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FOR ANFO

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Temperature-based reactive flow model for ANFO

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Reactive flow models for explosives are usually developed by choosing an empirical form for the reaction rate and calibrating parameters against initiation experiments. In shock wave initiation, experimental data almost always comprise mechanical measurements such as shock speed, material speed, compression, and pressure. However, we know from chemistry that reaction rates depend on temperature as well as on the mechanical state. This is one reason why mechanically-based reaction rates do not extrapolate well outwith the range of states used to normalize them. For instance, mechanical reaction models which match single-shock initiation generally fail to reproduce multiple-shock initiation phenomena.

We have previously developed reactive flow models for military explosives which include temperature as well as the mechanical state. These models reproduced multiple-shock initiation behavior much more accurately than did reactive flow models with a purely mechanical reaction rate, and they were also capable of being used to simulate cook-off problems.

We have recently extended the temperature-based model for use with ANFO-type formulations. Reactive material is treated as a heterogeneous mixture of components, each of which has its own model for response to dynamic loading (equation of state, strength model, reactions.) A finite-rate equilibration model is used to determine the overall response of the mixture to dynamic loading. In the initial model of ANFO, the ammonium nitrate and the fuel oil are treated as separate components in the unreacted mixture. The ammonium nitrate reacts with a rate that depends on its thermodynamic state, with an additional contribution for brittle failure caused by shear under non-isotropic strain. The reaction products are oxygen-rich. The fuel oil decomposes as a function of its thermodynamic state, and the decomposition products are allowed to react with the excess oxygen from the ammonium nitrate with a diffusion-limited rate which depends on the thermodynamic state. This model is also suitable for other oxidizer-fuel mixtures.

There is a relative paucity of data on initiation in ANFO formulations, so our calibrations and simulations to date are to an extent sensitivity studies of a set of equations. More experiments are needed before the model can be regarded as accurate for predictive work.

Temperature-Based Reactive Flow Models for ANFO

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Damian Swift
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Outline

- Motivation
- Overview of Model
- Equations of State
- Reaction Rate
- Performance

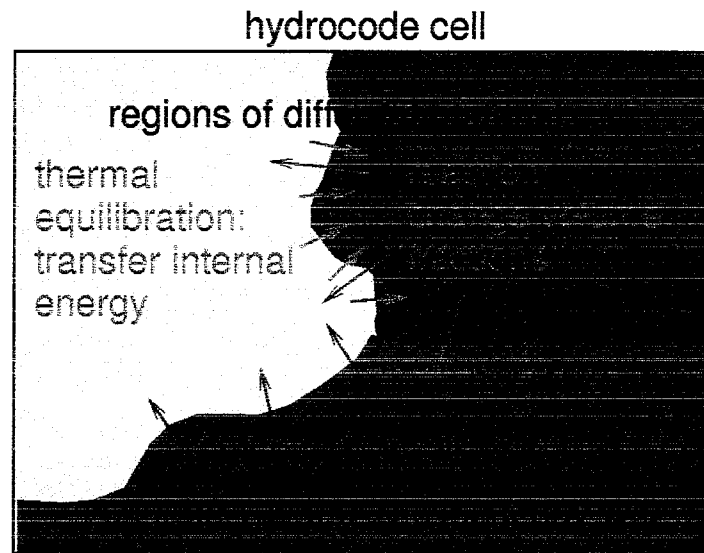
Developing a predictive capacity motivates mesoscale model

Want to predict initiation and blast given:

- Variations in composition
- Variations in morphology
- Different loading conditions

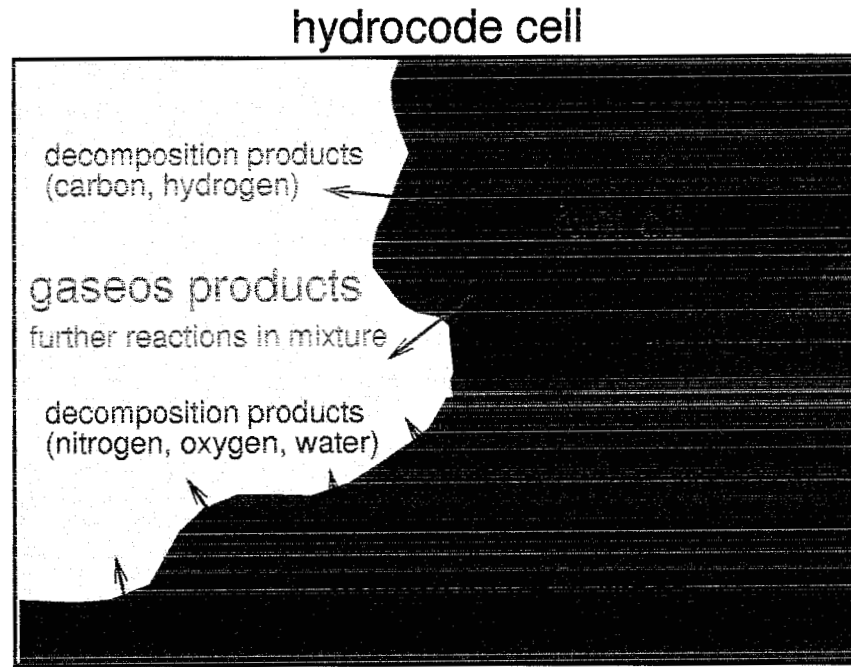
Previous work on military explosives:
need physically-based model rather than just
mechanical calibrations

Model encompasses various spatial regions



- Equation of state for each component (spatial region)
- Equilibration process for temperature and stress.
- Chemical reactions transfer mass between components.
- Regions may comprise separate chemical components.
- Oxidiser/fuel process: oxidiser decomposes leaving oxygen-rich products; the oxygen reacts with the fuel.

Heterogeneous model for ANFO



- Initial porosity modelled as product fraction (at STP).
- Ammonium nitrate reacts with temperature-dependent rate.
- Fuel oil heated by reaction.
- Fuel oil reacts with AN products with temperature-dependent rate
- Pore collapse → increased heating.

