One-Dimensional Dense-Fluid Detonation Wave Structure

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Ree provided an accurate representation of the thermodynamic properties of the Lennard-Jones fluid. This equation of state is used to calculate the Chapman–Jouguet state and the wave structure of steady-state plane dense-fluid detonation. The basic detonation equations are set up for a dense fluid in which a single irreversible bimolecular reaction 2A → B + C takes place with the release of chemical energy. The reactants and products are described by the same equation of state. The Enskog theory is used to provide the transport coefficients and to calculate the collision rate.

Introduction

The study of liquid explosives is currently of great interest.[1,2] However, the theory of condensed media detonation lags considerably behind the theory of gaseous detonation. The complexity of the problem is due to the

(1) W. Witt and K. Reinel, *Int. Defense Rev.*, 14, 64 (1981).

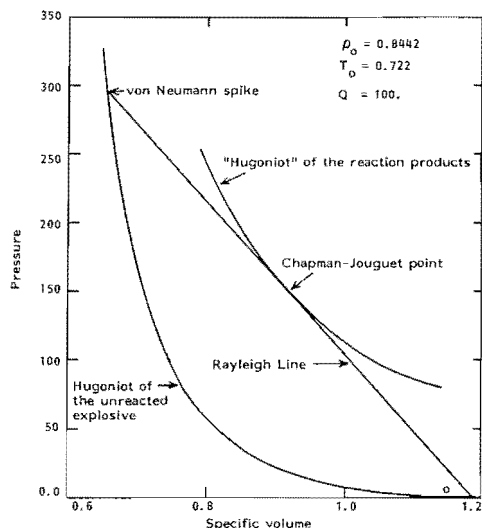(2) J. B. Ramsay and W. C. Chiles, *Proc., Symp. Detonation, 6th*, 723 (1976).

Figure 1. Dense-fluid Hugoniot of unreacted explosive and the reaction products.

fact that the detonation products are obtained at high pressure and density (pressure of hundreds of thousands of atmospheres and density which can reach[3] about 2 g/cm³). Therefore, the reaction products can no longer be described by the ideal gas equation of state. Knowledge of an equation of state for dense fluids, therefore, becomes essential. The Becker–Kistiakowsky–Wilson (BKW) equation of state is widely used to calculate detonation properties. It is, however, an empirical equation and is not based on a molecular microscopic model. In general, the BKW equation of state is at best only adequate for engineering purposes.

Recently Ree[4] provided an accurate representation of the thermodynamic properties of the Lennard-Jones fluid. In the present work this equation of state is used to calculate the Chapman–Jouguet state and the detonation wave structure with and without the inclusion of the transport effects.

Calculation of Chapman–Jouguet State

The shock Hugoniot curve can be calculated by finding those (P, V, E) points which satisfy the Hugoniot relation

$$E - E_0 = (1/2)(P + P_0)(1/\rho_0 - 1/\rho) \qquad (1)$$

where E is the internal energy per unit mass, P is the pressure, and ρ is the density. The subscript 0 refers to the initial state. (Units of the molecular mass m for mass, the "collision" diameter σ for distance, and the potential depth ϵ for energy are used throughout the calculations. The Boltzmann constant k is set equal to one.)

To produce the "Hugoniot" curve for the reaction products the heat of reaction Q should be included, so that E in 1 is replaced by $E - Q$ (where Q is a positive quantity). In the present work, it is assumed that the reactants and products are described by the same Lennard-Jones equation of state.

Figure 1 shows the Hugoniot of the unreacted explosive (shock Hugoniot) and the reaction products "Hugoniot". The initial state is triple-point liquid. The Rayleigh line (tangent to the reaction products "Hugoniot" from the initial state) intersects the shock Hugoniot at the von Neumann spike. The point of tangency represents the final state of a steady-state detonation, the Chapman–
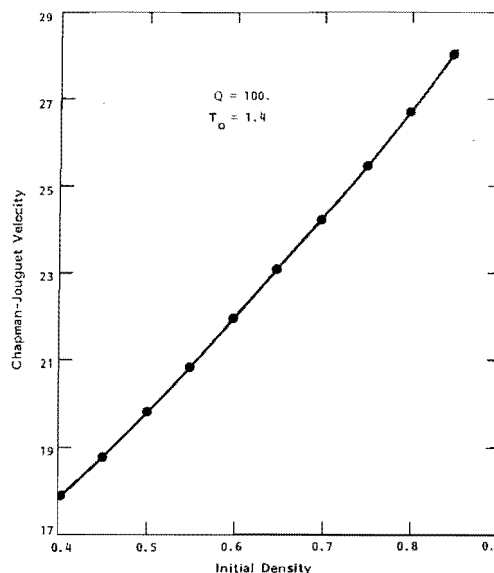

