PREPARATION DEVELOPMENT AND PRELIMINARY APPLICATION OF NOVEL EQUATIONS OF STATE FOR GEOLOGICAL MATERIALS AND ICE

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ABSTRACT

This paper describes the use of Quantitative Structure/ Property Modelling (QSPM) to derive physically-based equations of state directly, from knowledge of the constituents of the material. For geological materials this is based on an implicit assumption that many geological materials are a derivative of different crystal forms of silica (i.e. crystobalite, coesite, α-quartz, and stishovite) based around packing of the Si-O tetrahedra. This approach is validated by predicting shock Hugoniot data for various materials. These crystal forms are present in craters after impact, but the link to each phase during the impact process is largely unknown. Equations of state have been developed for each of these forms and simulations have been performed in the QinetiQ GRIM Eulerian hydrocode to investigate their effect on the initial cratering phase. These have been compared to standard geological models in GRIM and AUTODYN SPH. The QSPM approach has also been used to investigate the equation of state for ice in its various forms and compared to published experimental data.

1. INTRODUCTION

There are an abundance of planetary and asteroid type bodies in the solar system which consist of either geological materials or ice or a mixture of both. This can cause a great disparity in the behaviour of these objects when subject to a significant impact leading to crater formation in terms of crater dimensions, ejecta and subsequent momentum transfer to the body. Given this uncertainty it is important to understand the effect of the material composing the body on the cratering process. Modelling combined with precise experimentation is the key to providing this understanding. This requires the development of physically based models where the constants are either measured or derived.

This paper describes the use of Quantitative Structural Property Modelling (QSPM) in deriving physically based equations of state directly, from knowledge of the constituents of the material. For geological materials this is based on an implicit assumption that many geological materials are a derivative of different crystal forms of silica (i.e. crystobalite, coesite, α-quartz, stishovite). Equations of state have been developed for each of these forms and simulations have been performed to investigate their effect on the initial cratering phase.

2. QUANTITATIVE STRUCTUR/PROPERTY MODELLING OF SILICA

Silica is a molecule which exhibits 4 main crystal forms. These are in ascending order of density: cristobalite, quartz, coesite and stishovite and their molecular structure is illustrated in Fig 1. CASTEP [1] reproduced the minimum energy structures of the different polymorphs of silica with the specified space group of the crystal forms and predicted their correct density values. However, CASTEP was unable to simulate changes in the crystal structure of silica with different boundary conditions such as pressure or volume imposed. The practical consequence of this problem was that the predicted bulk elastic modulus of all four polymorphs was identical, with a value of about 100 GPa.
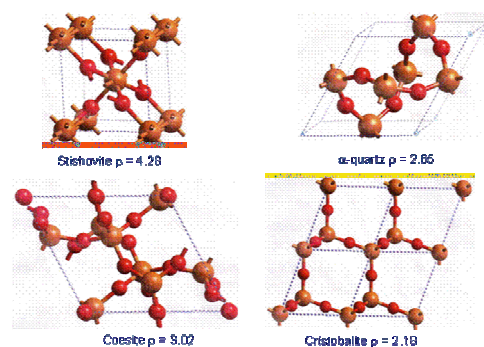

Fig 1 – Different crystal forms of silica

Most quantum mechanics programs try to change the length or angle of a chemical bond to simulate a change in structure, since the energy associated with these changes is large. However, the Si-O bond is very

mobile and can rotate easily around relatively rigid chemical bonds with very small changes in energy. Thus, changes in crystal structure or dimensional changes in silica are dominated by rotation of torsional bond angles that are very difficult to reproduce with programs such as CASTEP, unless a crystal structure is specified in advance to direct the calculations.

The failure of molecular mechanics or quantum mechanics to predict the volumetric properties of silica polymorphs requires a different modelling technique that can predict properties associated with the relatively small changes in energy associated with physical (van der Waal's) bonding between atoms that are not chemically bonded in a structure. This type of bonding dominates the properties of polymers, since the preferred mode of deformation is through the weak van der Waal's bonding normal to the chemical bonding in the chain axis of the polymer macromolecules.

