# Equations of State

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# Outline

- What is the equation of state and why should we care?
- Theoretical basis
- Complete and incomplete EOS
- Predicting the EOS
- Experimental measurements
- Corrections, limits, and other issues

# Nomenclature for thermodynamics

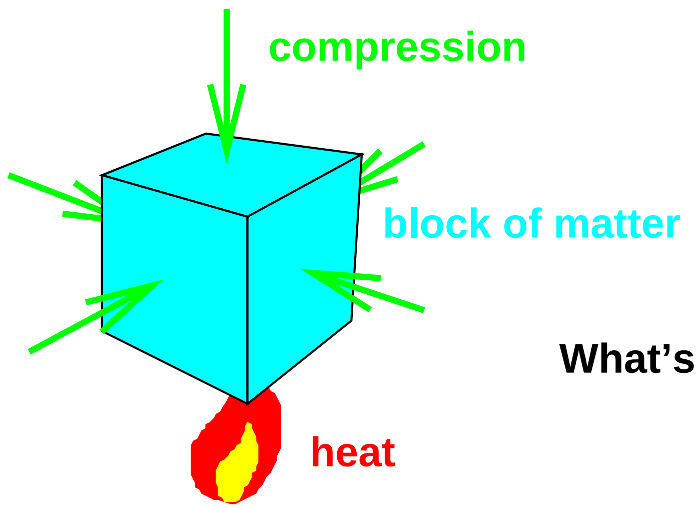
Mass density $\rho$ and specific volume $v$: $\rho = 1/v$.

| **intensive** | | **extensive** | |
|---|---|---|---|
| $p$ | pressure | $e$ | internal energy |
| $T$ | temperature | $s$ | entropy |

Extensive quantities: can integrate over system to find total.

Convention here: use specific quantity (per mass).

# What is the equation of state?




What's the pressure'

**Material-dependent** property, relating **thermodynamic potential** and its **natural parameters**, e.g. $de = Tds - pdv$. EOS is the relation $e(s, v)$ for a material.

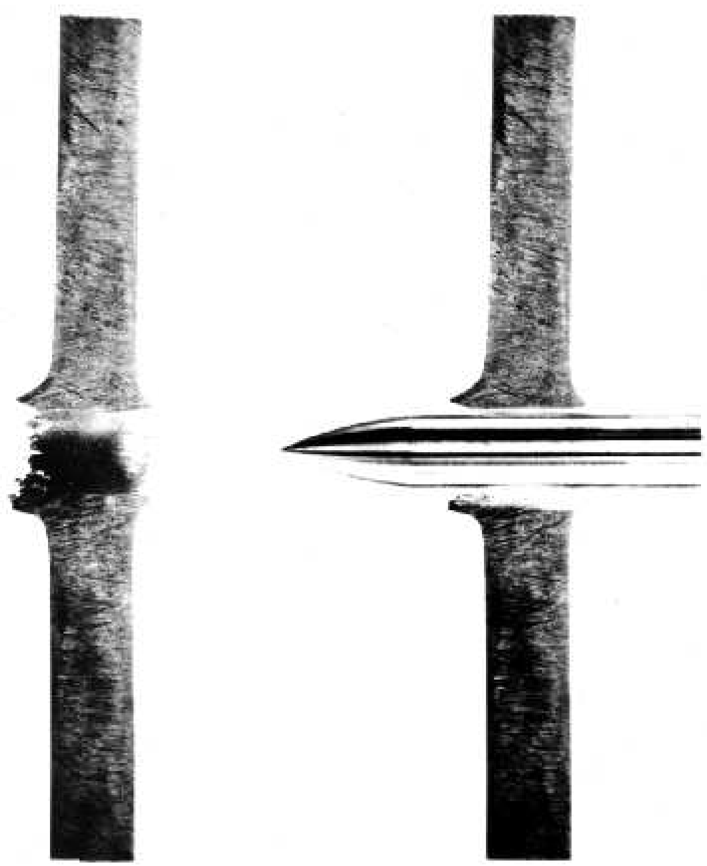
Derivatives and other functions of EOS give other quantities: $p$, $T$, sound speed $c^2$, heat capacity $c_v$, ...

Perfect gas EOS:

$$p = nk_B T \quad p = (\gamma - 1)\rho e$$

# Uses of the equation of state

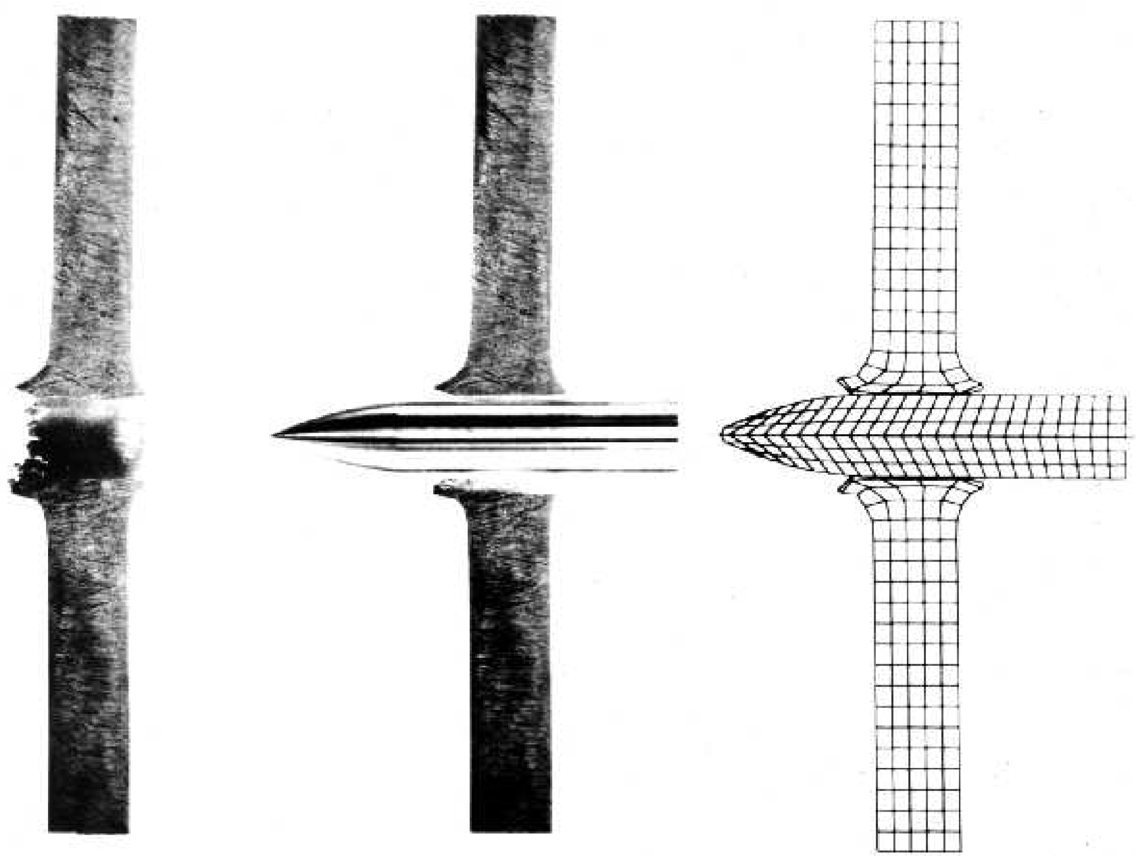
Hydrocode / continuum mechanics simulations of impact-type problems:



Cross-section of armor after perforation by projectile.