Figure 2. Chapman–Jouguet velocity as a function of initial density. Points are calculated with Ree's equation of state.
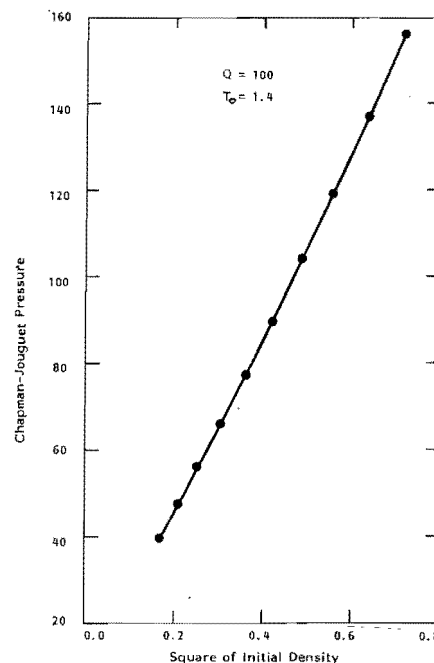

Figure 3. The Chapman–Jouguet pressure as a function of the square of initial density. Points are calculated by using Ree's equation of state. The solid line is a guide to the eye.

Jouguet state (CJ). This final state can be determined either graphically or numerically.[5]

The Chapman–Jouguet velocity D_{CJ} and pressure P_{CJ} have been calculated as a function of ρ_0 at a temperature slightly higher than the Lennard-Jones critical temperature. The heat of reaction Q is held constant ($Q = 100$). The results shown in Figures 2 and 3 indicate that both D_{CJ} and P_{CJ} are roughly linear functions of ρ_0 and ρ_0^2, respectively. This simple functional dependence agrees with empirical fits[6] to a large set of BKW calculations for many explosives. Experimental results[7] reveal the same behavior for D_{CJ} and P_{CJ}.

(3) R. Chirat and G. Pittion-Rossillon, *J. Chem. Phys.*, **74**, 4634–42 (1981).
(4) F. H. Ree, *J. Chem. Phys.*, **73**, 5401–53 (1980).

(5) M. S. Abdelazeem, Ph.D. Thesis, University of California, Davis, 1982.
(6) M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, **48**, 23–35 (1968).
(7) R. Chirat and G. Pittion-Rossillon, *Combust. Flame*, **45**, 147–59 (1982).
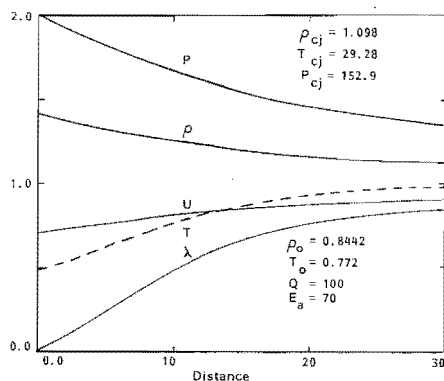
Figure 4. Dense fluid detonation profiles for P, ρ, U, T, and λ from the Zeldovich–von Neumann–Doering model (values of P, ρ, U, and T are reduced by the corresponding Chapman–Jouguet values). The ideal gas contribution to the internal energy is $(7/2)RT$. Energy and momentum are conserved throughout the calculations. Energy flux is 9180 and momentum flux is 664.

Figure 5. Coupled wave profiles of P, ρ, U, T, and λ for dense-fluid detonation. Values of P, ρ, U, and T are reduced by the corresponding Chapman–Jouguet values. Energy and momentum are conserved throughout the profile calculations. The momentum and energy fluxes are 663 ± 3 and 9170 ± 5, respectively.

