AB INITIO MODEL OF POROUS PERICLASE

Neil D. Drummond[1], **Damian C. Swift**[2], **and Graeme J. Ackland**[3]

[1]*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, UK*
[2]*P-24 Plasma Physics, Los Alamos National Laboratory, Los Alamos, NM 87545*
[3]*Department of Physics and Astronomy, University of Edinburgh, Kings Buildings, Edinburgh, UK*

Abstract. A two-phase equilibrium equation of state (EOS) for periclase (MgO) was constructed using ab initio quantum mechanics, including a rigorous calculation of quasiharmonic phonon modes. Much of the shock wave data reported for periclase is on porous material. We compared the theoretical EOS with porous data using a simple 'snowplough' treatment and also a model using finite equilibration rates suitable for continuum mechanics simulations. (This model has been applied previously to various heterogeneous explosives as well as other porous materials.) The results were consistent and matched the data well at pressures above the regime affected by strength - and ramp-wave formation - during compaction. Ab initio predictions of the response of porous material have been cited recently as a novel and advanced capability; we feel that this is a fairly routine extension to established ab initio techniques.

INTRODUCTION

Ab initio techniques based on quantum mechanics are now capable of predicting thermodynamically complete equations of state and equilibrium phase diagrams for crystalline materials. We have used numerical electronic ground states to calculate equations of state (EOS) for a variety of materials.(1,2)

High pressure EOS are constructed empirically using shock wave data, and such data are valuable for comparing with theoretical EOS. However, in many shock wave measurements the samples have a mass density lower than that of a perfect crystal, intentionally or because of practical difficulties in preparing samples. Experiments on porous materials are also valuable for exploring states with temperatures higher than the principal Hugoniot. It is therefore desirable to predict the shock properties of porous material from the EOS of material at the theoretical crystal density.

A combination of ab initio EOS and porous model was reported at the last meeting.(3) Various porous response models have been developed over the years,(4,5) and can be used with equal ease with ab initio EOS as with empirical EOS, so we would not regard the combination of ab initio EOS and porous compaction model as novel in itself.

Here we apply a simple porous compaction model and a more general equilibration model to shock propagation in porous periclase (MgO), modelled using an EOS based on previously-reported ab initio calculations.(2) The equilibration model allows the simulation of systems where the grain size is significant, and has been used for calculations of the shock initiation of heterogeneous explosives.(6,7) The calculations were compared with published data on shocks in single crystal and polycrystalline periclase.(8,9) Polycrystalline or ceramic samples were generally porous.

CRYSTAL EQUATION OF STATE

As reported previously,(2) quantum mechanical calculations were performed of the ground state of electrons in MgO, using a Schrödinger

Hamiltonian with a plane-wave basis set for the outer electrons and the inner electrons subsumed into a nonlocal pseudopotential centered on each atom. Exchange and correlation effects were estimated by the local density approximation (LDA).(10) These calculations were used to predict the frozen-ion cold curve and restoring forces on atoms displaced from equilibrium, and hence the specific Helmholtz free energy f tabulated against specific volume v and temperature T, for face-centered cubic and simple cubic crystal structures. The tabulated $f(v,T)$ was then used to calculate the pressure EOS, suitable for simulating the response to shock loading, by applying the laws of thermodynamics in numerical form as described previously.(1)

This ab initio EOS was found to give an STP mass density ρ_0 of about 3.41 g/cm^3, compared with about 3.58 g/cm^3 for single-crystal periclase.(8) Interestingly, the ab initio EOS thus underpredicts the STP density, in contrast to most experience with the LDA. An ab fere initio EOS was constructed as before by tilting the free energy by an amount p_r, equal to the pressure calculated from the ab initio EOS at the desired STP mass density. p_r was found to be ~8.1 GPa – a fairly large correction compared to the accuracy obtained on low Z elements, probably reflecting the relatively deep pseudopotential for Mg.