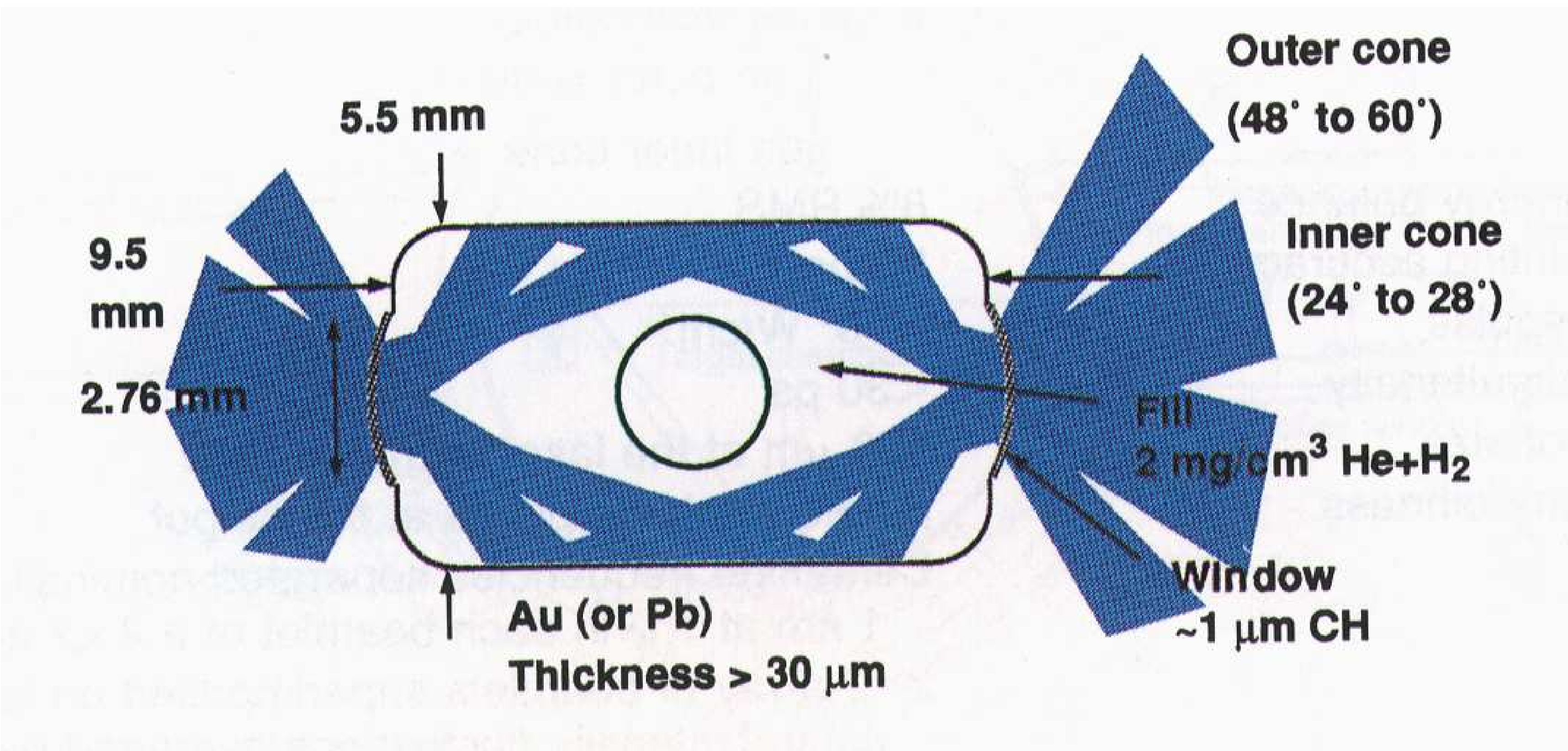
# Uses of the equation of state

Divide components into small cells, assume conditions are spatially uniform in each. Need material properties for simulations.



# Uses of the equation of state

Radiation-driven implosions, e.g. NIF hohlraum-driven fusion capsule:




Source: J. Lindl, "Inertial confinement fusion," Springer (1998).

# Simulation of dynamic loading problems

Initial value problem: given $\{\rho, \vec{u}, e\}(\vec{r}, t_0)$ over some region $\{\vec{r}\} \in \mathcal{R}$, what is $\{\rho, \vec{u}, e\}(\vec{r}, t > t_0)$?

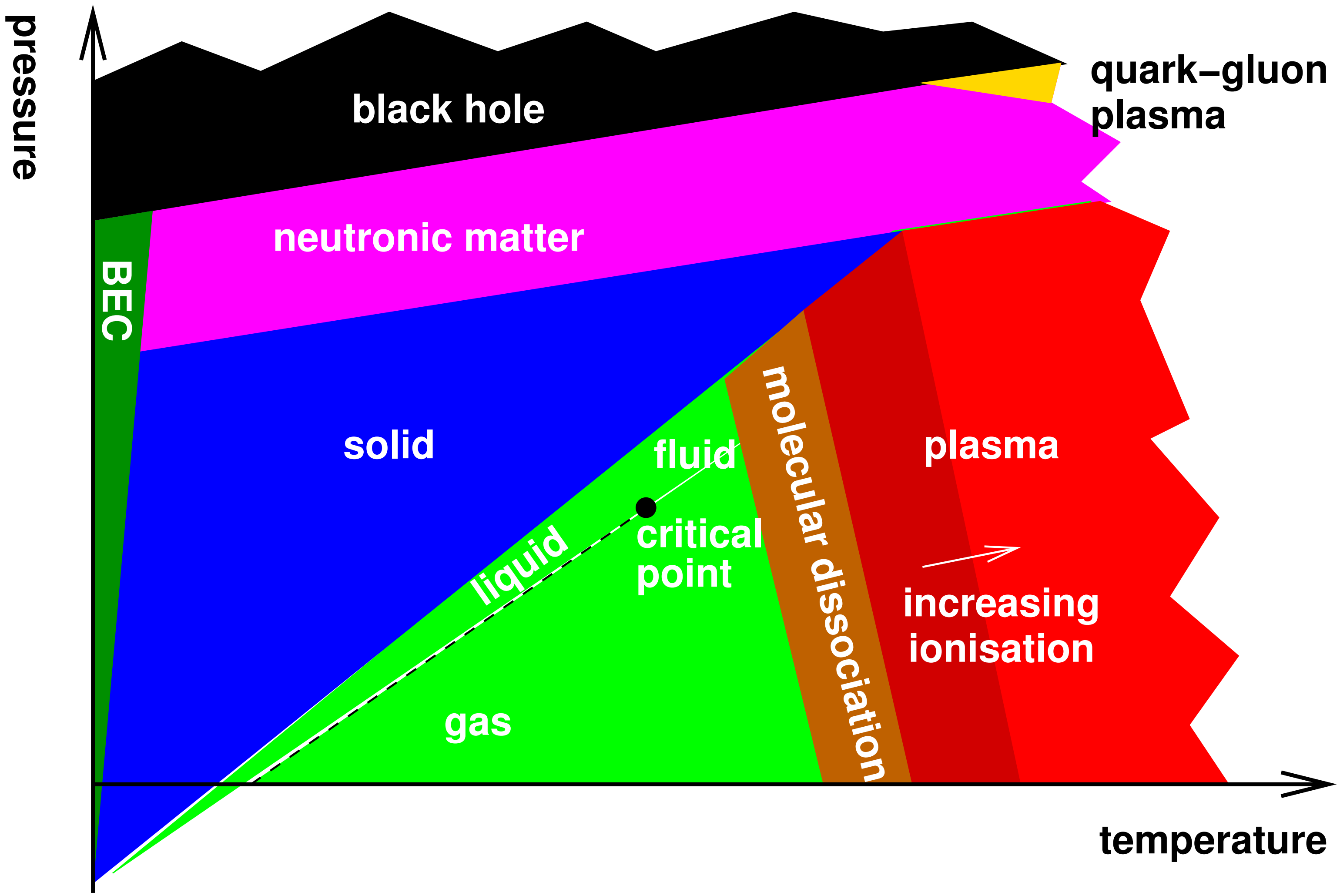
Continuum equations (Lagrangian, neglecting heat conduction):