Unreacted equations of state: quasiharmonic

Need accurate temperature

→ thermodynamically complete.

- Cold curve ($T = 0$ isotherm) + vibrational modes.
- Cold curve deduced from mechanical EOS fitted to shock data, with $\Gamma(\rho)$ model for off-Hugoniot states.
- Assumed value for $\rho(T=0)$ not particularly sensitive.
- Estimated vibrational modes ω_i from structure of molecule.
- Deduced $d\omega_i / dv$ to reproduce STP state.

Used to calibrate $\varepsilon(\rho, T)$ and $p(\rho, T)$.

Quasiharmonic equation of state

$T = 0$ isotherm $\varepsilon_c(\rho) \rightarrow p_c(\rho) = -d\varepsilon_c/dv$

Vibrational modes $\omega_i(\rho)$

Specific internal energy:

$$\varepsilon_c(\rho, T) = \varepsilon_c(\rho) + \frac{1}{m} \sum_i \hbar \omega_i(\rho) \left\{ \exp(-\hbar \omega_i(\rho) / k_B T) - 1 \right\}^{-1} + \frac{1}{2}$$

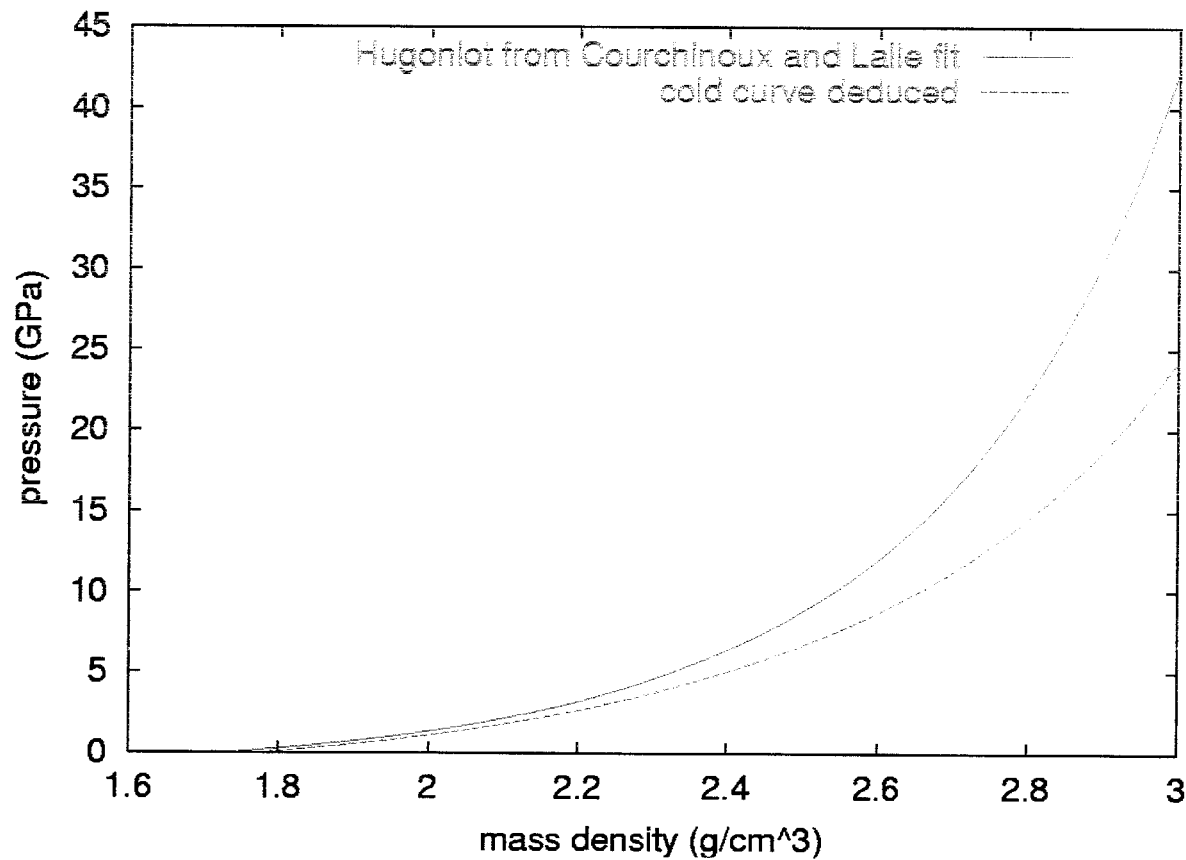
Pressure:

$$p(\rho, T) = p_c(\rho) - \frac{1}{m} \sum_i \hbar \frac{d\omega_i}{dv} \left\{ \exp(-\hbar \omega_i(\rho) / k_B T) - 1 \right\}^{-1} + \frac{1}{2}$$

Tabulated (Sesame format); used as (ρ, ε) EOS.

