SHOCK POLAR CALCULATION OF INERT NITROMETHANE BY MOLECULAR DYNAMICS SIMULATION

Laurent Soulard

CEA-DAM/Île-de-France, BP12, 91680 Bruyères-le-Châtel, France

Abstract. In the previous SCCM meeting (1999), we have shown that Gauss’ mechanics provides a very efficient method to evaluate the Hugoniot by purely classical molecular dynamics simulation. In this talk, we present an application of this method to a simple but realistic explosive, the nitromethane. In a first part, systematic computations are performed to obtain a large set of thermodynamic data of nitromethane under shock. A good agreement with experimental data is found for density and pressure and for various initial states. On the other hand, calculated temperatures are significantly lower than experimental or EOS data. This disagreement can be due to the classical treatment of intra-molecular interactions.

INTRODUCTION

In the classical model of Shock Detonation Transition (SDT) in homogeneous explosives, proposed initially by Chaiken, the overall decomposition of the explosive occurs after an induction time \( \tau \) which is strongly dependent of the temperature behind the shock front. Thus, the shock temperature (or, more generally, the equation of state) of the unreacted explosive is one of the keys for a quantitative description of SDT. Unfortunately, the corresponding experiments are rare, and very sensitive to the experimental conditions. An alternative is to built a theoretical equation of state and several ways of elaborating such an equation have been proposed in the literature. A very interesting approach is the Lysne and Hardesty’s development [1] which relies on a complete thermodynamic description of the 1 atm isobar and on measured Hugoniot data for a range of different initial temperatures. They generate the tabulated energy-entropy-volume equation for nitromethane by a numerical integration of the coupled differential equations governing the entropy and temperature variations along a Hugoniot. Their method is interesting because it is based on physical considerations. However its accuracy depends on the existence of a large set of experimental data. Such data base is often unavailable because of non stretch budgets and technical capabilities.

Recently, an alternative has been proposed, based on molecular dynamics (MD) simulations. Provided a good description of intra- and intermolecular forces, this method leads to a realistic representation of the shock states. In this paper, we use MD to compute the thermodynamic properties of an very usual explosive (nitromethane) and we compare the calculated Hugoniot to Lysne and Hardesty’s results.

METHOD

The more intuitive method to reach an Hugoniot state by molecular dynamics is the direct method, in which the shock propagation is due to an appropriate choice of initial and limit conditions. The thermodynamic properties can be then calculated directly behind the front. Furthermore, the shock velocity, the
jump of material velocity and the Hugoniot relations permit to verify the coherence of results. The direct method is very interesting to evaluate the characteristic time of the non equilibrium processes which occur in the shock front. It shows that these processes are not instantaneous for the time scale of molecular dynamics and reliable calculation of the Hugoniot state needs large systems, very expensive in CPU time. An alternative to the direct method is the use of constrained mechanics imposing on the system to reach equilibrium on a Hugoniot state. These method can use a Nose-Hoover like mechanic [2], or, alternatively, the Gauss'principle of least constraint [3] that we will use in this paper.

The Gauss'principle states that the time evolution of the system is such as [4, 5, 6]:

$$\frac{1}{2} \sum_{i=1}^{N} \left( m_i \left[ \frac{f_i}{m_i} - r_i \right] \right)^2 \text{minimum} \quad (1)$$

Given a specific volume $V$, we impose the system to move on the surface $H(E, P_{xx})$ which corresponds to an Hugoniot state at thermodynamic equilibrium:

$$H = E - \frac{1}{2} P_{xx} (V_0 - V)$$

$$= E_0 + \frac{1}{2} P_0 (V_0 - V) \quad (2)$$

$$\Rightarrow \dot{E} - \frac{1}{2} P_{xx} (V_0 - V) = 0 \quad (3)$$

$P_0$, $E_0$ and $V_0$ are the initial pressure, specific energy and specific volume, $P_{xx}$ the component of the tensor pressure along the shock axis propagation and $E$ the specific energy. We use for pressure the classical expression:

$$P_{xx} = \frac{N k_B T_x}{V} + \frac{\Phi(x)}{V} \quad (4)$$

$\Phi$ is the virial. By combining the conditions 1 and 3 via a Lagrange multiplier $\lambda$, we obtain the following equation of motion:

$$\ddot{r}_i = \frac{f_i}{m_i} - \lambda \dot{r}_i, \quad \lambda = \frac{1}{\frac{1}{2} \sum_{i=1}^{N} \dot{r}_i f_i^{(x)} + \frac{1}{2} \Phi^{(x)}}$$

$$= \frac{1}{\zeta} \frac{E_k^{(x)} - E_k}{2} \quad (5)$$

with $\zeta = V_0/V - 1$, $r_i$ and $m_i$ the position and mass of particle $i$, $E_k$ the total kinetic energy and $f_i$ the force on particle $i$. We call this molecular dynamics method NVHug. The first stage of the calculation of an Hugoniot is the determination of $P_0$ and $E_0$ by a standard NVT method. Then, calculation NVHug is to start by choosing specific volume $V$. Starting from a cubic system with simple cubic mesh, the density is reached by an instantaneous uniaxial in the $xx'$ direction. Note that this compression affects only the mass center of each molecule, no the internal geometry. Knowing the virial and the potential energy for $V$, temperature is calculated so as to satisfy equation 2. If the initial temperature is negative, system is relaxed during some hundred iterations until a positive temperature can be calculated from 2. NVHug simulation is performed during about $10^{-11}$ s, corresponding to the time to reach thermodynamic equilibrium of the system. For all calculations, we use $10 \times 10 \times 10$ molecules. The simulations are performed with the MD code S-TAMP from CEA-DAM.

The experimental vibrational spectra of nitromethane under high static pressures show that the internal geometry of the molecule is not strongly modified up to 30GPa [7, 8, 9, 10]. Thus the total potential energy can be split in two terms $E_p^{(intra)}$ and $E_p^{(inter)}$ which correspond to intramolecular and intermolecular interactions, respectively. $E_p^{(intra)}$ is an harmonic function of a set of 15 independent internal coordinates in which the constants of force are deduced from quantum chemistry calculations. We verify that the corresponding vibrational frequencies and geometry agree with experimental data [11, 12, 13]. The $E_p^{(inter)}$ term is a purely empirical function depending on the interatomic distances of two distinct molecules and are deduced from quantum chemistry calculations.

RESULTS

Three Hugoniot curves, corresponding to the Lysnes et Hardesty’s results ($T_1 = 297K$, $323K$ and $363K$) have been calculated (figures 4 and 5). We observe a good agreement with experimental measurements both for the $U_s(u_x)$ and $P(V)$ curves except for very low pressures. These disagreements probably are due to a lack of precision on $P_0$ and
On the other hand, shock temperatures calculated by molecular dynamics are markedly lower than Lysnes and Hardesty’s results i.e. experimental results and physical EOS) and Delpuech’s measurements [14] (figure 6).

Note that if molecular dynamics results are used instead of the experimental results, we find MD temperatures. Shock pressure is not very sensitive to temperature because the thermal contribution is small (∼15%, see figure 7) in comparison with potential contribution (see equation 4).

A possible improvement would consist in calculating intra-molecular potential in a quantum way. Indeed, $C_v$ corresponding to the purely classical treatment, as in this study, is much more high than the quantum $C_v$, leading so a too-weak temperature variation.

**CONCLUSION**

This study showed so that NVHug molecular dynamics allows a rather precise calculation of $U_s (u_p)$ and $P (V)$ curves. However, the very big sensitivity of the temperature with the pressure requires a
very fine description of both inter and intra molecular interactions. Anyway, this sensitivity shows that direct shock temperature measurements are essential for assessing the validity of the unreacted NM equation of state.

REFERENCES