$$\begin{aligned}
\frac{\partial \rho(\vec{r}, t)}{\partial t} &= -\rho(\vec{r}, t)\,\mathrm{div}\,\vec{u}(\vec{r}, t) \\
\frac{\partial \vec{u}(\vec{r}, t)}{\partial t} &= -\frac{1}{\rho(\vec{r}, t)}\mathrm{grad}\,p(\vec{r}, t) \\
\frac{\partial e(\vec{r}, t)}{\partial t} &= -p(\vec{r}, t)\,\mathrm{div}\,\vec{u}(\vec{r}, t)
\end{aligned}$$

Boundary conditions $p(\vec{r}, t)$ and/or $\vec{u}(\vec{r}, t)$ for $\{\vec{r}\} \in d\mathcal{R}$.

Use EOS $p(\rho, e)$ – derived from $e(s, v)$ – to complete equations and allow integration to proceed.

# Structure of the equation of state



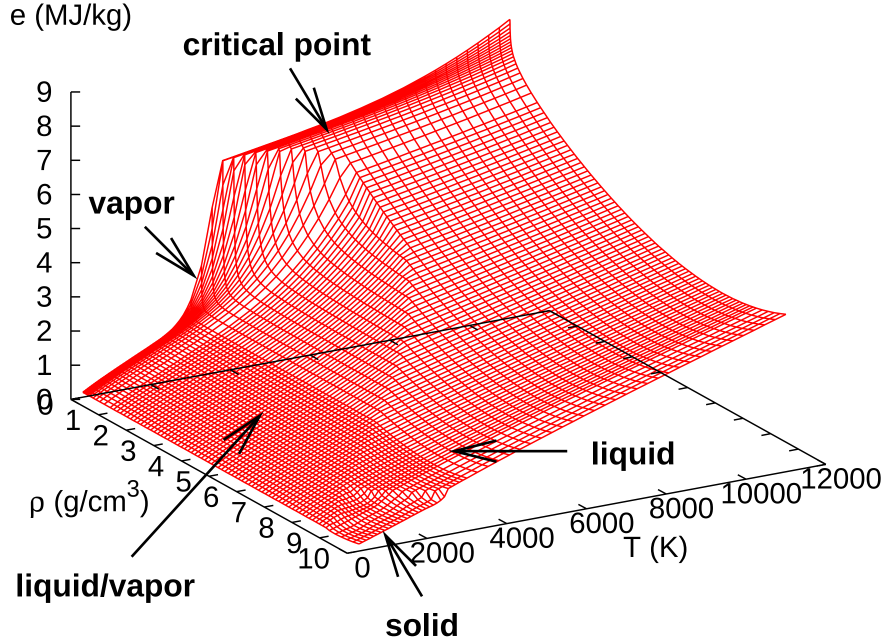

Details depend on the material composition.

# ‘Moderate’ pressure and temperature

Geophysics, hypervelocity impact, terrestrial explosions, ICF, ...

$-$GPa ($p_{\text{spall}}$) $< p <$ PPa (Gbar); $\sim 10\,\text{K} < T <$ MeV; ps $< t <$ Gyr

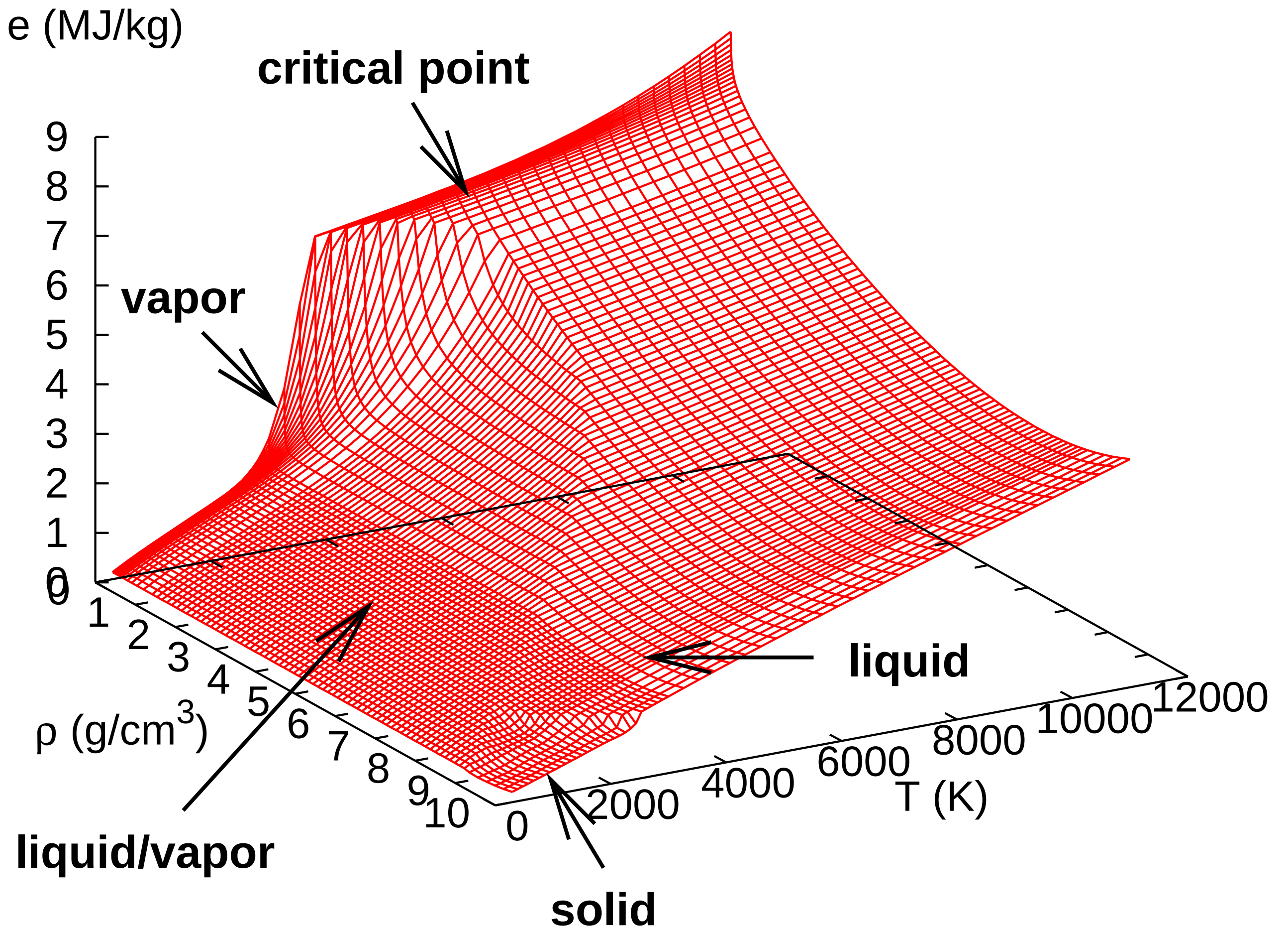
e.g. Cu:




$$e(\rho, T) = e_{\text{cold}}(\rho) + e_{\text{ion-thermal}}(\rho, T) + e_{\text{electron-thermal}}(\rho, T)$$