The tabular EOS were interpreted using bilinear interpolation. This is numerically robust, but typically results in oscillations in the shock Hugoniot. The Hugoniots calculated for periclase showed such oscillations at lower pressures. The presence of these oscillations does not affect the accuracy with which the Rankine – Hugoniot equations are solved; in particular, the error does not accumulate as the shock pressure increases. However, where oscillations are evident, the most accurate points on the shock Hugoniot are at the minimum of each cycle (for regions of the EOS in which the bulk modulus increases with compression). The ab initio EOS matched the bulk sound speed of single crystal periclase quite well, and passed among the points for shocked crystals up to particle speeds ~1.5 km/s (corresponding to pressures up to ~48 GPa and temperatures up to ~545 K). At higher pressures, the ab initio EOS fell slightly below the locus of the experimental data. The EOS lay well above the locus of shock data for polycrystalline material of the initial porosities reported, though these included values of ρ_0 both lower and higher than that deduced from the ab initio EOS. The ab fere initio EOS also matched the bulk sound speed quite well. It passed somewhat above the points for shocked crystals up to particle speeds ~1.5 km/s, but passed more closely to the locus of the experimental data at higher pressures. (Fig. 1.)

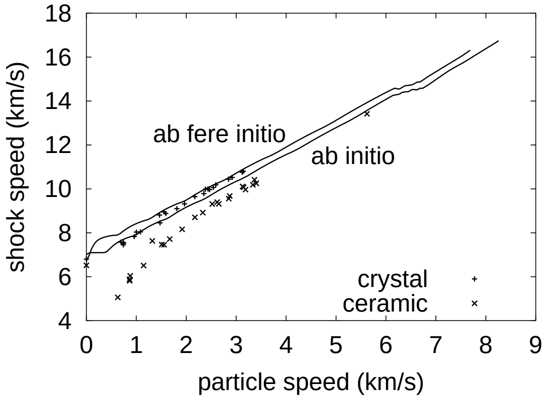

FIGURE 1. Comparison between theoretical Hugoniots and shock wave data for periclase.

Both theoretical EOS exhibited essentially linear relations between shock and particle speeds up to a particle speed ~6 km/s (corresponding to a pressure ~300 GPa and temperature ~7800 K), above which point there was a kink suggestive of a phase transition. No experimental data were found in this regime. The data at lower pressures have been described by a quadratic.(9) They could be interpreted with equal validity as a pair of straight lines, the upper line (for particle speeds over 1.5 km/s) matching the gradient of the theoretical Hugoniots.

“SNOWPLOUGH” COMPACTION

The simplest treatment of shock waves in porous materials is to assume the pressure to be zero until the material has been recompacted to its crystal density or greater(4); this is sometimes known as the “snowplough” model. A consequence of the assumption is that shock waves are predicted to travel with vanishing speed as the pressure tends to zero. The Rankine-Hugoniot shock relations can be solved simply to find the shock state as a function of compression, for a given initial porosity.

Often, porous materials have some structural strength, so the pressure in the material is not zero. The snowplough model is valid in the limit of pressures much greater than necessary to recompact the material. Alternatively, the model is valid for loading conditions which overdrive recompaction, in the sense that no precursor wave (such as sound) travels faster than the recompaction shock wave.

In order to calculate shock Hugoniots for porous material, the pressure from the solid equation of state was not allowed to fall below zero, and shocked states were calculated only for compressions at least great enough to recompact the material.

Using the ab fere initio EOS, Hugoniots calculated for porous material were fairly consistent with data on porous material, at pressures high enough to recompact the material. Hugoniot curves were calculated for porosities representative of each group of experimental data. Because of the properties of the snowplough model, the calculated Hugoniots gave a sound speed which tended to zero with the particle speed. In contrast, the experimental data showed sound speeds in porous material which were of similar order to the bulk sound speed for nonporous material. (Fig. 2.)

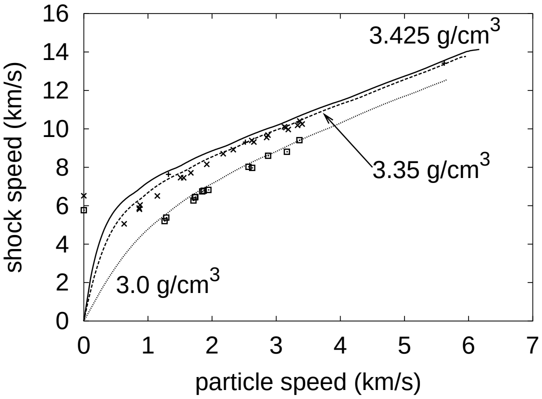

FIGURE 2. Shock conditions in porous periclase, observed and predicted using the snowplough model.

