Rubbers under high triaxial loads

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Impact against propellant – Insensitive Munitions

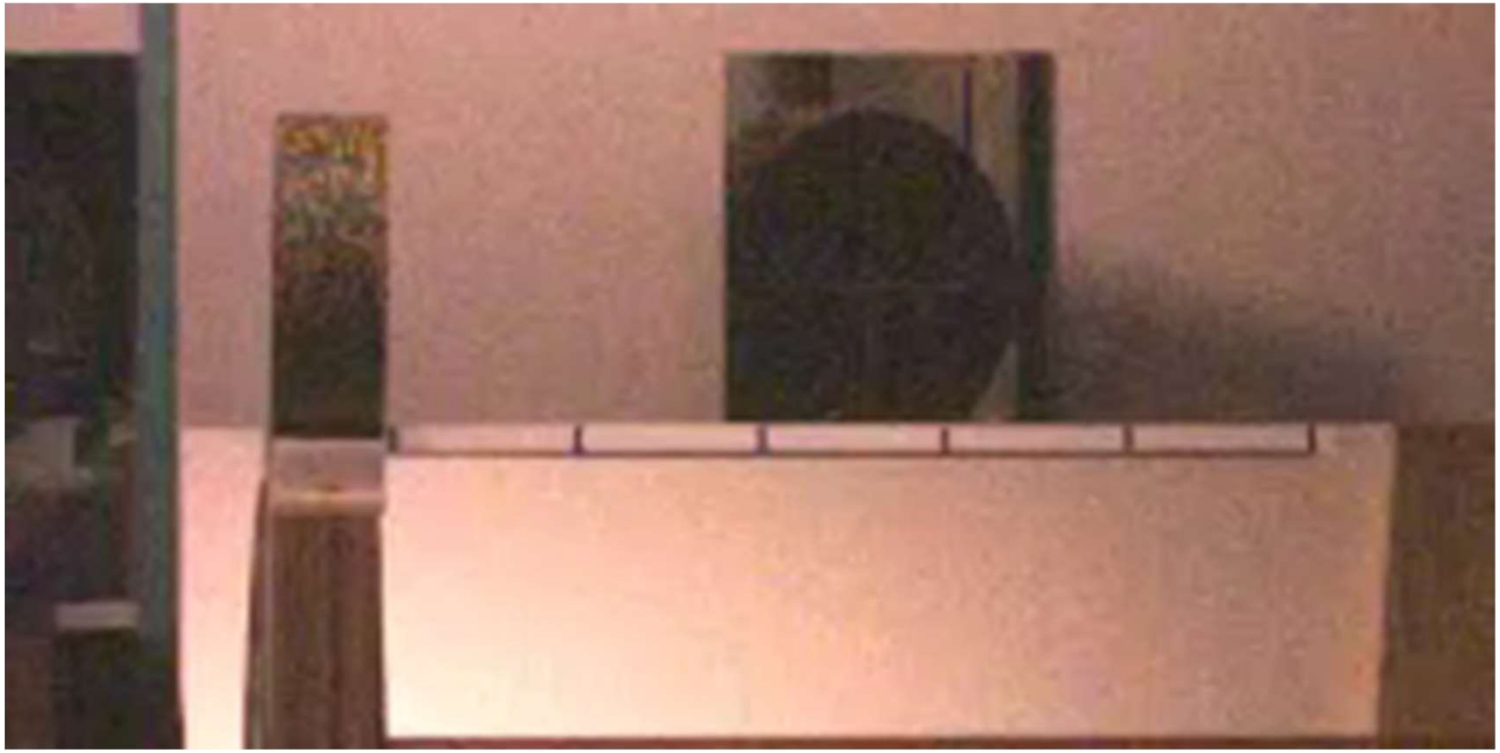
- We have a duty of care for our armed forces
- Our weapons should only explode when and where we want them to
- NATO standard for Insensitive Munitions response
  - Fragmenting munitions attack (Fragment Impact)
  - No response more severe than Type V (Burning)
  - Steel fragment from 15 g with velocity up to 2600m/s and 65 g with velocity up to 2200m/s.
- These tests are really expensive and a cost-effective approach to assurance is needed
- Small-scale approach using highly-instrumented tests on small amounts of material
  - Still expensive and needs material to be available
- Ideally we would be able to predict response from chemistry and physics