# Cu phase diagram

SESAME #4:



# Energy, EOS, and phase diagram

Given $e(\rho, T)$ – *for a given atomic arrangement* – can construct EOS using 2nd law of thermodynamics:

$$de = Tds - pdv \quad \Rightarrow \quad s(v,T) = s(v,0) + \int_0^T \frac{dT'}{T'} \frac{\partial e(v,T')}{\partial T'}$$

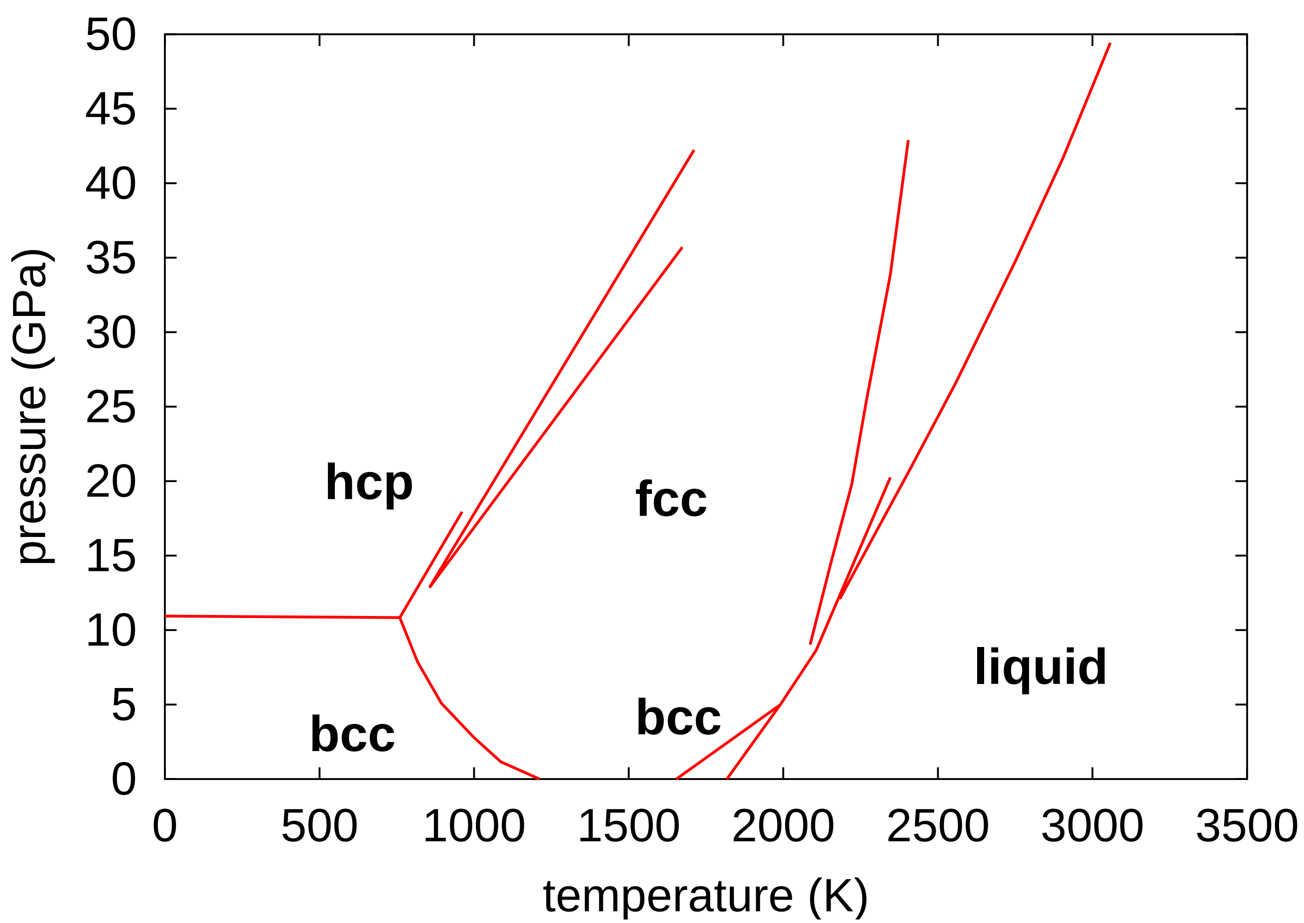
from which calculate $f(\rho, T) = e(\rho, T) - Ts(\rho, T) \Rightarrow$ EOS for this phase.

$s(v, 0)$: 'configurational entropy' – may vary between phases.

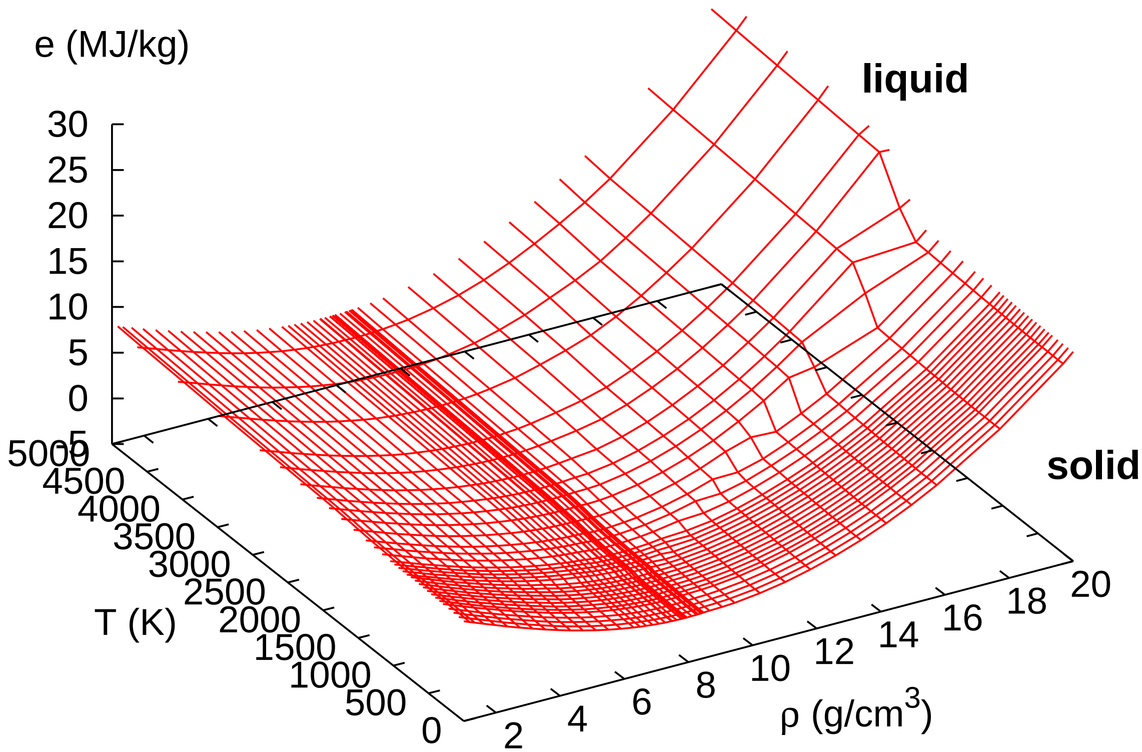
At any $p, T$, equilibrium phase has lowest Gibbs free energy $g = e - Ts + pv$ (natural parameters $g(T, p)$ as $dg = -sdT + vdp$)

