is illustrated in Fig. (A1.b). Since going from o to o' is a constant volume process, we obtain

$$I_{o'} = I_o - \frac{p_o v_o}{\gamma} \quad , \qquad \text{(A1.9)}$$

where $p_o' = 0$ by definition. Also,

$$T_{o'} = T_o + \frac{I_{o'} - I_o}{C_v} \quad . \qquad \text{(A1.10)}$$

Now the path o' to c' is a constant zero-pressure process, so that the enthalpy, H, is equal to the internal energy, I. We then can write

$$\left(\frac{\partial I}{\partial v}\right)_p = \frac{(\partial I/\partial T)_p}{(\partial v/\partial T)_p} = \frac{(\partial H/\partial T)_p}{(\partial v/\partial T)_p} \; .$$

The numerator is the specific heat at constant pressure, C_p, while the denominator is related to the coefficient of volummetric expansion $\alpha_v \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$. For zero pressure, $C_p \cong C_v$. Moreover, for condensed phases (solid or liquid), v_c is expected to be close in value to v_o. Thus

$$\left(\frac{\partial I}{\partial v}\right)_p \cong \frac{C_v}{3\alpha\, v_o} \quad , \qquad \text{(A1.11)}$$

where α is the coefficient of linear expansion ($\alpha_v = 3\alpha$). Integrating

Eq. (A1.11), we obtain

$$I_{c'} = I_{o'} + \frac{C_v}{3\alpha\, v_o}(v_c - v_o) \; . \tag{A1.12}$$

Also, since $C_p \cong C_v$ along o' - c',

$$T_{c'} = T_{o'} + \frac{I_{c'} - I_{o'}}{C_v} \; . \tag{A1.13}$$

Combining Eqs. (A1.9) and (A1.12) yields

$$I_{c'} = I_o - \frac{p_o v_o}{\gamma} + \frac{C_v}{3\alpha\, v_o}(v_c - v_o) = I_o - \frac{p_o v_o}{\gamma} - \frac{C_v \eta}{3\alpha} \; . \tag{A1.14}$$

Combining Eqs. (A1.10) and (A1.13) yields

$$T_{c'} = T_o + \frac{I_{c'} - I_o}{C_v} \; . \tag{A1.15}$$

Finally for the constant volume process c' - c,

$$p_c = \frac{\gamma}{v_c}(I_c - I_{c'}(v_c)) \tag{A1.16}$$

and

$$T_c = T_{c'}(v_c) + \frac{I_c - I_{c'}(v_c)}{C_v} \; . \tag{A1.17}$$

Equations (A1.14) to (A1.17) are referred to as the Gruneïsen equation of state.

In summary, $p\,(v_c,I_c)$, $T(v_c,I_c)$ are expressed in terms of a reference state, denoted from now on by a subscript r, namely

$$p(v_c,I_c) = p_r(v_c) + \frac{\gamma}{v_c}\,(I_c - I_r(v_c)) \qquad \text{(A1.18)}$$

$$T(v_c,I_c) = T_r(v_c) + \frac{I_c - I_r(v_c)}{C_v}\;. \qquad \text{(A1.19)}$$

For $v < v_o$, $r \equiv H$; while for $v > v_o$, $r \equiv c'$.

It remains, finally, to define a standard state at which the internal energy is set equal to zero by definition. Here we pick $I_o = 0$. As mentioned earlier, this is the undisturbed state, namely $p_o \equiv 1$ bar, $T_o \equiv 300K$.

A2. Equation of State of the Gas Products

The gas products are assumed to reach chemical equilibrium instantaneously after their production. To solve for an equilibrium state we need an equation of state for the mixture of gas products in terms of the composition. According to Cowan and Fickett [11], the BKW equation of state for a mixture of gases can be written in the form

$$\frac{p_g v_g}{RT} = 1 + x\, e^{\beta x} \qquad \text{(A2.1)}$$

where

$$x \equiv \frac{k}{v(T+\theta)^{\alpha}} \quad ,$$

k being the average covolume defined in terms of the individual covolumes, k_i, as $k \equiv \kappa \sum_i x_i k_i$, where x_i is the molar fraction of species i. The α, β, θ and κ are constants adjusted to reproduce the detonation Chapman-Jouguet pressure and velocity obtained experimentally. If we know the internal energy and entropy of the mixture of products at the ideal gas limit (p=0), we can extend their validity to the hundreds of Kilobars pressure range by using the thermodynamic relations

$$\left(\frac{\partial I}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

together with Eq. (A2.1). The equilibrium state is then obtained by minimizing the Gibbs free energy. Note that because of the possible presence of solid carbon in the products, a solid equation of state for graphite is needed. According to Cowan and Fickett, the carbon pressure is expressed in terms of a second degree polynomial in T, the coefficients of which are themselves polynomials in the compression of the solid carbon relative to its normal crystal density.