Ammonium nitrate: mechanical EOS

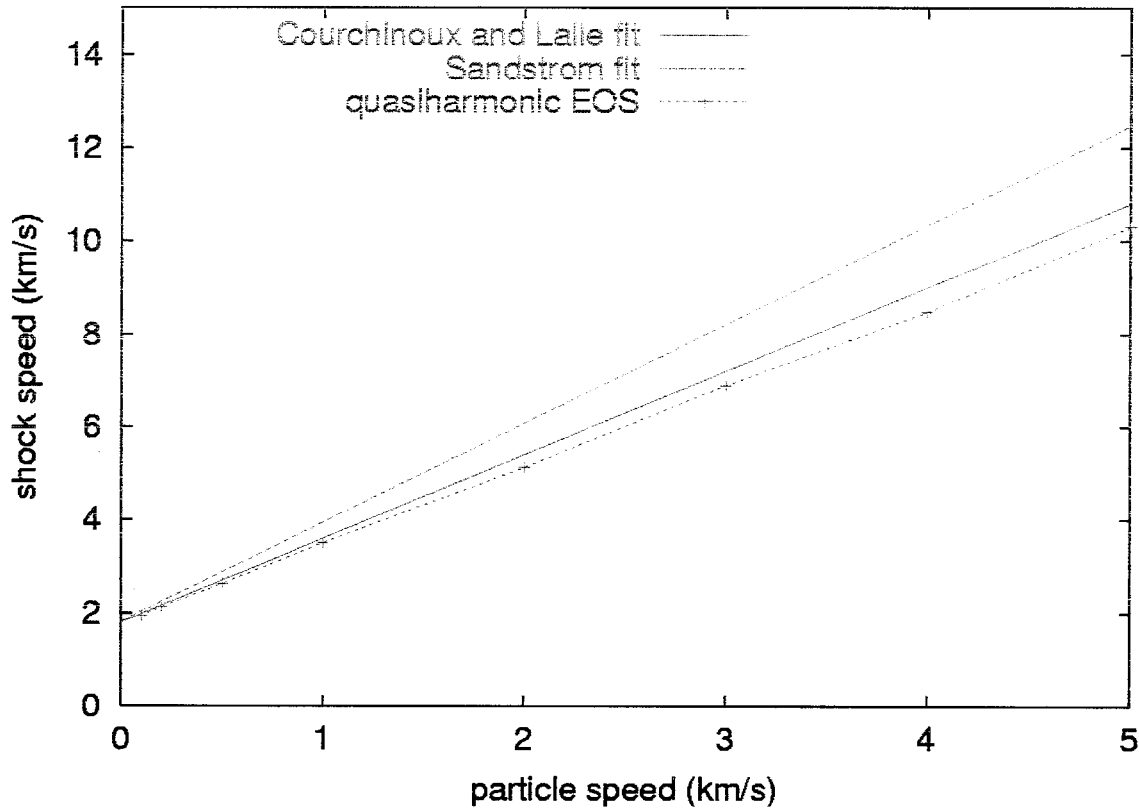
Steinberg-style Gr neisen form:



Ammonium nitrate: thermal contributions

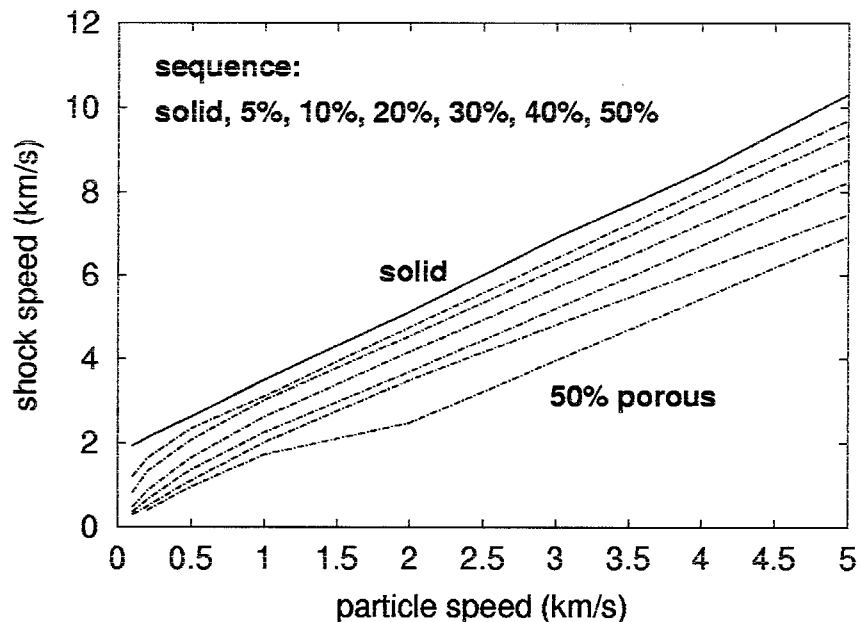
mode	wavenumber, cm ⁻¹	degeneracy (modes per molecule)
O-H bending	1300	1
O-H stretching	3700	1
NH ₃ umbrella	1400	3
NH ₃ stretch (as)	3145	3
NH ₃ scissor	1680	2
NH ₃ stretch (s)	3040	1
O-NH ₃ torsion	150	1
O-NO ₂ torsion	456	1
O-NO ₂ i.p. bend	710	1
O-NH ₃ bending	300	2
N-O bending	450	1
N-O bending	630	1
NO ₂ scissor	800	1
O-NH ₃ stretching	900	1
NO ₂ stretch (s)	1300	1
NO ₂ stretch (s)	1760	1