# Phase diagram: Fe

Different crystal structures occur in the solid state:

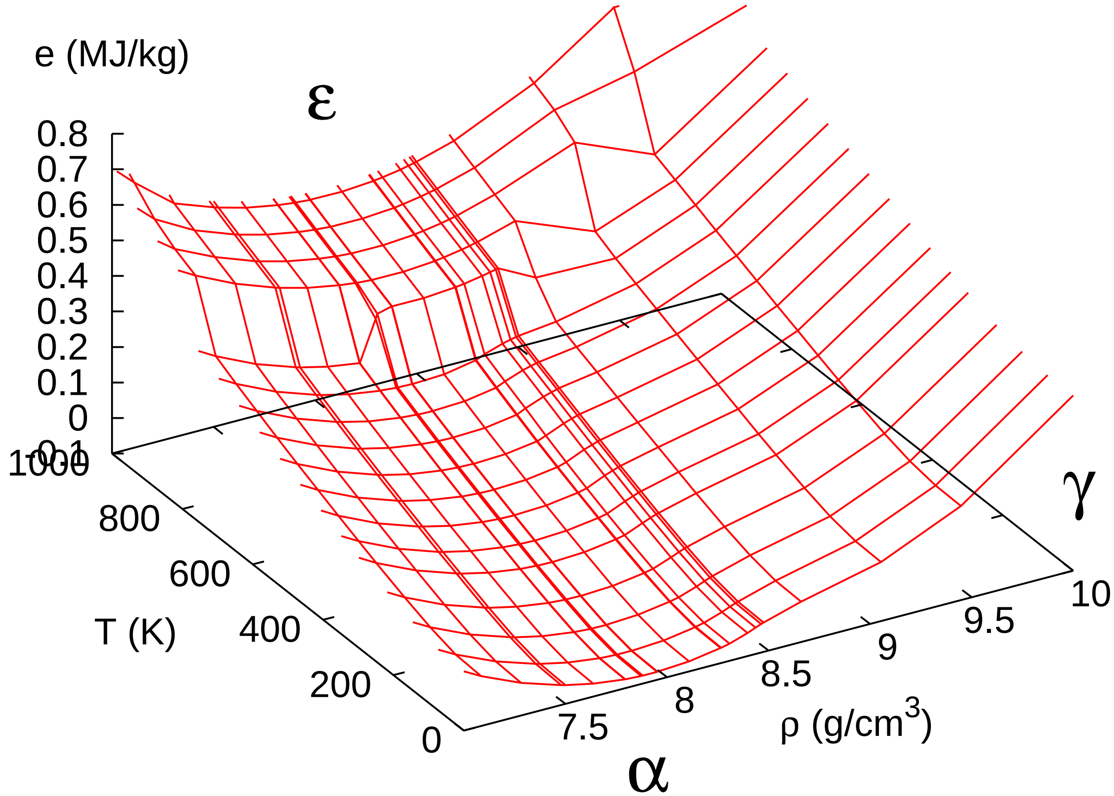


# Multiphase EOS: Fe




Source: J.T. Gammel, T-1.

# Multiphase EOS: Fe




Source: J.T. Gammel, T-1.

# Thermodynamic completeness

Complete EOS: thermodynamic potential expressed in natural parameters

$e(s,v)$, $f(T,v)$, $g(T,p)$, $h(s,p)$

Can derive any thermodynamic parameter from a complete EOS.

Continuum mechanics:

$$\partial\rho/\partial t = -\rho \mathsf{div}\,\vec{u}, \quad \partial\vec{u}/\partial t = -(1/\rho)\mathsf{grad}\,p, \quad \partial e/\partial t = -p\mathsf{div}\,\vec{u}$$

only require $p(\rho,e)$.

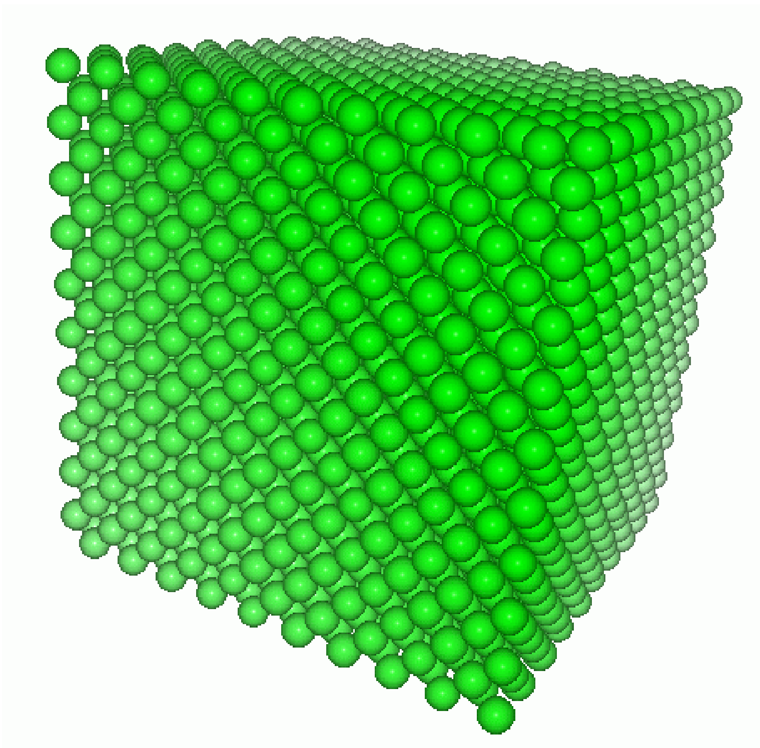
Also: easiest to deduce $p(\rho,e)$ from mechanical measurements.

Incomplete EOS: $p(\rho,e)$ with no information about $T$.

'SESAME' EOS: $e(\rho,T)$ and $p(\rho,T)$: a complete EOS – but may be inconsistent.

# Predicting the EOS

$$e(\rho, T) = e_{\text{cold}}(\rho) + e_{\text{ion-thermal}}(\rho, T) + e_{\text{electron-thermal}}(\rho, T)$$



– solve for electron states for a given set of ion positions (Dirac or Schrödinger equation).

Electrons are indistinguishable fermions: quantum many-body problem...

# Quantum many-body problem

Ground state of collective wavefunction $\Psi$: $\hat{H}\Psi = E_0\Psi$.

Numerical quantum mechanics: based on single-particle wavefunctions $\{\psi_i\}$. Fermions: antisymmetric with respect to particle exchange (Pauli exclusion principle), e.g. for 2-particle wavefunctions $\Psi(1,2) = -\Psi(2,1)$, can be satisfied if

$$\Psi(1,2) = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)].$$

More generally,

$$\Psi(1,2,...n) = \sum_{\chi} \epsilon(\chi)\psi_{\chi(i)}(i) = \det \psi_i(j)$$

where $\epsilon$ is a permutation operator – 'Slater determinant' approach; in practice prohibitive in computer time.

Differences in the phase of the wavefunctions $\Rightarrow$ correlation effects: another complication.