2.1 Potential Function Method

A modelling technique has been developed by the author to predict the structural properties of polymers, called Group Interaction Modelling, GIM [2]. This technique has been used to predict equations of state for polymer based materials [3]. The technique uses an empirical equation to describe the relationship between energy and separation distance between adjacent (but not chemically bonded) groups of atoms in a molecular structure. Fortunately, a very simple power-law function called the Lennard-Jones function works very well for most polymers that are based upon carbon or silicon lattices. To a first approximation, the method assumes that chemical bonds do not deform significantly, relative to the weak physical bonds, due to electronic interactions between atoms or molecules. Note that, although the potential function here is an empirical relation for simplicity, all the fundamental contributions to bond energy are embodied in that function, and a potential function can be constructed from 'first principles' by a series of quantum mechanics simulations.

Fig 2 shows the general form of a potential energy well for Van der Waal's bonding. Energy, E, is expressed relative to the depth of the potential energy well, E_o, and dimensions are given as volume, V, relative to the volume at the absolute depth of the potential energy well, V_o. Note that energies for bonding are negative.
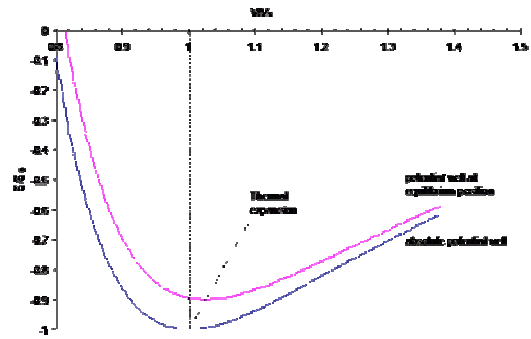

Fig 2 - A potential well for intermolecular energy

As positive energy (such as thermal energy, HT) is increased, the interaction dimensions move away from the minimum energy position to two possible values on either side of the minimum. Generally, the potential well is asymmetric, such that the equilibrium mean position of the new well minimum moves to higher volumes to cause thermal expansion in a material.

The energy E can be expressed either as a Lennard-Jones power function in separation distance, r, (or volume proportional to r^3) or in terms of the positive and negative contributions to total energy

$$E_T = E_o \left(\left(\frac{r_o}{r} \right)^{12} - 2 \left(\frac{r_o}{r} \right)^6 \right) = E_o \left(\left(\frac{v_o}{v} \right)^4 - 2 \left(\frac{v_o}{v} \right)^2 \right) = -E_o + H_T + H_c \quad (1)$$

where Hc is the configurational energy due to metastable non-zero energy configurations in the chains of atoms (a sort of entropy term) and ET is the energy at a temperature T. If we take the new equilibrium function at T to have the same mathematical form as the absolute zero-point potential function with a new minimum energy ET at a position VT

$$E = E_T \left(\left(\frac{v_T}{v} \right)^4 - 2 \left(\frac{v_T}{v} \right)^2 \right) \quad (2)$$

then we can express pressure as a function of volume through the highly non-linear relation

$$P = \frac{dE}{dV} = \frac{4 E_T}{V} \left(\left(\frac{v_T}{v} \right)^2 - \left(\frac{v_T}{v} \right)^4 \right) = \frac{6 E_T}{v_T} \left(\left(\frac{v_T}{v} \right)^3 - \left(\frac{v_T}{v} \right)^5 \right) \quad (3)$$