Impact against propellant

- Shock-to-Detonation Transition and No reaction

Impact against propellant

- Unknown (X) to Detonation Transition



Impact against propellant

- Need to predict – consider the material response
- Impact conditions
  - Uniaxial strain
    - Implies Poisson's ratio is zero but these are large volumetric deformations
  - Sub microsecond response: strain rates 10^7 /s
  - Pressure 6 GPa
  - Temperature?
    - Mechanical work with heat capacity
    - Entropic effects with high hoop strain at rear of block
- What are the things we need to predict?

Group Interaction Modelling

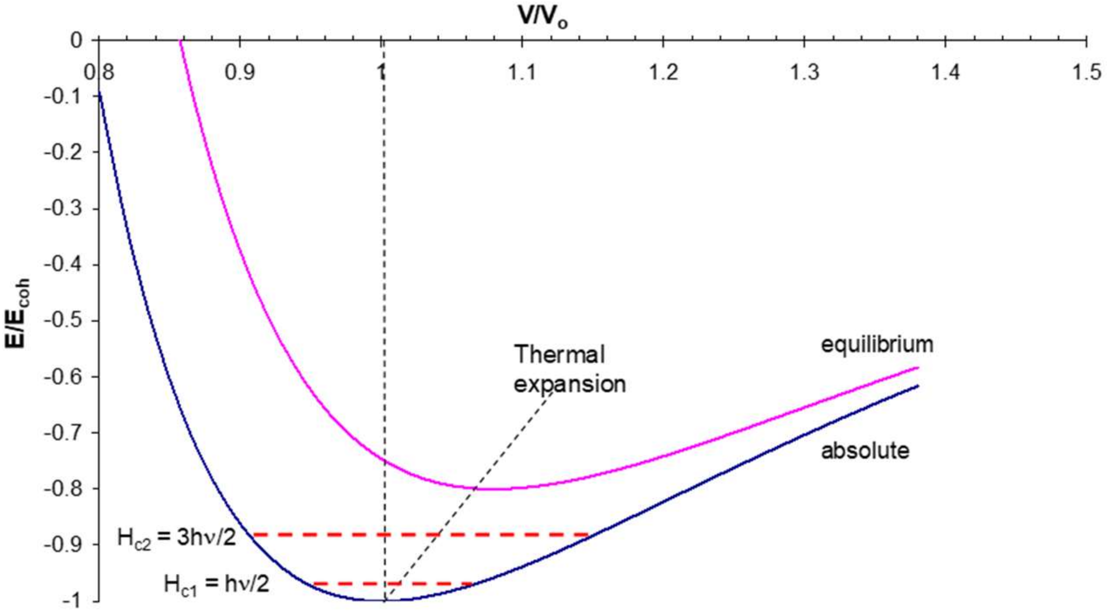
- Group Interaction Modelling (GIM) is a group contribution method for predicting properties of polymers without need for synthesis or measurement.
  - Originated in polymer industry
  - Significant evidence of predictive capability
  - Can predict physical and mechanical properties as a function of rate and temperature through the glass transition
- Mean Field description of energy-deformation response
  - Van der Waals and Hydrogen bonding
  - Can be predicted via quantum mechanics codes
  - Account for vibrational modes and conformational state
  - Equivalence of thermal and mechanical energy
- Interacting groups have characteristic contributions to parameters used:

– M	molecular weight of a group
– V_w (cc/mol)	van der Waal’s volume of a group
– E_{coh} (J/mol)	cohesive energy of intermolecular forces
– θ_D (K)	1-D Debye reference temperature related to polymer chain stiffness
– N	skeletal degrees of freedom per group