To avoid solving the chemical equilibrium relations every time the equation of state of the products is needed, it assumed that the states encounterd in a typical calculation are close to those encountered in a steady Taylor-type detonation wave, i.e. states on the equilibrium isentrope through CJ point. Mader [1] fit the equilibrium isentrope through the CJ point for different explosives to a set of polynomials of the form

$$\ln p_i = A + B(\ln v_g) + C(\ln v_g)^2 + D(\ln v_g)^3 + E(\ln v_g)^4 \qquad (A2.2)$$

$$\ln I_i' = K + L(\ln p_i) + M(\ln p_i)^2 + N(\ln p_i)^3 + O(\ln p_i)^4 \qquad (A2.3)$$

$$\ln T_i = Q + R(\ln v_g) + S(\ln v_g)^2 + T(\ln v_g)^3 + U(\ln v_g)^4. \qquad (A2.4)$$

The shifted internal energy $I_i' \equiv I_i + Z$, where Z is a constant used to change the standard state to be consistent with the condensed explosive one.

For points off the isentrope, the definition of Gruneisen γ' and c_v' (for gases we use an apostrophe) provide the transition from point i to g, as shown in Fig. (A2). Since we need the equilibrium p(v,I) and T(v,I), and we do not need to obtain the composition of the products, the change in composition along the constant volume process i-g in Fig. (A2) can be absorbed in the definition of γ' and C_v'. As for γ', since g is expected to be near i, we can take $\gamma'_{average} = \gamma_i'$ where γ_i' takes into account the change in $\delta p/\delta I$ due