The potential function relation of equation (3) for pressure as a function of volume requires two reference parameters of energy and volume that can be calculated in terms of chemical composition, crystal structure, and temperature for any polymer-like material such as

silica. Equation (3) for pressure can be used to predict the bulk modulus

$$B = -V \frac{dP}{dV} = \frac{6\,E_T}{V_T}\left(3\left(\frac{V_T}{V}\right)^3 - 5\left(\frac{V_T}{V}\right)^5\right) = \frac{12\,E_T}{V_T} \quad (4)$$

at Vt = T

Since the required model predictions are for high rate properties that are conventionally expressed as Hugoniot parameters from impact experiments, we need expressions for the particle and shock velocities Up and Us in terms of pressure and volume

$$U_p = \sqrt{\frac{P\left(1 - V/V_T\right)}{\rho_T}} \quad (5)$$

$$U_s = \sqrt{\frac{P}{\left(1 - V/V_T\right)\rho_T}} \quad (6)$$

2.2 Application of Model to Geological Materials

On close inspection, the parameters show a qualitative trend that the reference parameter of volume for the different silica forms scales with the inverse of the density of the polymorphs and the energy parameter stay remarkably constant. The conclusion from this observation is that the many polymorphs of silica can be modelled as a single material in terms of a single adjustable parameter of volume at zero pressure, VT, and two absolute reference parameters of energy and molar volume of an underlying polymeric form of silica, Er and Vr respectively. The key point is that each polymorph adopts a crystal structure as if it were constrained by an energy or pressure, Pr, of configuration associated with the non-zero energy of each particular set of metastable chemical bond angles in the polymorph structure.

The remarkably simple conclusion from the pressure-volume relations for silica can be translated into a single predictive equation for any given silica polymorph of the following form

$$P = 0.34\left(\left(\frac{V_r}{V}\right)^3 - \left(\frac{V_r}{V}\right)^5 - \left(\frac{V_r}{V_T}\right)^3 + \left(\frac{V_r}{V_T}\right)^5\right) \quad (7)$$

This implies that the only variable required to predict the equation of state is the initial density of the material. The prediction using this approach for the pressure/volume relationship for each of the crystal

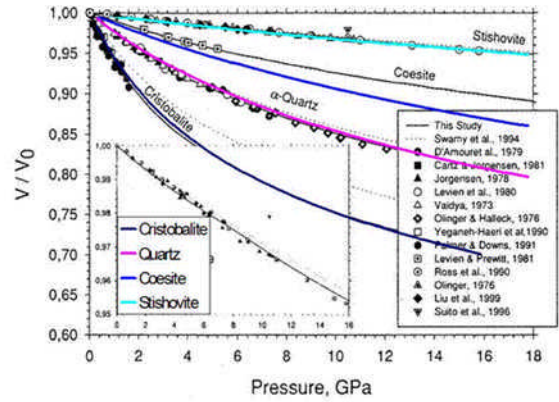forms compared to experimental data is shown in Fig 3.

Fig 3 - Comparison of predicted pressure/volume relationship compared with experimental data for different crystal forms.

An interesting feature of the model is the radical difference in shock velocity versus particle velocity as shown in Fig 4. This has quite significant implications for the impact behaviour of the materials as discussed later. In addition the approach is also capable of predicting tensile states up to the point of failure.
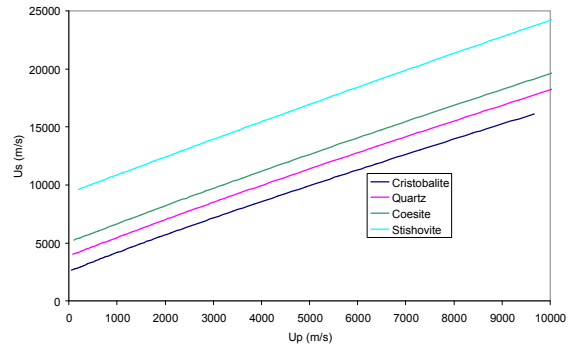

Fig 4 – Predicted Shock velocity versus particle velocity for different crystal forms