Dense-Fluid Detonation Wave Structure Using the Zeldovich–von Neumann–Doering Model

The Zeldovich–von Neumann–Doering model[8] is used to calculate the detonation wave structure of steady-state plane dense-fluid detonation when the transport effects are ignored.[5]

In the present work, it is assumed that the chemical energy is released by a single irreversible bimolecular reaction of the form

$$2A \rightarrow B + C \tag{2}$$

An example of such a reaction is the explosive decomposition of nitric oxide, $2NO \rightarrow N_2 + O_2$. The elementary reaction 2 follows the rate law

$$d[A]/dt = -K(\rho,T)[A]^2 \tag{3}$$

The above rate equation can be written[5] in terms of the extent of chemical reaction λ (the "progress variable" λ is 0 for no reaction and 1 when the reaction is completed)

$$\frac{d\lambda}{dx} = \frac{(1-\lambda)}{\rho}\frac{d\rho}{dx} + \frac{K(\rho,T)}{U}(1-\lambda)^2\rho \tag{4}$$

We introduced the independent variable x into (3) through the transformation $dx/dt = U$, to obtain (4).

Using eq 4 and the conservation of mass, momentum, and energy, with $P = P(\rho,T)$ and $E = E(\rho,T)$, we can write three coupled differential equations

$$d\lambda/dx = f_1(\rho,T,\lambda)$$
$$dT/dx = f_2(\rho,T,\lambda) \tag{5}$$
$$d\rho/dx = f_3(\rho,T,\lambda)$$

where $f_1(\rho,T)$, $f_2(\rho,T)$, and $f_3(\rho,T)$ are (relatively complicated, but explicit) algebraic functions of ρ and T. These differential equations with the initial condition that is determined by the thermodynamic conditions right behind the shock (the von Neumann spike) are solved numerically by using the fourth-order Runge–Kutta Method. The numerical solution is shown in Figure 4. The extent of chemical reaction λ varies smoothly from zero right behind the von Neumann spike and approaches the Chapman–Jouguet state very closely ($\lambda = 0.99$). Both pressure and density decrease and approach the Chapman–Jouguet point asymptotically, while the temperature increases as chemical energy is released. Our numerical solution in-
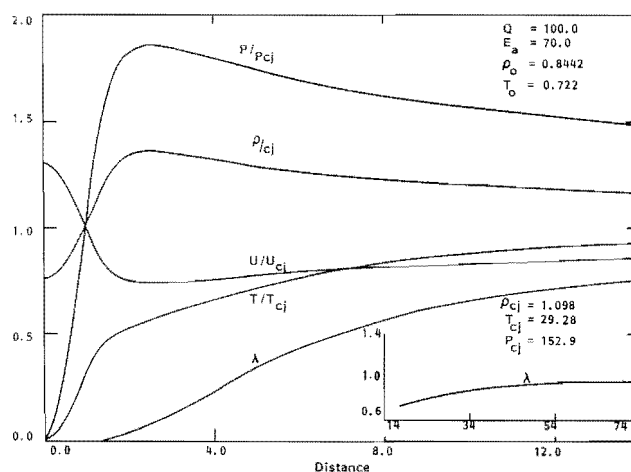
dicates that the temperature approaches the Chapman–Jouguet state ahead of the density while the pressure approaches behind.

Dense-Fluid Detonation Wave Structure Including Transport Effects

A complete description of the processes occurring in a stationary detonation wave involves a simultaneous solution of the conservation equations including transport phenomena. In this case the entire profile is continuous. It is not possible to identify one portion of the profile to be strictly shock with the remainder a reaction zone.

In the present calculations, diffusion is ignored. This is a reasonable assumption for simple single irreversible bimolecular reaction when the reactants and the products are not very different. Ignoring diffusion reduces the number of the differential equations to be solved from four to three.