GIM

- Potential function method
  - Lennard-Jones and self-similar
  - Born criterion for instability
  - Stress and bulk modulus from derivatives of E(V)
  - Put P vs V into Rankine-Hugoniot equations
    - Shock equation of state
  - Also get tensile response which is hard to measure

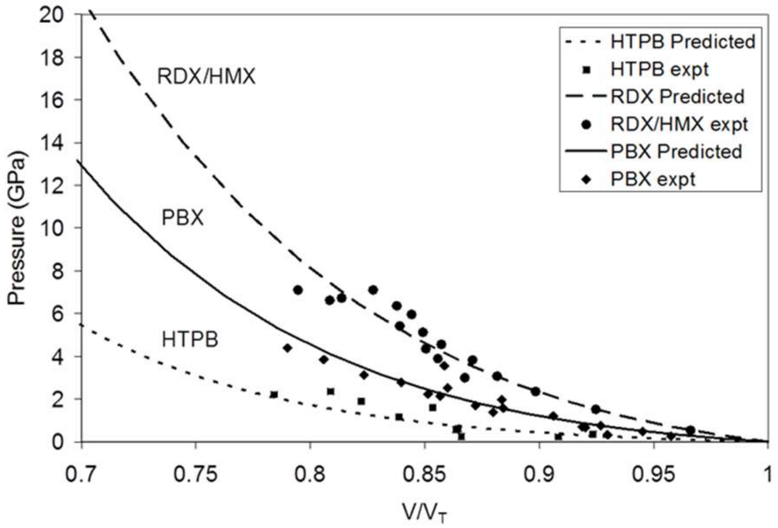
$$P = -\frac{dE}{dV}$$

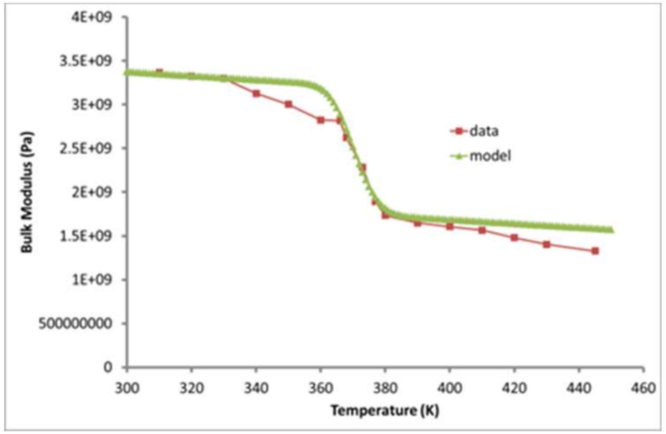


- Point of inflection correlated with glass transition
  - Is L-J sufficient for this?

Pressure vs volume

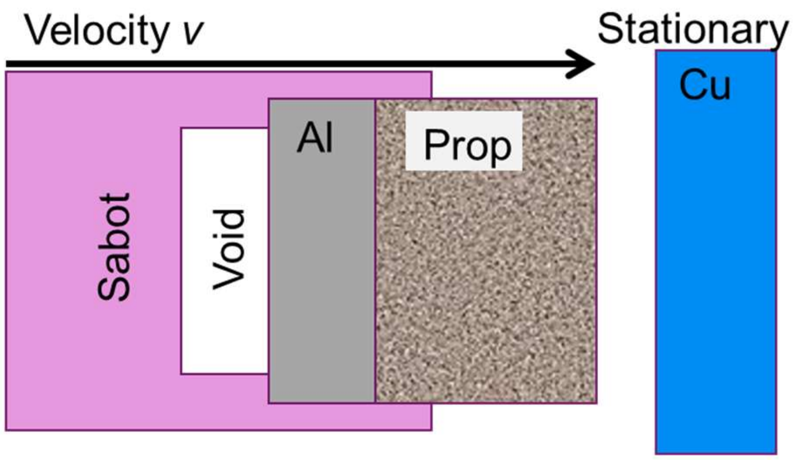
- Rubbers are not incompressible
- Hugoniot from GIM potential function
  - Allows shock propagation to be predicted
- Some questions arise about volumetric loss through glass transition
  - In particular: how does one predict the factor 2 in bulk modulus change?
  - Link to thermal expansion
  - Further questions then about thermal expansion coefficient of plasticized rubbers