The model has also been used to predict shock Hugoniot data for a range of geological materials as shown in Fig 5
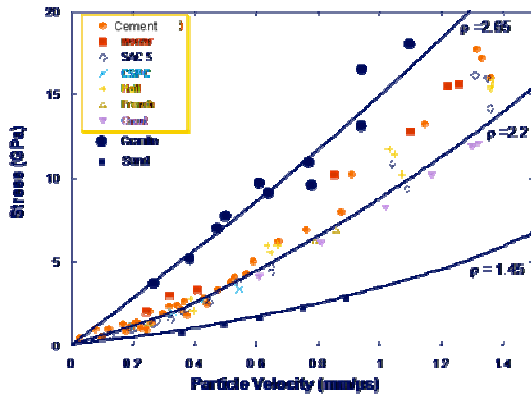
Fig 5 – Comparison of model with experiment

At present this approach generates a SESAME type equation of state format in terms of P, V, T and is used in combination with an existing constitutive relation, such as the Johnson-Holmquist model for brittle materials [4]. The model is referred to as the QinetiQ Porter-Gould Equation of State (EOS).

3. APPLICATION OF MODEL APPROACH TO ICE

The case of ice presents a novel problem, since it is a solid material consisting of hydrogen-bonded small molecules, which can adopt a wide range of different molecular structures, with a commensurate range of different physical properties such as density and elastic modulus. If we assume that water/ice behaves as a simple solid, with intermolecular interactions represented by a Lennard-Jones function, and positive energy terms HT and Hc that are the thermal energy of molecular vibrations and energy of configuration (zero point energy) respectively.

$$E = E_o \left(\left(\frac{V_o}{V} \right)^4 - 2 \left(\frac{V_o}{V} \right)^2 \right) = -E_o + H_T + H_C \quad (8)$$

where Eo is the depth of the potential energy well at a volume Vo. Pressure is then the differential, with Eo and Vo now at a specified temperature.

$$P = -\frac{dP}{dV} = 4 \frac{E_o}{V} \left(\left(\frac{V_o}{V} \right)^5 - \left(\frac{V_o}{V} \right)^3 \right) \quad (9)$$

The cohesive energy for water/ice is simply the dispersion energy for oxygen (6300 J/mol) plus any hydrogen bonding, with 10,000 J/mol for each hydrogen bond per molecule. For liquid water or any dynamic form of the H_2O molecule, we assume that the hydrogen bonds are not active, and for solid ice we assume that there are generally two hydrogen bonds per molecule. This suggests two values of cohesive energy: 6300 and 26300 J/mol for liquid and solid H2O respectively.

Let us take the melting point of ice as the transition point, where an energy instability occurs as $d^2E/dV^2 = 0$ at E = 0.84 Ecoh and V = 1.29 Vo on the absolute potential well. This suggests a value of Vo ≈ 14 cc/mol using the density of water as 1 g/cc and V = 18 cc/mol.

The review by Stewart and Ahrens [5] shows that ice is a complex material with many different structural forms. At its most simple we reduce these to porous and compacted ice. Porous ice is composed of water molecules that are arranged in the attractive multitude of different H-O hydrogen bonding structures, which are also seen as pentagons and hexagons in materials such as clathrates that encapsulate methane under the sea. We take this porous form to be the Ih form with a density 0.93g/cc or specific volume 1.08cc/g. The compact form should have a density approximately M/Vo ≈ 18/14 = 1.3g/cc, which is approximately that of the VI and VII forms with densities of 1.3 and 1.46 respectively.

Table 1 suggests the parameters required to predict P-V relations for the specified three different ice forms, and also suggests a transition form of ice where the structures are compacting from Ih to the compacted structures and the hydrogen bonds are not active in the real part of the complex cohesive energy (effectively a 'yield' state). These predictions are performed using the QinetiQ Porter-Gould EOS.