# Local density approximation

Assume can approximate exchange and correlation by modifying the potential energy contribution in the Hamiltonian to include functions of the local electron density

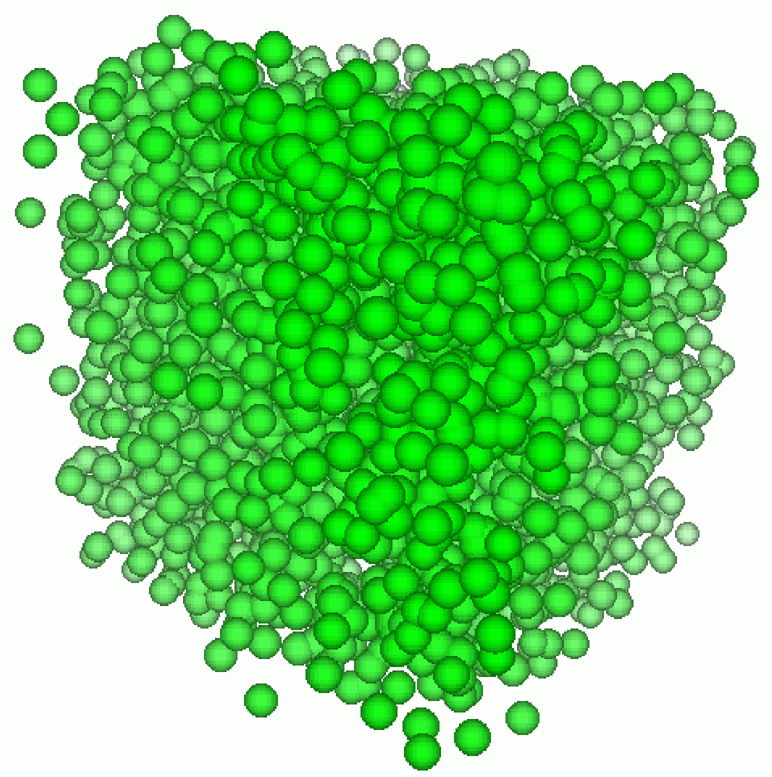
$$n(\vec{r}) = \sum_i \psi_i^\dagger(\vec{r})\psi_i(\vec{r}).$$

These functions are then calibrated against detailed exchange and correlation calculations for simple systems e.g. uniform electron gas.

Typical accuracy: a few percent in density at $p = 0, T = 0$.

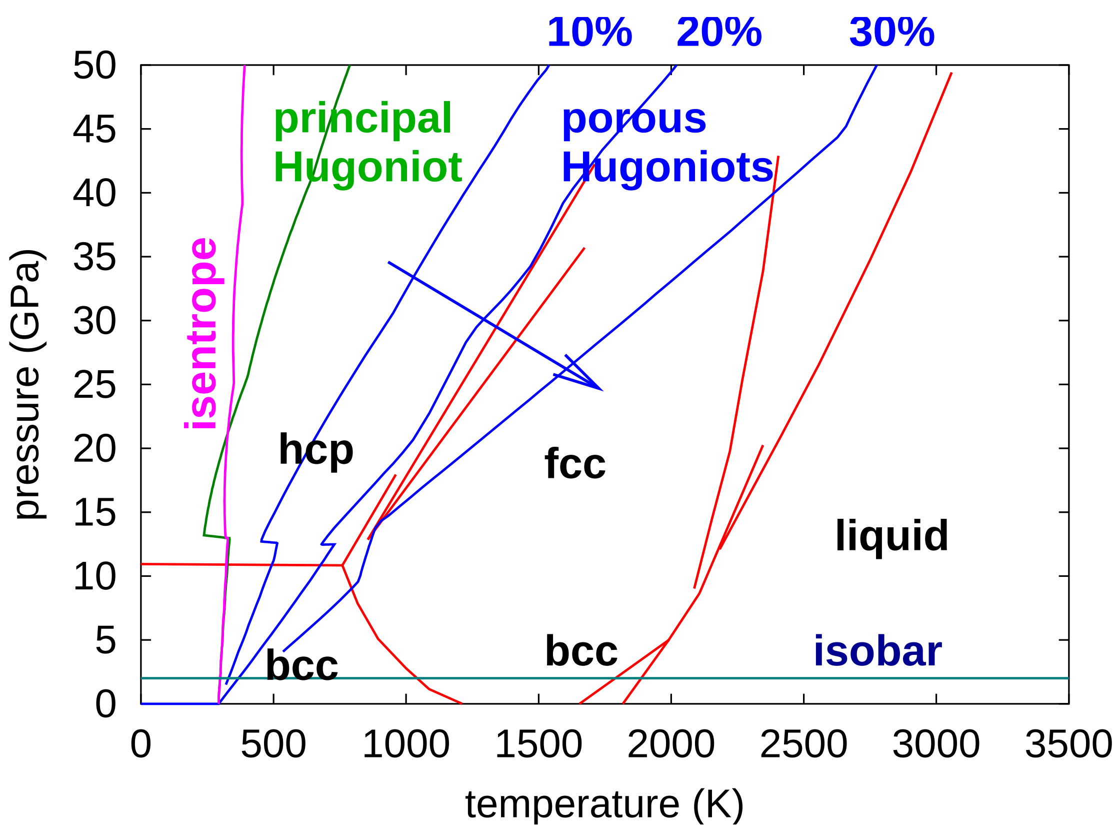
# High temperature EOS

Below $\sim$1 eV: ion-thermal from phonons (Bose-Einstein) and electron-thermal from band structure around Fermi surface (Fermi-Dirac).



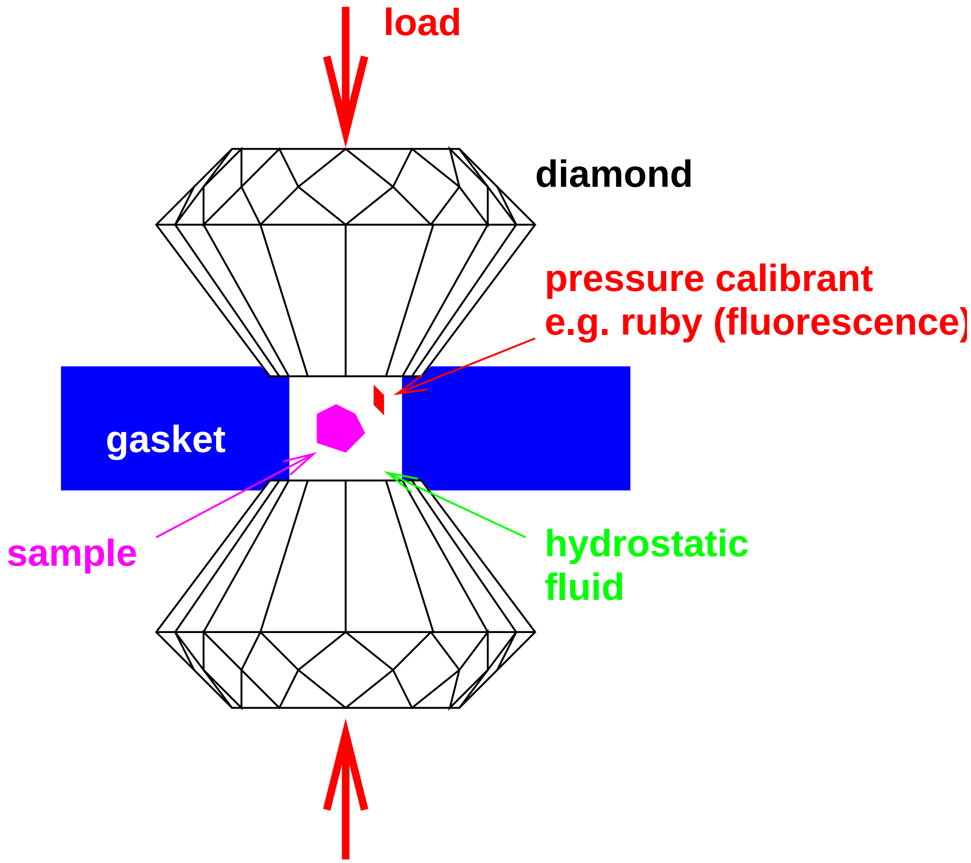
Different ion positions (may be small effect: dominated by $\rho$); excited electrons / ionization; band structure consistent with $T$. Treats plasma seamlessly. Spherical atom model.