Ammonium nitrate: comparison with Hugoniot



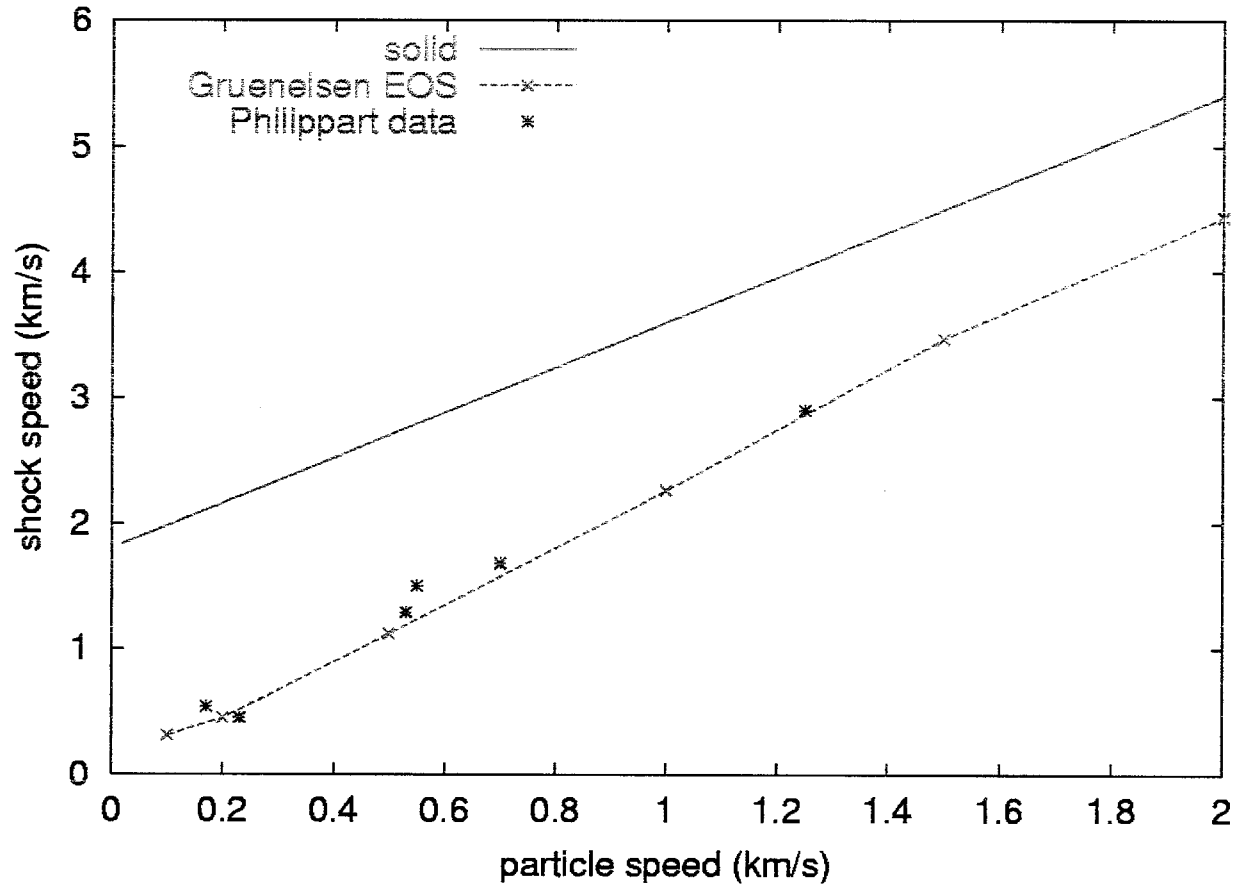
-- quasiharmonic EOS is reasonably consistent with Gr neisen ;
temperatures are probably accurate.

Ammonium nitrate: porous Hugoniot



- Heterogeneous mixture model → treats porosity automatically.
- Particle size → equilibration rates.
- More useful for simulations than empirical rules for adjusting Hugoniot.
- Developed for military explosives: porosity ~1%, works well to > 45%.
- Example: air in pores, infinitesimal particles (ideal mixture).

Porosity model compares well with Hugoniot data

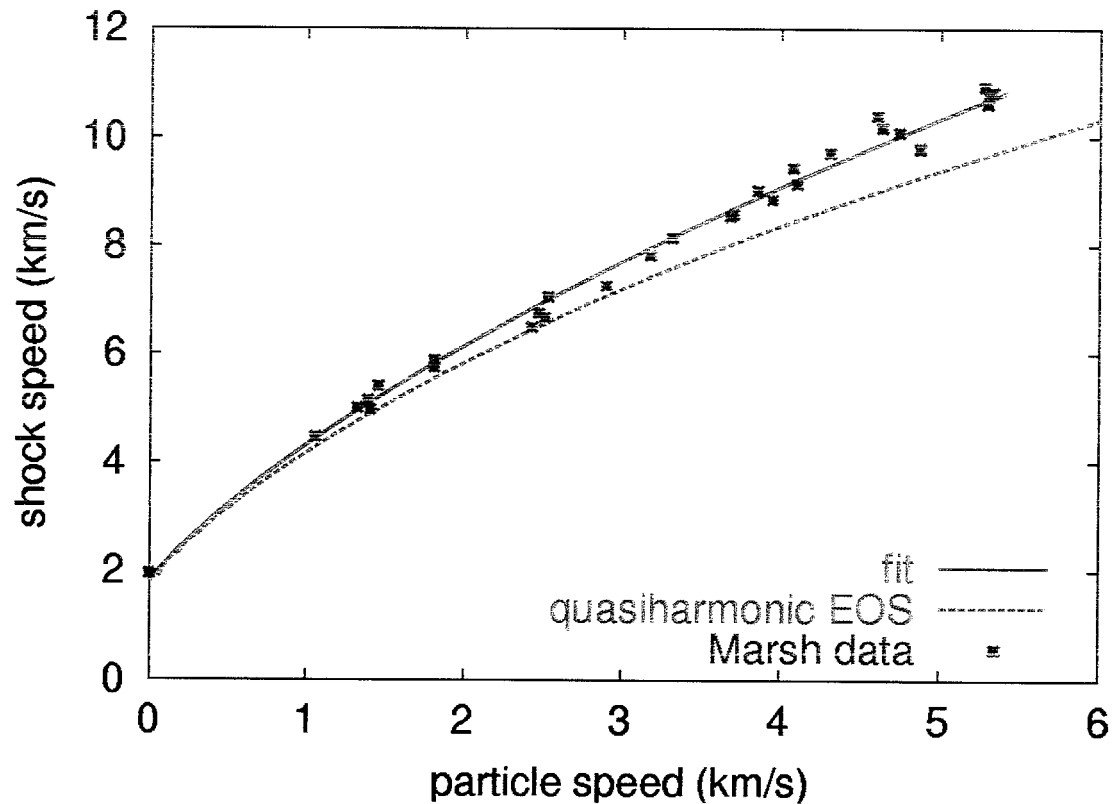


45% porous, compared with ANFO Hugoniot data

Paraffin: mechanical EOS

Steinberg-style Gr neisen EOS, fitted to Hugoniot data:

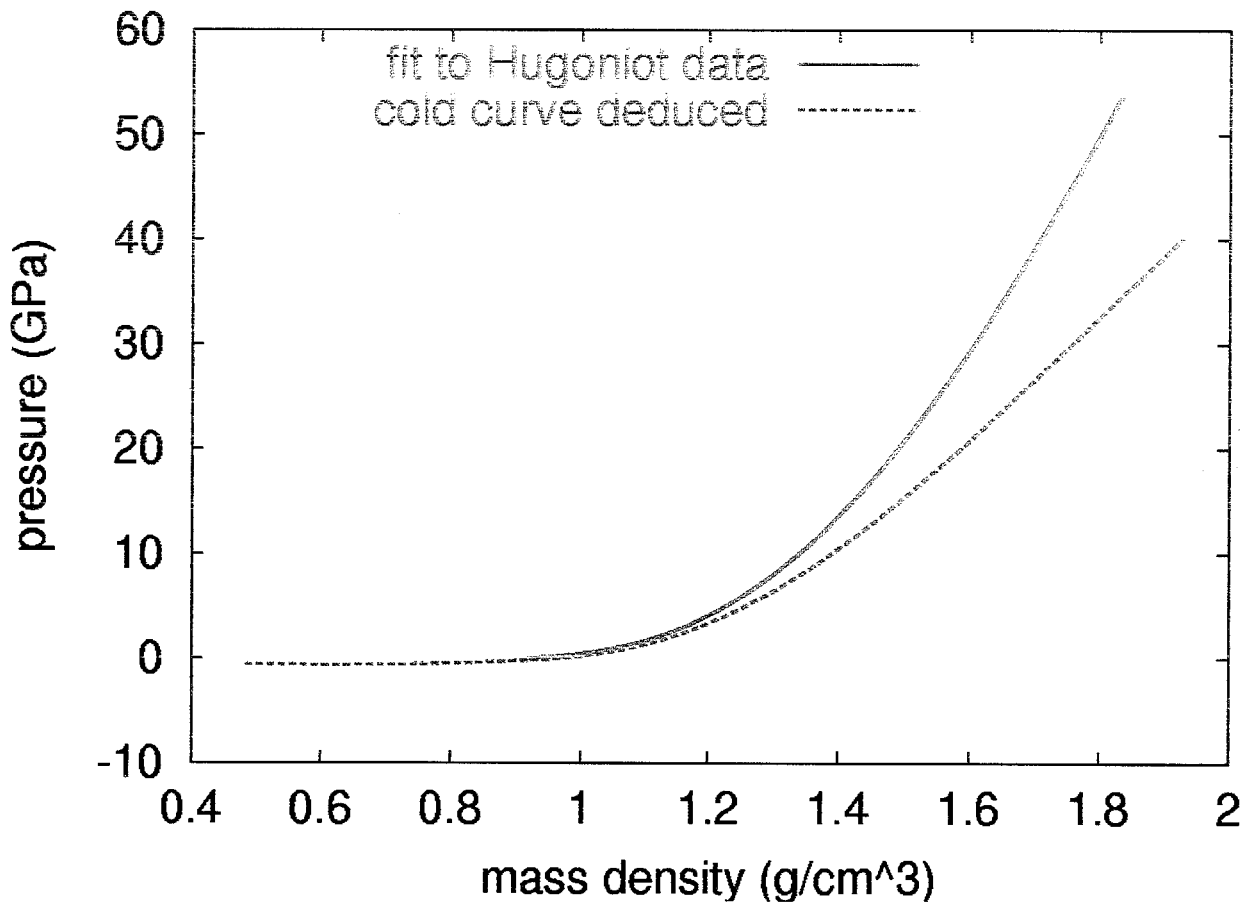
$$u_s = c_0 + \sum_{i=1}^n S_i \left[\frac{u_p}{u_s} \right]^{i-1} u_p$$



$\Gamma(\rho)$ estimated from du_s/du_p .

Paraffin: mechanical EOS

Steinberg-style Gr neisen EOS:



Paraffin: thermal contributions

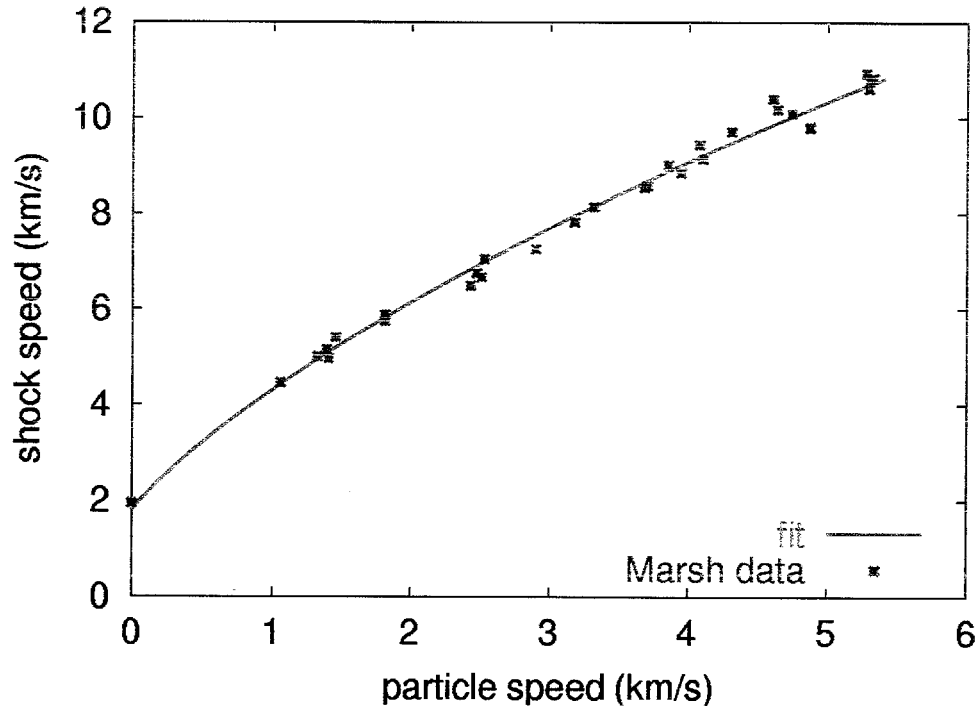
mode	wavenumber cm^{-1}	width cm^{-1}	degeneracy (modes per molecule)
translation	0		6
Torsion	200	100	$n-1$
skeletal bends	400	100	$n-1$
CH_2 rock	760	40	$n/2$
CH_3 rock	900	50	$n/2$
C-C stretches	1050	140	$n-2$
CH_3 deform	1140	10	2
CH_2 twist	1250	30	$n/2$
CH_2 wag	1350	10	n
CH_2 scissor	1450	30	$n+2$
CH stretches	2900	50	$2n+2$