When the mass flux equation is used, the momentum and energy equations can be written in a suitable form for integration:

$$\frac{d\rho}{dx} = \frac{\rho_0 U_0}{\eta_L}\left(\frac{\rho^2}{\rho_0^2 U_0^2}[P_0 - P] + \frac{\rho^2}{\rho_0} - \rho\right) \tag{6}$$

$$\frac{dT}{dx} = \frac{\rho_0 U_0}{\kappa}\left[E - E_0 - \lambda Q + P_0\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right) + \frac{U_0^2}{2}\left(\frac{2\rho_0}{\rho} - \frac{\rho_0^2}{\rho^2} - 1\right)\right] \tag{7}$$

Here $\eta_L = \eta_v + (4/3)\eta_s$, where η_s is shear viscosity, η_v is the bulk viscosity, and κ is the thermal conductivity. Viscosity and thermal conductivity are provided by the Enskog theory[9,10] where the real dense gas is considered to be equivalent to a rigid sphere gas in which the external pressure is replaced by the thermal pressure. Calculations of the Enskog theory transport coefficients require a low-density collision integral given by Neufeld et al.[10]

(8) W. Fickett and W. C. Davis, "Detonation" University of California Press, Los Angeles, 1979, Chapter 2.

(9) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1964, Chapter 9.

(10) D. A. McQuarrie, "Statistical Mechanics", Harper + Row, New York, 1976, Chapter 19.

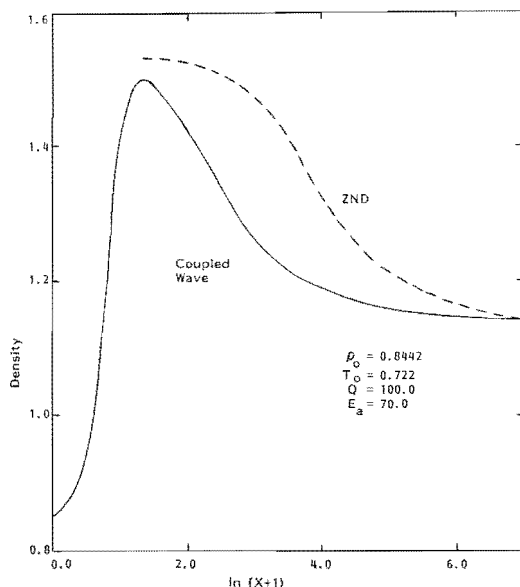(11) P. D. Neufeld, A. R. Janzen, and R. A. Aziz, *J. Chem. Phys.*, **57**, 1100–2 (1972).

Figure 6. Density profiles of dense-fluid detonation (——— for the coupled wave calculations and − − − for the ZND model calculations). The starting of the ZND profile corresponds to the peak point of the coupled wave calculations. At the end of the profiles, the two calculations agree within 0.3%. Note that the distance X is shifted by one.

The system of coupled first-order differential equations [eq 4, 6, and 7] along with the initial condition and the specified heat of reaction represents a well-posed problem. A numerical solution[5] is shown is Figure 5. Both pressure and density rise sharply but smoothly to their peaks and decrease toward the Chapman–Jouguet point. The peak pressure and peak density are reduced somewhat from those of the corresponding von Neumann spike. The extent of chemical reaction λ and the temperature increase smoothly and monotonically toward the Chapman–Jouguet point. At the end of the profile the temperature reaches almost twice that which corresponds to the peaks in pressure and density. Finally, we notice that the temperature approaches the Chapman–Jouguet point ahead of the density while the pressure approaches it behind. The same behavior was noticed for the Zeldovich–von Neumann–Doering model calculations of Figure 4.

In Figure 6 the density profile for the coupled wave is compared with that from the Zeldovich–von Neumann–Doering model. The effect of including the viscosity and thermal conductivity is clearly manifested by the reduction of the density peak from the Neumann spike value (comparison of the Zeldovich–von Neumann–Doering model calculations of Figure 4 and those of the coupled wave in Figure 5 indicates similar behavior for the pressure). Away from the peak, however, the two solutions are similar. When the transport effects are included, the numerical solution shows strong coupling between the shock and the reaction zones. This coupling is associated with the occurrence of the chemical reaction in the overlapping region between the shock and reaction zones. The dependence of the coupling upon the physical parameters of the problem has been studied extensively.[5]

Conclusion

Our numerical solutions reveal a linear relationship between the Chapman–Jouguet velocity and the initial density ρ_0. They also show that the Chapman–Jouguet pressure is roughly proportional to $\rho_0{}^2$. This simple functional dependence agrees with experimental results and other numerical calculations.

Comparison between the Zeldovich–von Newmann–Doering profile calculations and those of the coupled wave shows that, away from the overlapping region, the two calculations are similar.