# Measuring the EOS




**Isobaric expansion:** exploding wire in pressure vessel.
**Isotherm:** static presses (special case).
**Hugoniot:** locus of states accessible by a single shock wave (can vary its strength).

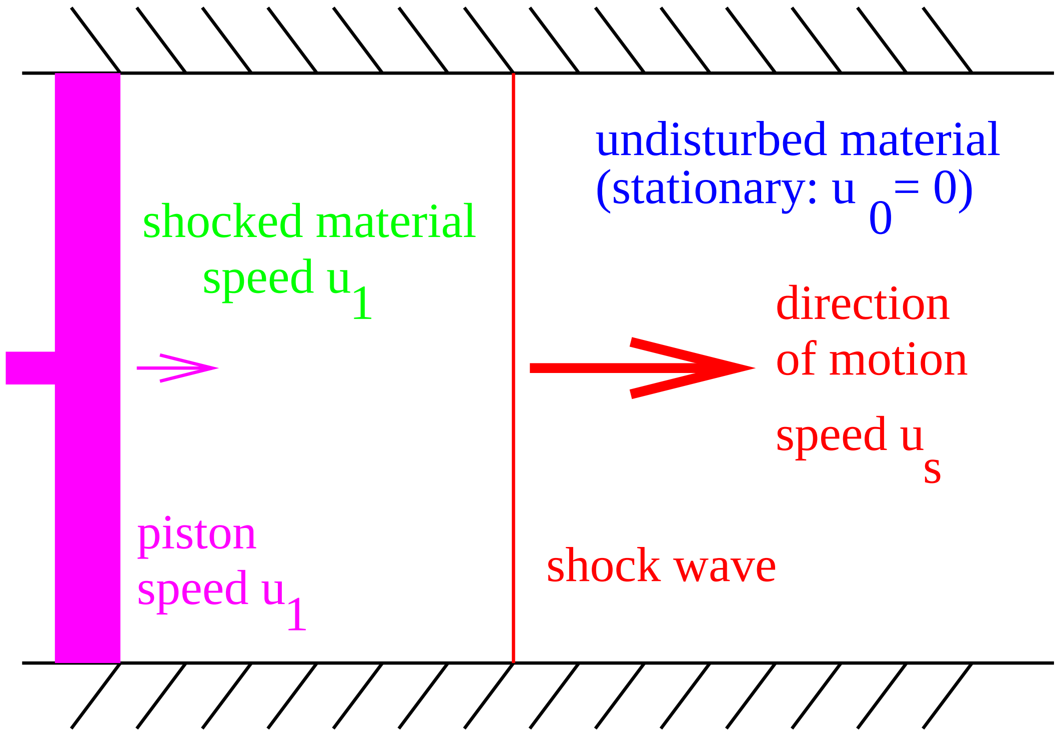
# Static high pressure




Apply load at known temperature; measure pressure, mass density, structure, etc. Diagnostics: x-ray diffraction, optical properties.

$p$ to $\sim$400 GPa, steady $T$ to 2500 K, higher by laser heating.

# Steady shock waves




Rankine-Hugoniot relations (conservation laws):

$$u_s^2 = v_0^2 \frac{p - p_0}{v_0 - v}, \quad u_p = \sqrt{[(p - p_0)(v_0 - v)]}, \quad e = e_0 + \frac{1}{2}(p + p_0)(v_0 - v)$$

– 3 equations, 5 unknowns ⇒ measure 2 quantities to determine state on shock Hugoniot.

# Shock wave experiments

– ways to launch and measure a steady shock:

- Impact experiments (gas gun, powder gun, electromagnetic flyer, explosively-driven flyer, laser flyer)

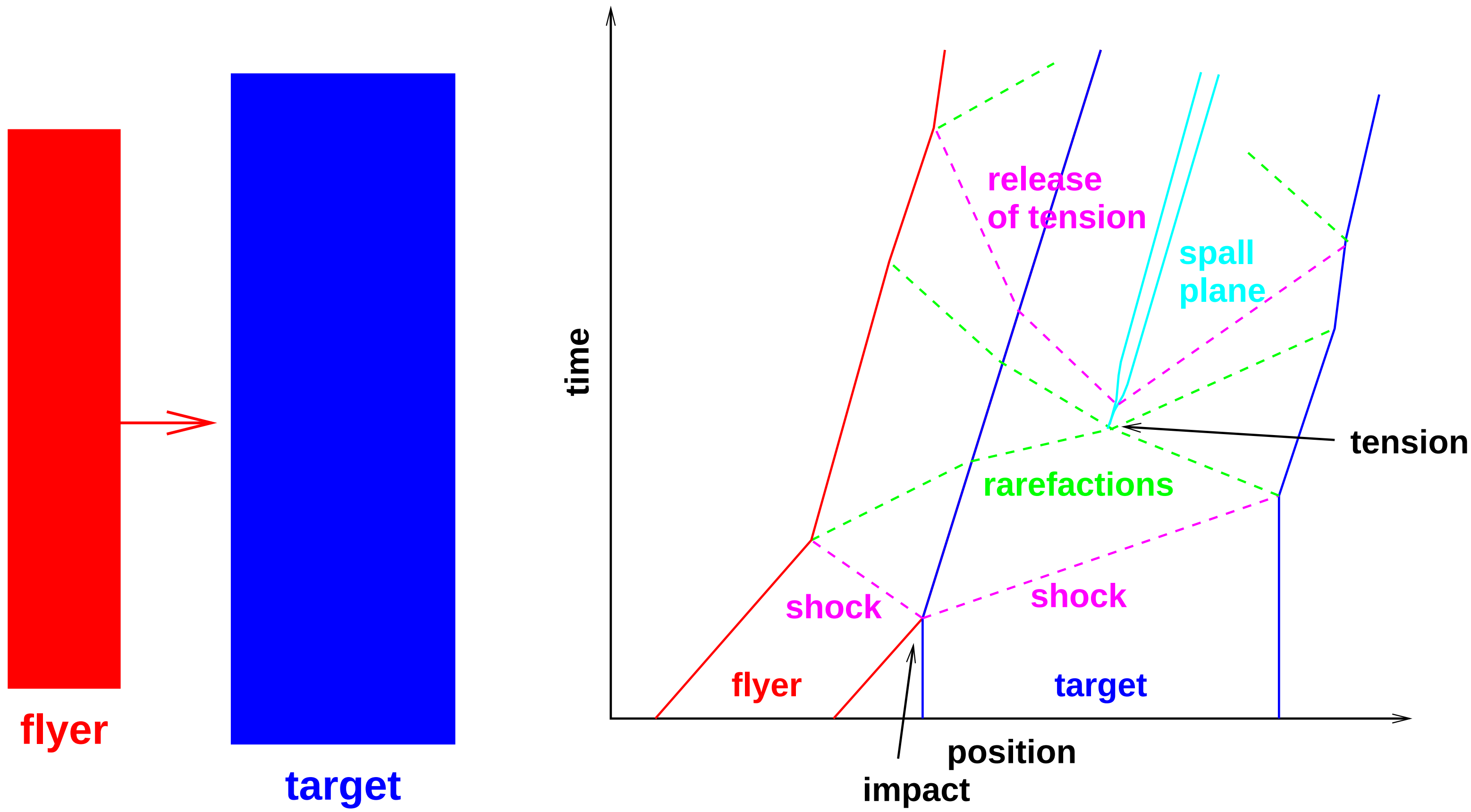
- Detonation-driven shock

- Radiation-driven shock (nuclear explosion, laser hohlraum)

- Laser ablation

Aspect ratio: thin samples to preserve 1D region in center.