Ice Type	Density (g/cc)	Sp. Gravity (cc/g)	E_o (J/mol)	V_o (cc/mol)	$4 E_o/V_o$ (GPa)
Ih	0.93	1.08	25600	19.4	5.28
VI	1.3	0.769	25600	13.8	7.39
VII	1.46	0.685	25600	12.3	8.29
Transition	0.93	1.08	4800	19.4	1.00

Table 1 – Predicted parameters for ice

The prediction for the shock velocity v particle velocity for the different ice forms compared to experimental data is shown in Fig 6 and PV data in Fig 7.
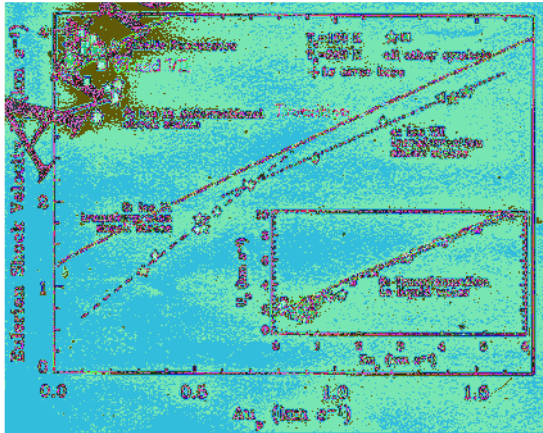
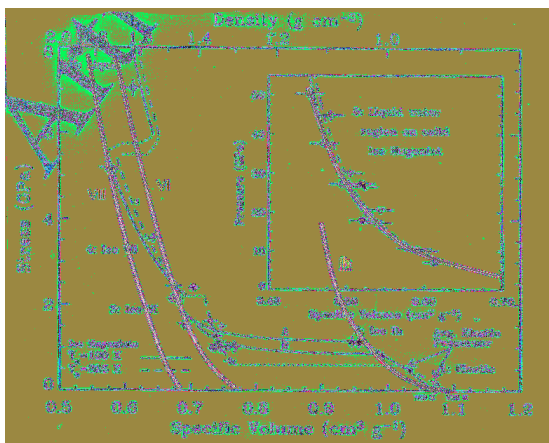Fig 6 – Comparison of prediction (red) with experimental Hugoniot data

Fig 7 – Comparison of prediction (red) with experimental PV data

4.   SIMULATIONS

The main purpose of the simulations was to perform scoping studies for initial crater formation using the new silica models compared to standard models for concrete. The crater formation was simulated using the QinetiQ Eulerian hydrocode GRIM which is capable of multi-material analysis and is 3rd order accurate in the transport of material variables (advection) through the mesh. In addition the AUTODYN Smooth Particle Hydrodynamics (SPH) model was used using a Johnson-Holmquist concrete model.

The simulations comprised a 1500kg aluminium sphere normally impacting a semi-infinite target at 10km/s. The models used were the QinetiQ Porter-Gould EOS for the different silica forms combined with a Johnson-Holmquist type model for concrete. The standard model for concrete was a tabulated EOS combined with the same constitutive model. Thus the only

difference between the simulations was the EOS. The simulations were run to a maximum of 10ms after impact to investigate the initial crater formation. In addition the runs were performed without a failure model, other than a simple volumetric strain cut-off so as not to confuse the spallation effects with the basic crater dimensions. The crater formation for coesite is illustrated in Fig 8 after 10ms, which shows a zoomed in plot of the crater interface. It was established that the target was large enough such that reflections from the boundaries did not significantly affect the results.

Fig 8 – Crater formation using GRIM for Coesite 10ms after impact

The results for the crater dimensions after 10ms are given in Table 2. These show the surprising result that the lower density crystal form (i.e. cristobalite) results in the least penetration. The prediction of the crater dimensions is also shown on the universal cratering curve [6] and fits quite well as shown in Fig 9.

	Depth (m)	Diameter (m)
Cristobalite	3.07	7.4
Quartz	3.85	7.2
Coesite	3.95	7.3
Stishovite	4.08	7.3
Concrete	3.47	6.2