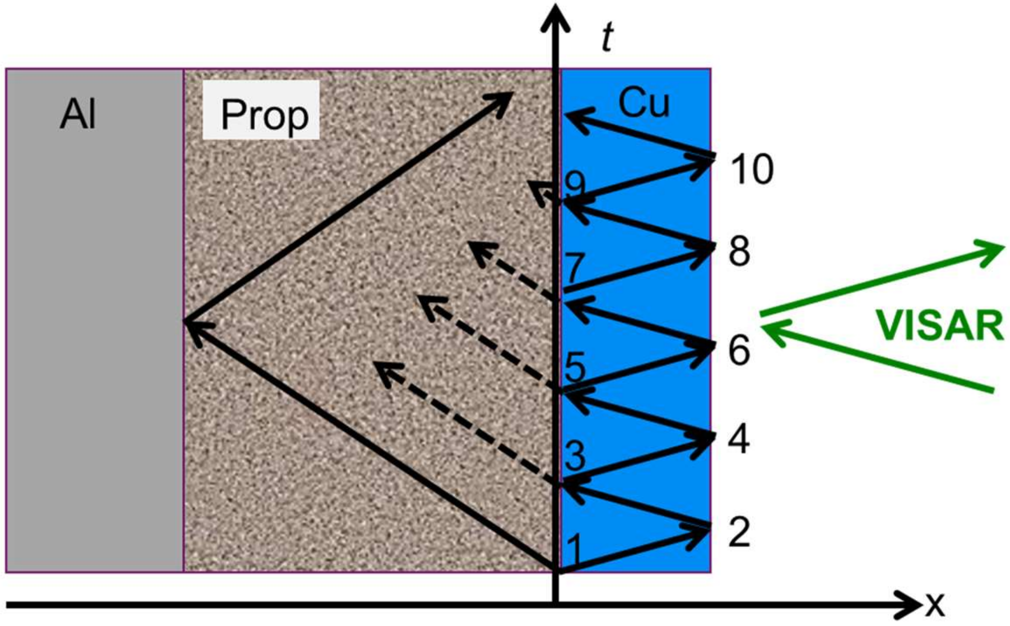




Pressure vs volume

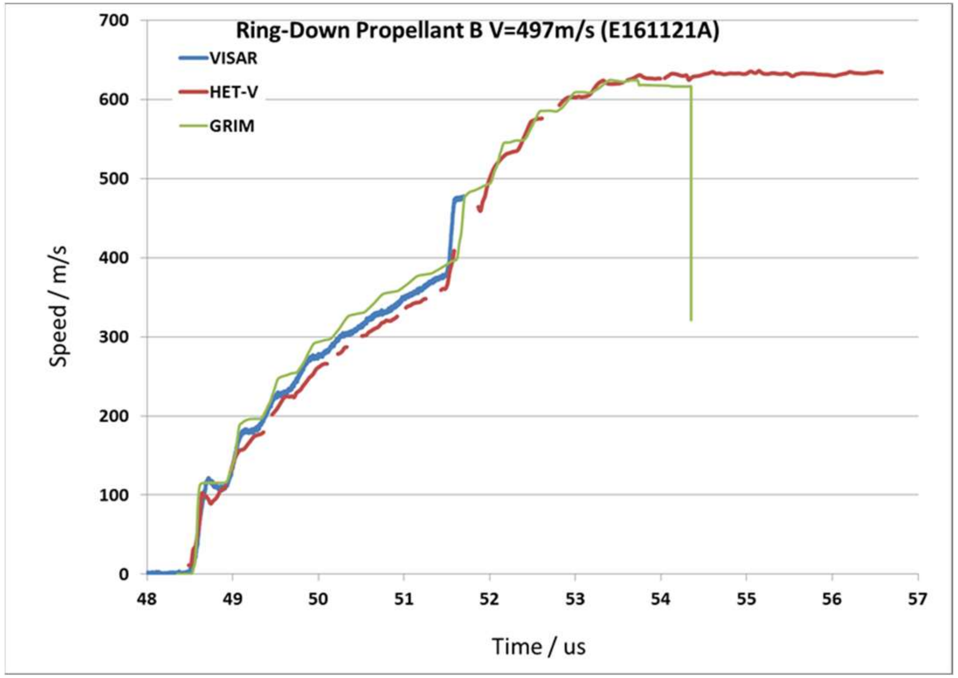
- Validation against ring-down





Pressure vs volume

- Comparison of VISAR and HetV with numerical simulation (GRIM)
- The differences reflect details of the experimental arrangement not being included in the simulation and known physics missing from the material model



Heat Capacity

- 1-D Debye Theory
  - VV Tarasov, Russian Journal of Physical Chemistry **39** (1965) 1109
  - B Wunderlich: ATHAS database
- Chain skeletal modes contribute directly to potential function and thermal energy
- At glass transition need extra 0.5N degrees of freedom
- Group optical modes treated as Einstein oscillators