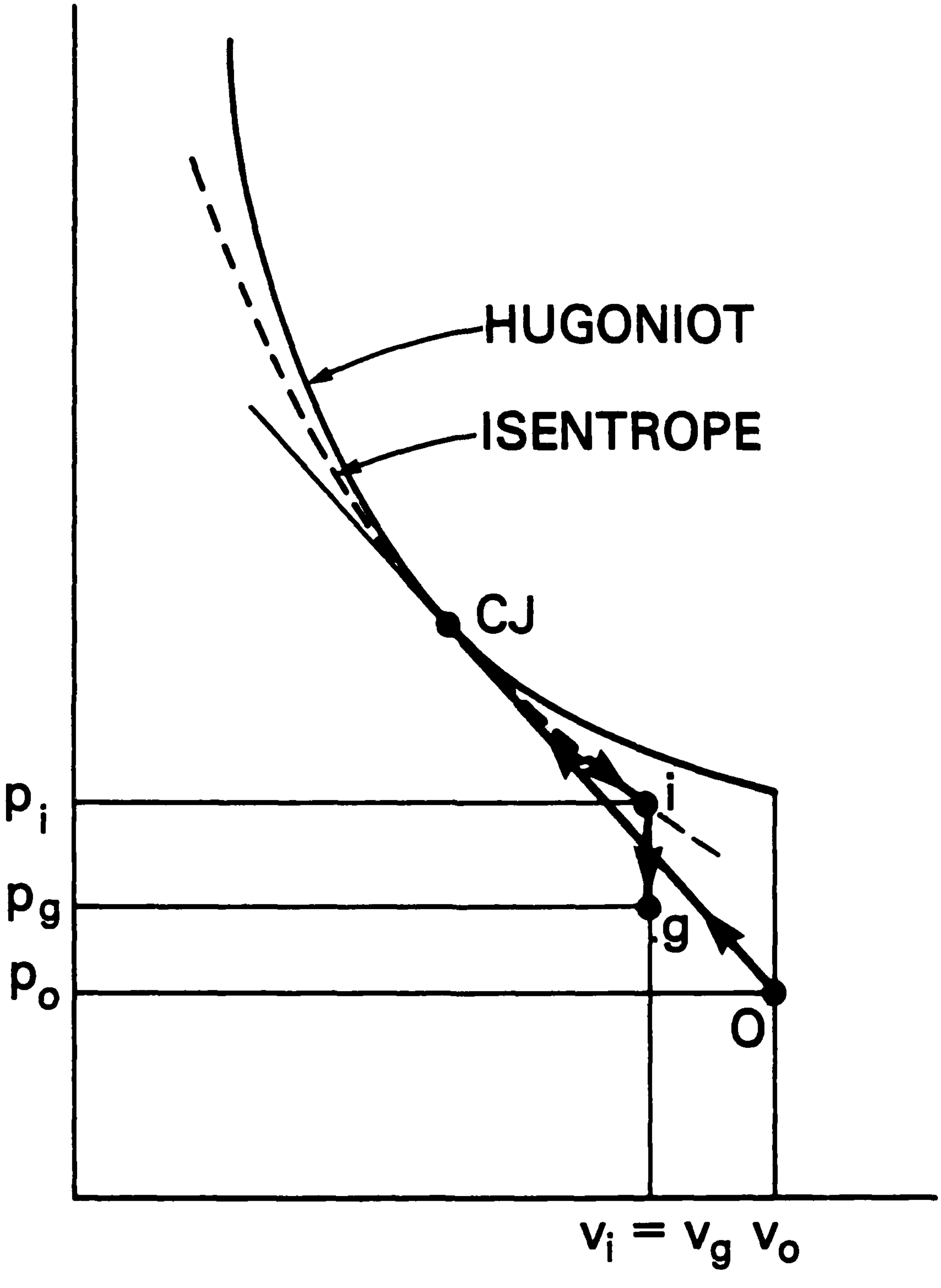

Figure A2 Path used in deriving the equation of state of an explosive's gas products beginning from its undisturbed state.

to change in composition along the equilibrium constant volume process. First, we write

$$\gamma' \equiv v\left(\frac{\partial p}{\partial I}\right)_v = \frac{v\left(\frac{\partial p}{\partial s}\right)_v}{\left(\frac{\partial I}{\partial s}\right)_v} , \tag{A2.5}$$

then substitute for $(\partial p/\partial s)_v$ and $(\partial I/\partial s)_v$ from the first law of thermodynamics ($dI = Tds - pdv$), yielding

$$\gamma' = v\left(-\frac{\partial T}{\partial v}\right)_s/T = \left(\frac{\partial \ln T}{\partial \ln v}\right)_s .$$

Thus γ_i' is expressed as

$$\gamma_i' = \frac{d\ell nT_i}{d\ell nv_g} = -\{R + 2S(\ell nv_g) + 3T(\ell nv_g)^2 + 4U(\ell nv_g)^3\} \tag{A2.6}$$

therefore inferring the change in compositon along the constant volume process i-g in Fig. (A4) from the change along the constant entropy process through i, expressed in Eqs. (A2.4). Integrating Eq. (A2.5), we get

$$p_g = p_i(v_g) + \frac{\gamma_i'}{v_g}\left(I_g - I_i(v_g)\right) . \tag{A2.7}$$

Finally, we assume that C_v' is insensitive to the change in composition, giving

$$T_g = T_i(v_g) + \frac{I_g - I_i(v_g)}{C_v'} . \tag{A2.8}$$

A3. Expressions for the Sound Speed

Generally, the sound speed, c, is defined as

$$c^2 = (\frac{\partial p}{\partial \rho})_s = -v^2(\frac{\partial p}{\partial v})_s \ .$$

Since $p = p(v,I)$, let $I = I(v,s)$, so that

$$(\frac{\partial p}{\partial v})_s = (\frac{\partial p}{\partial v})_I + (\frac{\partial p}{\partial I})_v(\frac{\partial I}{\partial v})_s \ .$$

Substituting for $(\partial I/\partial v)s$ by $-p$ ($dI = Tds - pdv$) we get

$$c^2 = - v^2(\frac{\partial p}{\partial v})_s = v^2[p(\frac{\partial p}{\partial I})_v - (\frac{\partial p}{\partial v})_I] \ . \qquad (A3.1)$$

Condensed Phase

The pressure is expressed in terms of a reference pressure, p_r, and a reference internal energy, I_r, both functions of specific volume only:

$$p = p_r(v) + \frac{\gamma}{v}(I - I_r(v)) \ .$$

Substituting the above relation in Eq. (A3.1) we obtain

$$c^2 = v[\gamma p - v\frac{dp_r}{dv} + (p - p_r) + \gamma\frac{dI_r}{dv}] \ . \qquad (A3.2)$$

Since the reference state r depends on whether the condensed explosive is compressed or expanded we consider the two cases:

(1) $v < v_o$, $r \equiv H$: From Eq. (A1.3) and the definition of η in Eq. (A1.2),

$$\frac{dp_r}{dv} \equiv \frac{dp_H}{dv} = -\frac{1}{v_o}\left(\frac{p_H - p_o}{\eta}\right)\left(\frac{1 + s\eta}{1 - s\eta}\right) = \frac{(\rho_o c_o)^2(1 + s_o\eta)}{(1-s_o\eta)^3} , \qquad \text{(A3.3)}$$

whereas Eqs. (A1.2) and (A1.4) give

$$\frac{dI_r}{dv} \equiv \frac{dI_H}{dv} = \frac{1}{2\rho_o}\left[\eta \frac{dp_H}{dv} - (p_H + p_o)\rho_o\right] \qquad \text{(A3.4)}$$

At the undisturbed state (p_o, T_o), $\eta = 0$. Eq. (A3.2) gives then $c^2 = c_o{}^2$, as it should be. Note that c_o and s_o are replaced by c_l, s_l when dealing with a solid that exhibits a kink in the linear relation between the particle velocity and shock velocity at the point where a phase change to a liquid occurs.

(2) $v > v_o$, $r \equiv c'$: Since $p_{c'} = 0$, $\frac{dp_r}{dv} = 0$. From Eq. (A1.14), $\frac{dI_r}{dv} \equiv \frac{dI_{c'}}{dv} = \frac{C_v \rho_o}{3\alpha}$. At the undisturbed state (p_o, T_o), Eq. (A3.2) yields

$$c^2 = (\gamma+1)\, p_o v_o + \frac{\gamma C_v}{3\alpha} ,$$

thus giving an estimate of c_o as

$$c_o = \left[(\gamma+1)\, p_o v_o + \frac{\gamma C_v}{3\alpha}\right]^{1/2} . \qquad \text{(A3.5)}$$

For liquid nitromethane, for example, Mader [1] gives the following set of parameters

$$c_o = 1.647 \times 10^{-1} \text{ cm/}\mu\text{sec}$$

$$\gamma = 6.805 \times 10^{-1}$$

$$\alpha = 3 \times 10^{-4}\ {}^{o}K^{-1}$$

$$C_v = 4.14 \times 10^{-1} \frac{\text{cal}}{\text{gm}\,{}^{o}K} = \frac{4.14 \times 10^{-1}}{23890} (\text{cm/}\mu\text{sec})^2$$

so that $[(\gamma+1)p_o v_o + \frac{\gamma c_v}{3\alpha}]^{1/2} \cong 1.145 \times 10^{-1}$ cm/μsec. The discrepancy between c_o given and that evaluated from Eq. (A3.5) indicates a kink in the thermodynamic properties at the interface between the two regimes $v < v_o$ and $v > v_o$. However, since the sound speed is only used to derive the Courant time step, which is an upper limit for the actual time-step used, this discrepancy presents no problem in the calculations.

Gas Phase

The equilibrium isentrope through the CJ point is the locus of reference states. Upon substituting Eq. (A2.7):

$$p = p_i(v) + \frac{\gamma_i'(v)}{v} [I - I_i(v)]$$

in Eq. (A3.1), we get a relation similar to Eq. (A3.2) except for a correction term attributed to the dependence of γ_i' on v, namely

$$c^2 = v[\gamma_i' p - v\frac{dp_i}{dv} + (p - p_i) + \gamma_i' \frac{dI_i}{dv} - (I-I_i)\frac{d\gamma_i'}{dv}] \quad . \qquad \text{(A3.6)}$$

Noting that $\ell n\, p_i$ and γ_i' are given in terms of $\ell n\, v$, whereas $\ell n\, I_i'$ is given in terms of $\ell n\, p_i$, Eq. (A3.6) can be rewritten as

$$c^2 = v[\gamma_i' p - \frac{d\ell n p_i}{d\ell n v} + (p - p_i)] + \gamma_i'(I_i + Z)\frac{d\ell n I_i'}{d\ell n p_i}\frac{d\ell n p_i}{d\ell n v} - (I-I_i)\frac{d\gamma_i'}{d\ell n v} \quad (A3.7)$$

where $\frac{d\ell n p_i}{d\ell n v}$, $\frac{d\ell n I_i'}{d\ell n p_i}$, and $\frac{d\gamma_i'}{d\ell n v}$ are obtained by direct differentiation of Eqs. (A2.2), (A2.3), and (A2.6), respectively.

Mixture of Condensed Phase and Gas Phase

Since the sound speed in the mixture is known a priori to be between the values of sound speeds of the condensed phase and gas products, it is satisfactory to assume

$$c_{mixture} = \max(c_c, c_g) \quad (A3.8)$$

when determining the Courant time step. Here, c_c and c_g are evaluated at the common temperature and pressure of the mixture.