Paraffin: complete equation of state

Comparison with Hugoniot data:

Comparison with Hugoniot data:

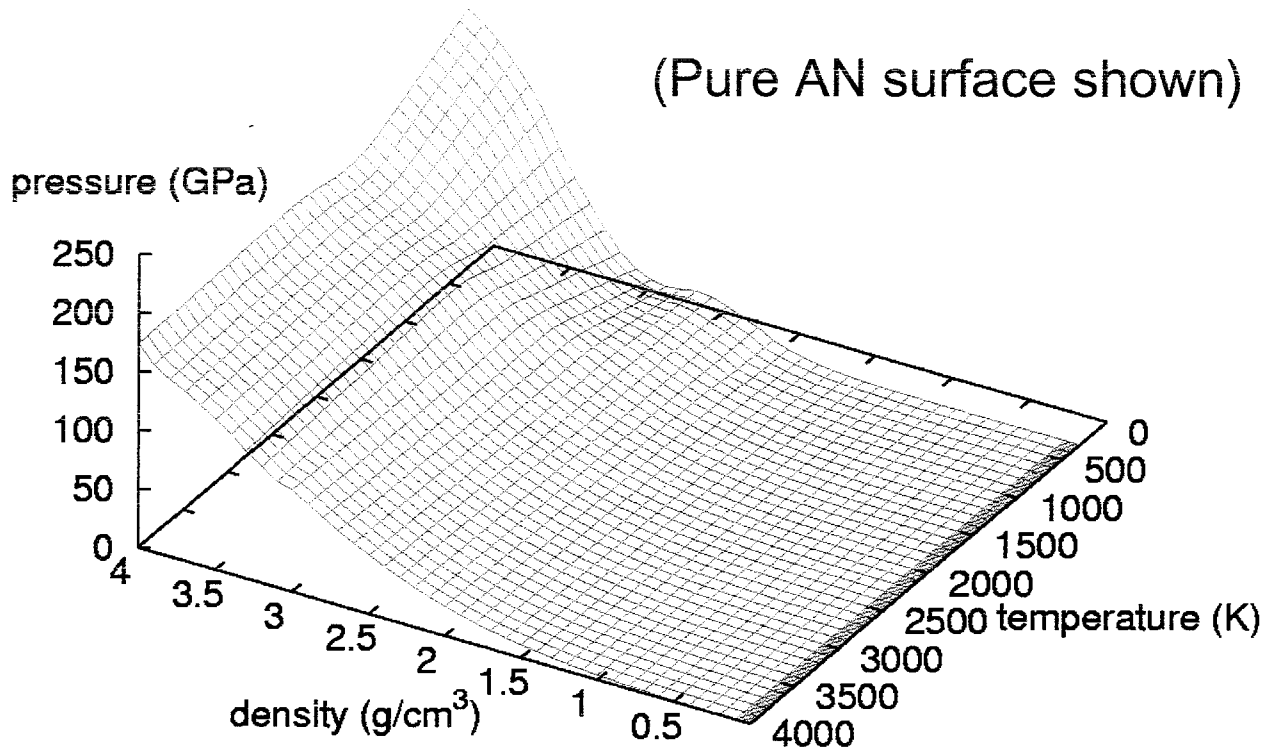
-- reasonably consistent below ~20 GPa;



probably need more accurate treatment
of frequencies at higher pressures.

Product Equation of State Generated with Cheetah

Varying AN/FO compositions
requires construction of surface in ρ , T and p



Reaction rates

- Generalised Arrhenius: $\lambda = R_0 e^{(-T/T^*)}$
 - T^* and R_0 may be functions of ρ , ε (not used here).
- Depletion terms for chemical species.
- T may include correction for non-equilibrium vibrations in a shock (not used here).
- Additional hotspot term using T for other components of mixture.
- R_0 estimated from typical atomic vibration frequencies for key bonds, $\sim 10^{14}/s$.
- Energy release calculated from heats of formation.
- AN: T^* estimated from (sparse) shock initiation data.
- FO: T^* chosen by comparison with RX-HD.

Continuum mechanics simulations

Based on Edinburgh C++ testbed hydrocode

- Lagrangian finite difference predictor-corrector scheme
- Equation of state, strength, spall, mixtures, reactions
- Object-oriented: state stored depends on material type
- Internal evolution (equilibration , reactions, plastic flow, etc. are operator-split from hydrodynamics

Heterogeneous reactive flow

- Material comprises a set of simple constituents ρ_i, T_i, f_i .
- Calculate p for each.
- Finite equilibration rates for p and T :
relaxation times τ_p and τ_T .
- Reaction: rate for each constituent to transform to other(s).
- Equilibration and reaction are subcycled.
- Rates: bulk + surface (homogeneous).
- Surface area depends on volume fraction f_i
through general function.
- Chemical reactions in products.