$$C \approx N\,R\,\frac{\left(\frac{6.7\,T}{\theta_D}\right)^2}{1+\left(\frac{6.7\,T}{\theta_D}\right)^2}$$

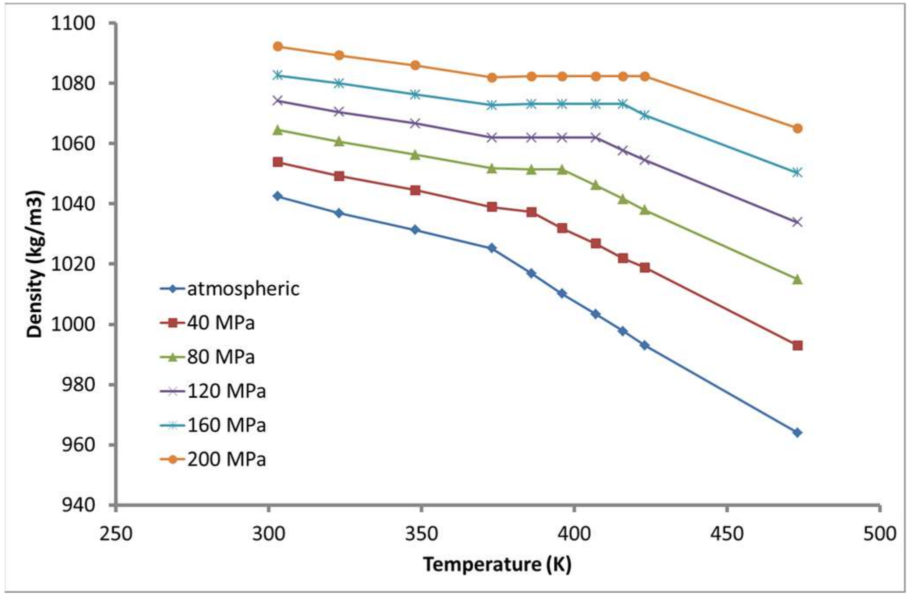
$$\mathrm{C_E} = \frac{\mathrm{R}\left(\theta_\mathrm{E}/\mathrm{T}\right)^2 \exp\left(\theta_\mathrm{E}/\mathrm{T}\right)}{\left[\exp\left(\theta_\mathrm{E}/\mathrm{T}\right)-1\right]^2}$$

$$H_T = \int_0^T C\,dT$$

Heat Capacity – pressure effect on heat capacity

- Movement of T_g as a function of pressure can be seen in poly(styrene) data*
  - Isothermal data
  - Loss peak appears to broaden
  - If T_g moves above current temperature then extra degrees of freedom should be suppressed
  - Would have a significant effect on heat capacity
  - What happens adiabatically?
  - How does this tie in with instability condition for glass transition?