ELASTIC PERCOLATION

One serious discrepancy between experimental data and Hugoniots calculated according to the snowplough model is the bulk sound speed: zero for the model (given at least an infinitesimally small porosity), compared with several kilometers per second in reality. As a preliminary step in developing a better model of porosity, we evaluate a simple percolation model for the effective sound speed in a porous medium.

Consider a material of porosity f. Assuming the pores are spherical and uniformly distributed, a cube of the material, side l, contains a pore of radius r, such that

$$\frac{4}{3}\pi r^3 = fl^3 \quad \Rightarrow r = \left(\frac{3f}{4\pi}\right)^{1/3} l \equiv \alpha l. \qquad (1)$$

Signals traveling at the solid sound speed c_0 in the bulk material travel further to pass around the pores, a distance d say compared with l if the material were non-porous. The effective sound speed in the porous medium is then

$$c_p = \frac{l}{d} c_0. \qquad (2)$$

Approximating for further simplicity, we estimate l as the distance to travel in a straight line to the maximum lateral displacement required to pass the pore. This cuts the corner of the pore, and is thus a slight under-estimate of the effect of porosity on the sound speed. The mean effect of the void can be estimated by averaging the displacement between pairs of points on opposite faces of the cube. Comparing with the bulk sound speed for periclase, the effect of porosity lies between the mean percolation contribution and the maximum contribution across the center of the void (Fig. 3). The percolation model predicts the effect of porosity to the correct order; the remaining discrepancy may reflect highly non-spherical voids. The result was not affected significantly by using a more rigorous calculation of the path length around a sphere.

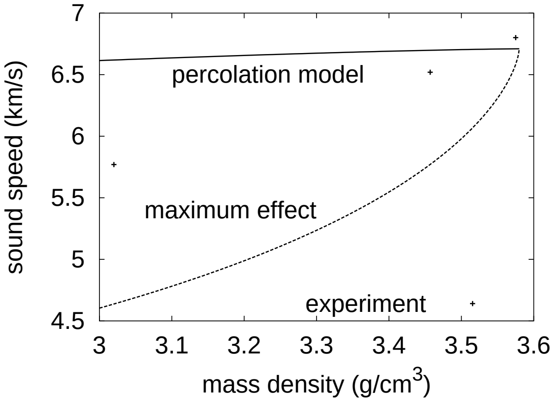

FIGURE 3. Sound speeds in porous periclase. Calculations are mean and minimum speed from percolation model with spherical pores; experimental data are bulk sound speeds.

HETEROGENEOUS MIXTURE MODEL IN CONTINUUM MECHANICS

More thorough calculations of the effect of porosity on shock propagation were made using an explicit stress equilibration model in a continuum mechanics program. Each spatial cell comprised a mixture of 'homogeneous' materials, each specified by a volume fraction and internal state (mass density, specific internal energy, elastic strain tensor, equivalent plastic strain, etc).(6,7) The shape of each constituent of the microstructure was represented by an overlap function ω (6-component real vector) describing the fractional area of the constituent connecting across the corresponding component of the stress tensor. The stress tensor and temperature were equilibrated between the constituents in the microstructure by adjusting the strain tensor and heat transfer to give an exponential approach to equilibrium. Instantaneous equilibration was treated by choosing a tiny value for the time constants of equilibration.

Porous periclase was modeled using an elastic-plastic model for the solid material, mixed with air. A series of simulations was performed with a velocity boundary condition; the solution was interpreted in terms of elastic, compaction, and plastic shock waves. This model was able to transmit elastic waves ahead of the bulk compaction wave, providing a closer match to the experiments than the snowplough model.

CONCLUSIONS

Using an EOS for periclase calculated by ab initio quantum mechanics, a shock Hugoniot was predicted which agreed fairly well with experimental data. Shock Hugoniots for porous material – which may be calculated easily using any EOS, theoretical or otherwise – matched the observed variation of the Hugoniot with porosity. The agreement could be extended to lower pressures by using an extension of a mixture model to include material strength.

ACKNOWLEDGMENTS

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