Mechanical equilibration

$$p_i \equiv p(s_i)$$

component pressure

$$p \equiv p(s) \text{ \&}$$

material mean pressure

$$\phi_r \equiv \phi_s (1 - e^{-\Delta t / \tau_m})$$

relaxation factor

$$\frac{\partial p_i}{\partial f_i} = \frac{c_i^2(s_i) \rho_i}{f_i}$$

stiffness (adiabatic)

$$\Delta f_i = \phi_r (p_i - p) \frac{\partial p_i}{\partial f_i}^{-1}$$

volume fraction change (raw)

$$p'_i \equiv p_i + \frac{\partial p_i}{\partial f_i} \frac{\Delta f_i}{2}$$

effective pressure

$$\Delta e_i = \frac{p'_i \Delta f_i}{f_i \rho_i}$$

energy change (raw)

(Volume and energy are adjusted for exact conservation)

Thermal equilibration

$$T_i \equiv T(s_i)$$

component temperature

$$\bar{T} \equiv T(s)$$

material mean temperature

$$\phi_r \equiv \phi_s \left(1 - e^{-\Delta\tau / \tau_T}\right)$$

relaxation factor

$$\Delta \varepsilon_i = \phi_r c_v(s_i) (T_i - \bar{T})$$

energy change (raw)

(Energy is adjusted for exact conservation.)

Heterogeneous reaction model

$$\lambda'_s \equiv R_b(s_i, p(s_j), T(s_j))$$

surface rate

$$V_f = V_f \rho_i T(s_j)$$

flame speed

$$A_s = A(f_i)$$

surface area

$$\Delta \lambda_s = A_s v_f \Delta t$$

surface burn fraction (raw)

$$\lambda'_b \equiv R_b(s_i, p(s_j), T(s_j))$$

bulk rate

$$\Delta \lambda_b = (1 - f_i - \Delta \lambda_s) \lambda'_b$$

bulk burn fraction (raw)

$$\Delta \lambda = \Delta \lambda_b + \Delta \lambda_s$$

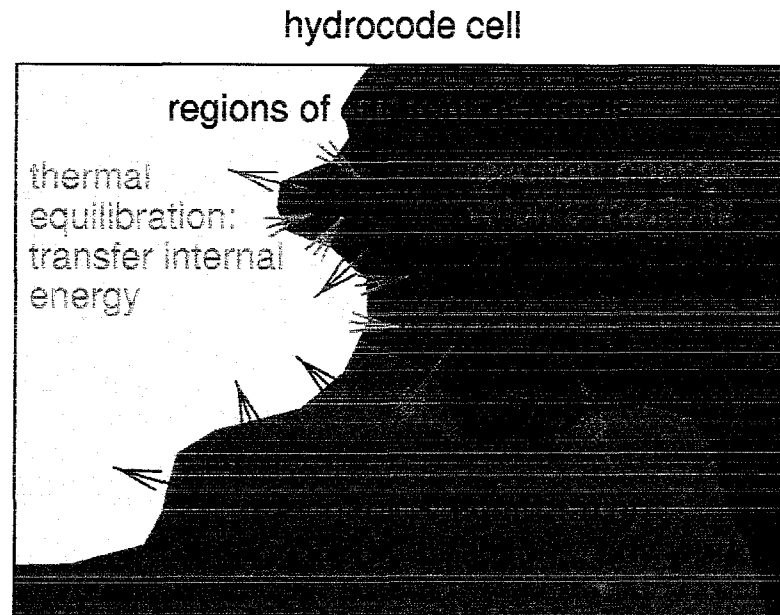
total burn

(Surface contribution ignored if $\lambda'_s \Delta t < 1$.

Burn fractions limited to ensure $0 < f_i < 1$
and $\sum_i f_i = 1$.)