  - HTPB would require imposed pressure of 400 MPa to move T_g above room temperature
  - Heat capacity would drop from 2 J/kg/K to 1.5 J/kg/K
  - Needs verification



$$\frac{dT_g}{dP} = 4\frac{P}{B}\frac{V}{Nk}$$

*T. Ougizawa, GD Dee, DJ Walsh, Polymer, **30** (1989) 1675

Heat Capacity – pressure effect on heat capacity

- Should be working with volume but this has practical issues
- Pressure/volume affects Debye θ temperatures which changes the vibrational modes
- This reduces heat capacity
- Use QM to calculate new vibrational modes for different pressures and new θ temperatures
- Additional to movement of glass transition but there is a feedback
  - Need to avoid double counting

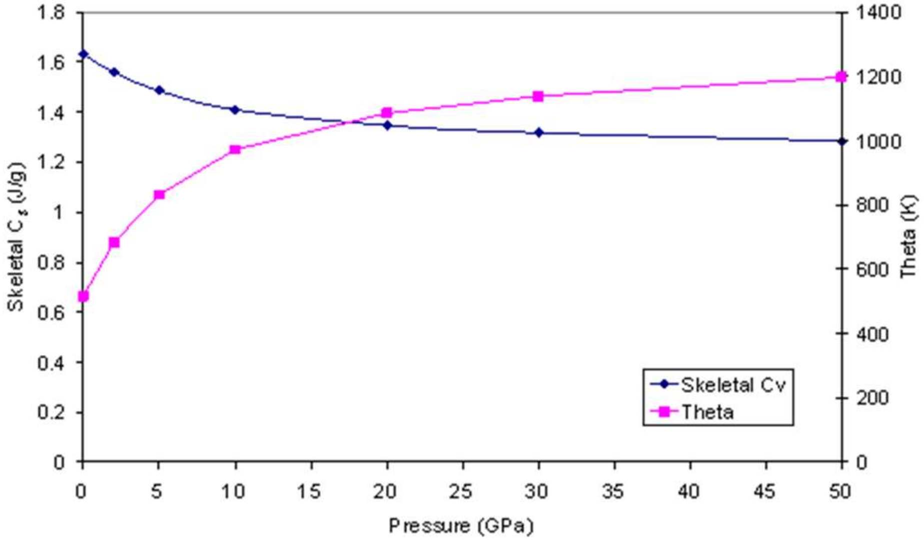
Debye temperatures can be included into model to suggest heat capacities at high pressures.

At 5 GPa and 300K

HTPB C_v = 1.0 J g^{-1} K^{-1}, RDX C_v = 0.79 J g^{-1} K^{-1}

Can use Dreger & Gupta measurements under same conditions to give RDX C_v = 0.81 J g^{-1} K^{-1}

ZA Dreger, YM Gupta, J. Phys Chem B 111 (2007) pp 3893 - 3903



Strength of rubber

- Good capability to predict rubber extension and failure in uniaxial tension
- Entropic stiffening treated as loss of degrees of freedom in modulus calculations
- Fracture when all degrees of freedom associated with glass transition have been lost
- Good prediction of silk properties – Vollrath & Porter
- How does this extend to 3D strain?
  - Particularly tensile
- How does it tie in to fracture mechanics and fragmentation?
  - And temperature?