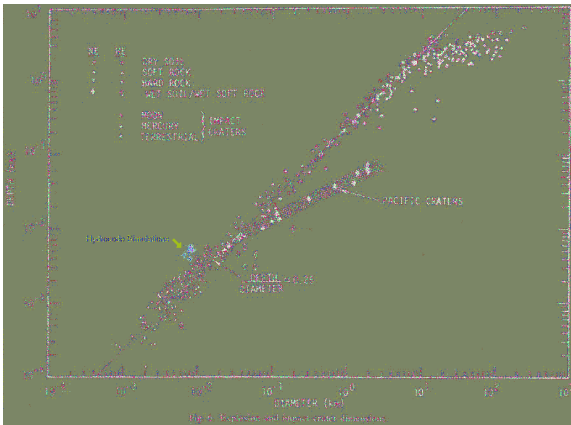Table 2 - Predicted Crater Depth and Diameters 10ms after impact for impact of 1500kg al sphere at 10km/s

Fig 9 – Position of simulation results on the Universal cratering curve

After extensive analysis there was no evidence of the model causing errors in the GRIM hydrocode or of wave reflections from the edge of the mesh influencing the results. On closer inspection there are potentially some complex mechanisms operating in the crater formation. This is illustrated in Fig 10, which shows a data point (station) indicating the penetration as a function of time and the cumulative pdv work input into the target.
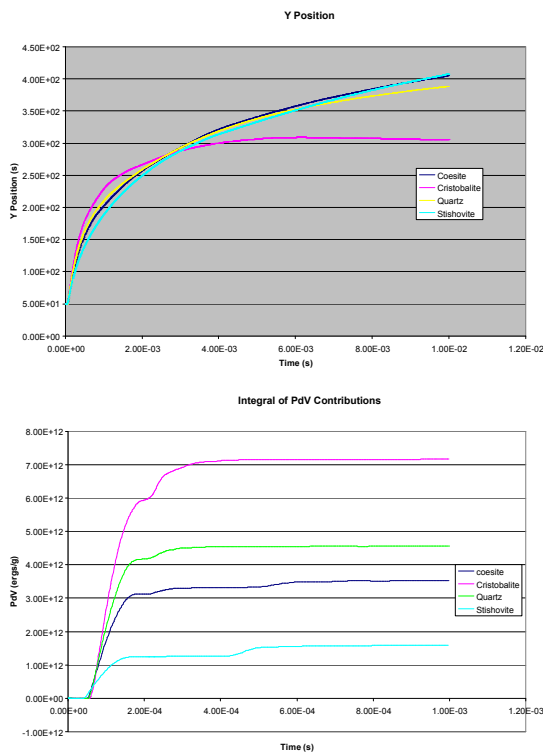

Fig 10 – predicted penetration v time (top) and cumulative pdv work (bottom) for each crystal form

It is very interesting that in the penetration v time curve the order for maximum penetration corresponds with that for maximum density. However, the order reverses after about 3ms. For the cumulative pdv work the stishovite starts off with the maximum, but again the trend reverses and the cristobalite has by far the largest pdv work. This could be an indication that the cristobalite is absorbing more energy from the impact and therefore deforming less resulting in a lower penetration depth. However, these results need more analysis.

It is also important to note that there will be solid-solid phase transitions during the impact. In particular the quartz will transition to stishovite at about 20GPa and thus the behaviour may be completely different. Development of a hybrid EOS is the subject of ongoing work and has recently been completed for concrete. Another very important factor is that the energy contribution leading to melt has not been explicitly accounted for these models. However, understanding the role of each crystal form is important since they can exist at different points in the crater away from the initial impact.

It is also interesting that the model prediction for quartz is very similar to that of concrete for both GRIM and AUTODYN, as would be expected. This indicates that the numerical scheme for this aspect of cratering is not particularly crucial, although it may have an effect at later times and for spallation effects.

5. CONCLUSIONS

A new approach using Quantitative Structure/Property Modelling (QSPM) has been described, which is capable of predicting shock Hugoniots for different crystal forms of silica. The approach has also been applied to various forms of ice and comparisons with available experimental data are highly encouraging.

The models have been applied in the QinetiQ Eulerian hydrocode GRIM to investigate the initial cratering phase. The results, which require further analysis, indicate that energy absorption in the material is critical in determining the final crater shape. Future studies will investigate the effect of phase transitions, particularly from quartz to stishovite on the cratering process.

6. REFERENCES

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