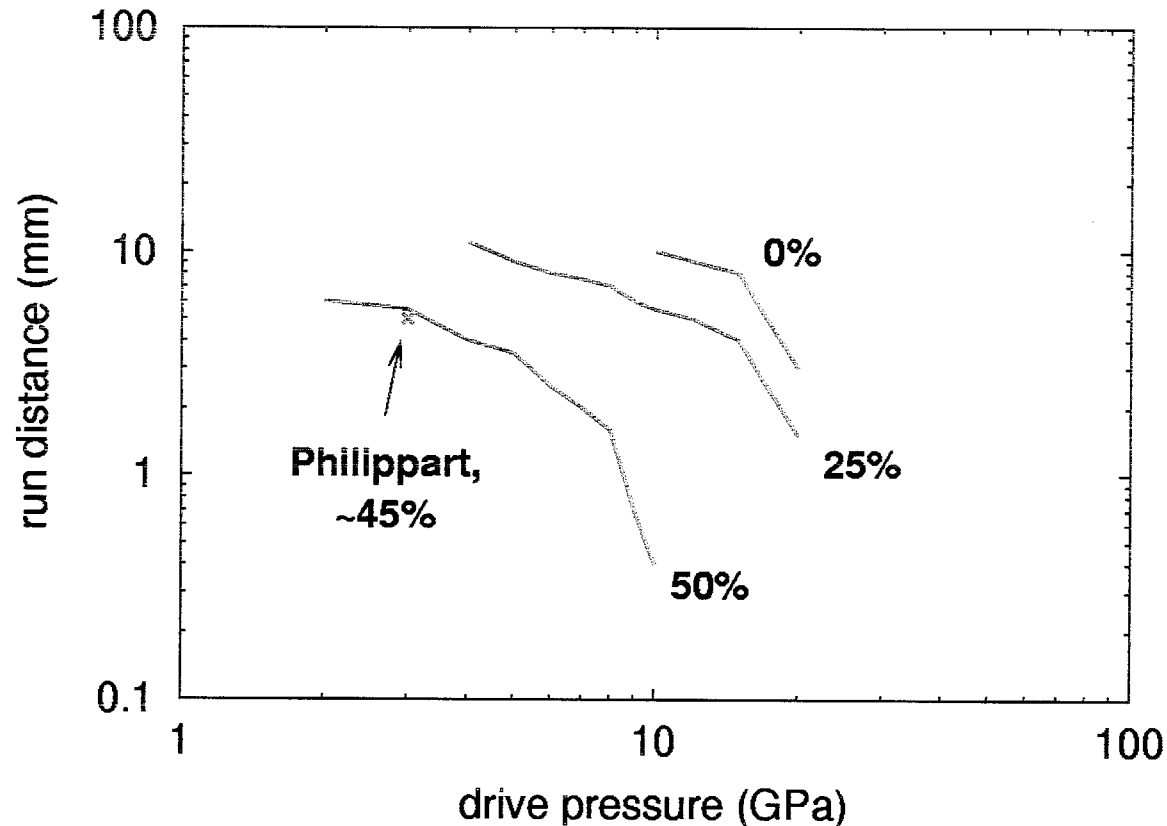
Hydrocode implementation

- Any number of materials per cell.
 - For each: volume fraction f_i , state (ρ_i, \dots) and EOS.
 - No further internal structure (shape functions etc).
 - State depends on material type: may include other parameters (e.g. plastic strain).
 - Explicit mechanical and thermal equilibration between regions; exponential time constant for each; operator-split from hydrodynamics and subcycled.
- EOS functions: $\rho, \varepsilon, p, T, c_v, c^2$
-- relatively simple requirement.- Reaction rates R_{ij} between each pair of regions; operator-split from hydrodynamics and subcycled.



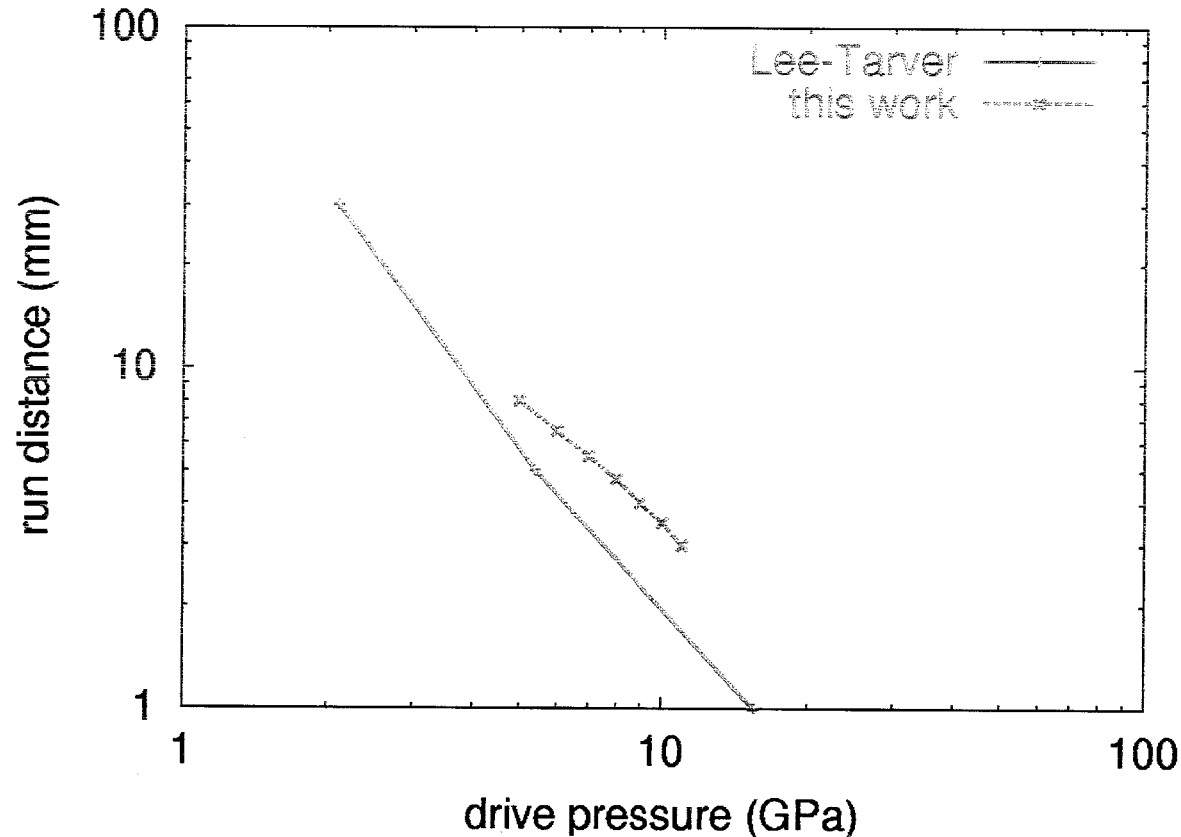
Predicted Pop plots fo AN

Variation with porosity, pore size, composition.



Parameters: $R_0 = 10^{14}$ /s, $T^* = 12500$ K,
 $\tau_p = 0.1 \mu\text{s}$, $\tau_T = 1.0 \mu\text{s}$, 0.1 mm mesh.

RX-HD Pop plots are Predicted



AN Parameters: $R_0 = 10^{14}$ /s, $T^* = 12500$ K,
FO Parameters: $R_0 = 10^{14}$ /s, $T^* = 15000$ K,
 $\tau_p = 0.1 \mu\text{s}$, $\tau_T = 1.0 \mu\text{s}$, 0.1 mm mesh.

Summary and Conclusions

- Physically-based reactive flow model for ANFO.
- Complete equations of state:
fairly rigorous, consistent with Gr neisen EOS.
- Model can predict effect of composition, porosity, particle size.
- Preliminary trials: comparable with empirical data / models.

Future work

- Minor adjustments to numerical scheme;
re-calculate parameters more carefully.
- Off-Hugoniot data for AN etc.
(e.g. Trident shots, diamond anvil, spectroscopy).
- Equilibrium chemistry for equation of state of reaction products.
- Use of / comparison with diameter effect data.
- Investigation of other fuels.
- Desensitisers as chemical species: model short-lived radicals.