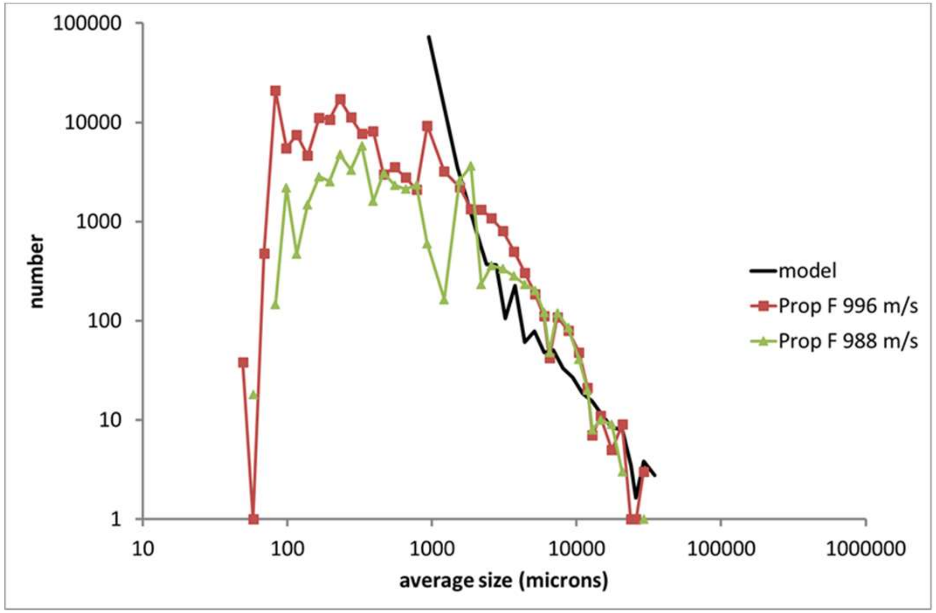
F Vollrath and D Porter, “Spider silk as archetypal protein elastomer”, Soft Matter, 2006, 2, 377–385

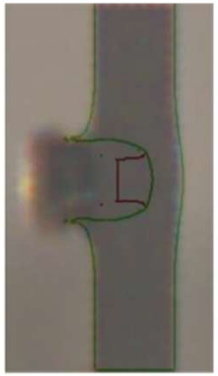
Fragmentation

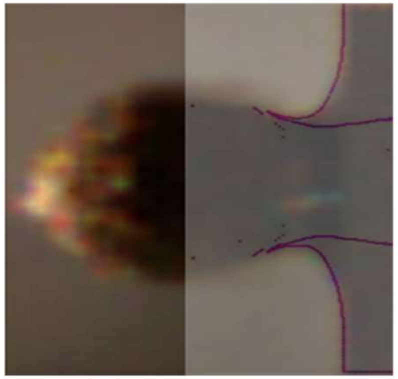
- There is an obvious lengthscale from microstructure
- So use a percolation model with energy-based failure criterion
  - Site percolation: bond is either failed or not
  - Site size is microstructural length
  - Energy gives probability of failure which translates to number of failure sites in 3D lattice
  - When there is no fully-bonded path material is fragmented
  - Gives fragment size distribution
- Allows other capability such as burn area calculation
- What happens if there is no obvious lengthscale?
  - Comminution limit of rubbers?
  - Link to fracture mechanics

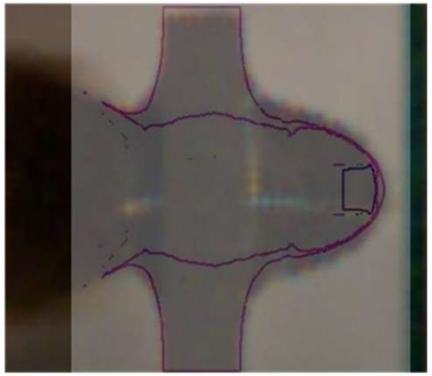
Fragmentation

- Validation against soft capture
- Compare model predictions with measured fragment distributions and shape of fragment cloud
- Importance of numerical scheme




26.4μs


52.8μs


79.2μs

Summary

- Some predictive capability
- Some fundamental questions still to be answered
  - Temperature
  - Time-dependence of volumetric properties
  - Configurational entropy in triaxial stress states
    - Particularly tensile

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