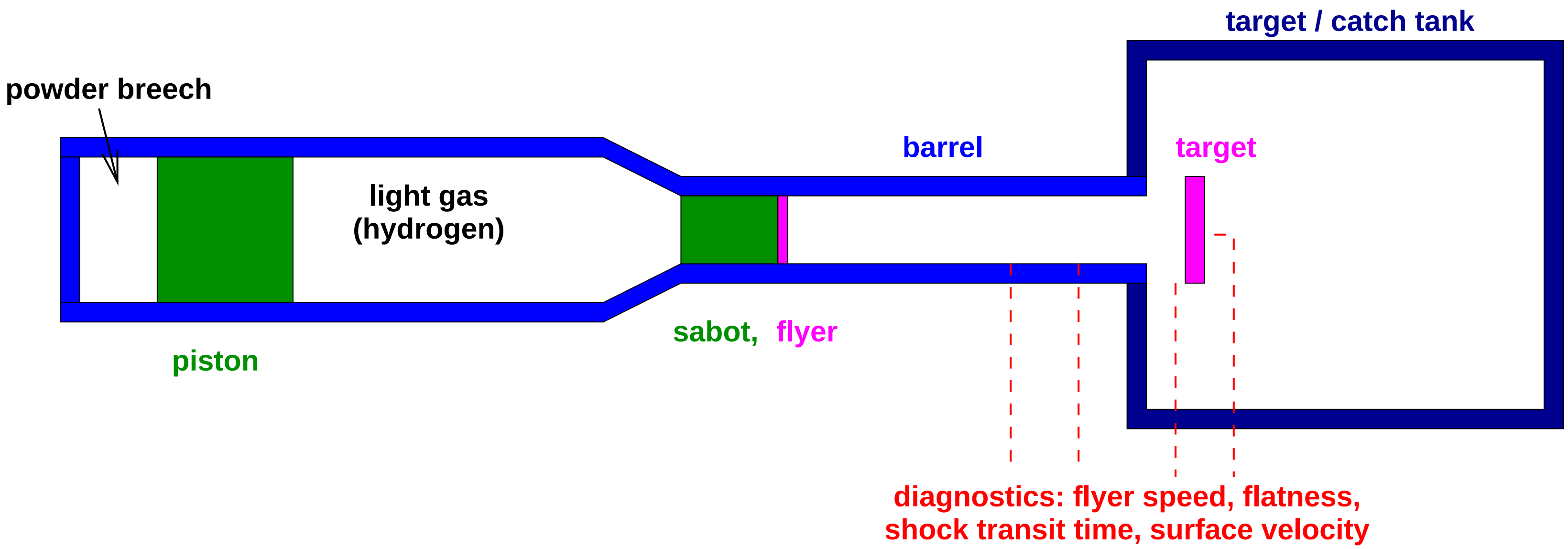
# Impact experiments




"Classical": same material for both; measure $u_{\text{flyer}} = 2u_p$ and $u_s$ from transit time.

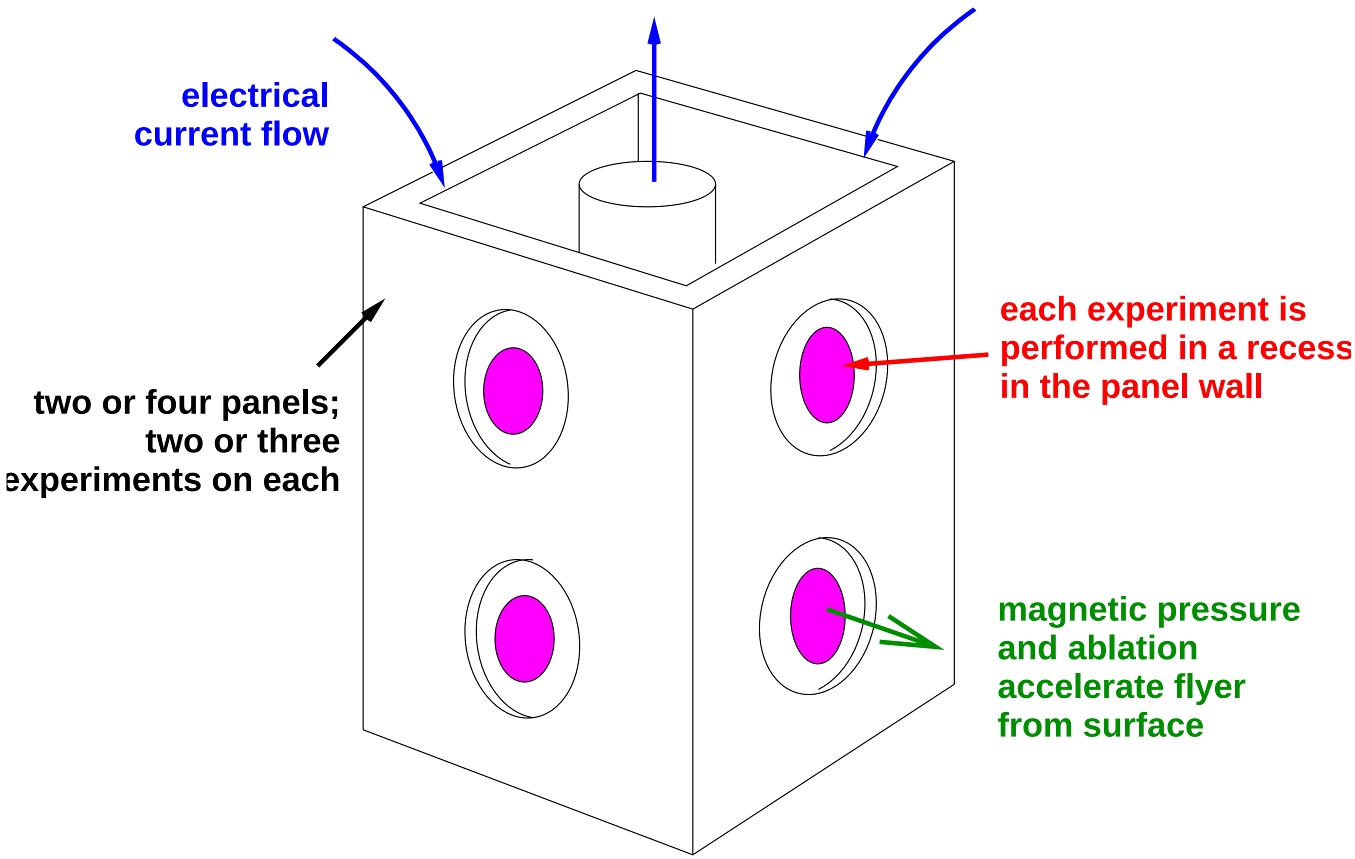
# Gas guns

e.g. two-stage light gas gun:

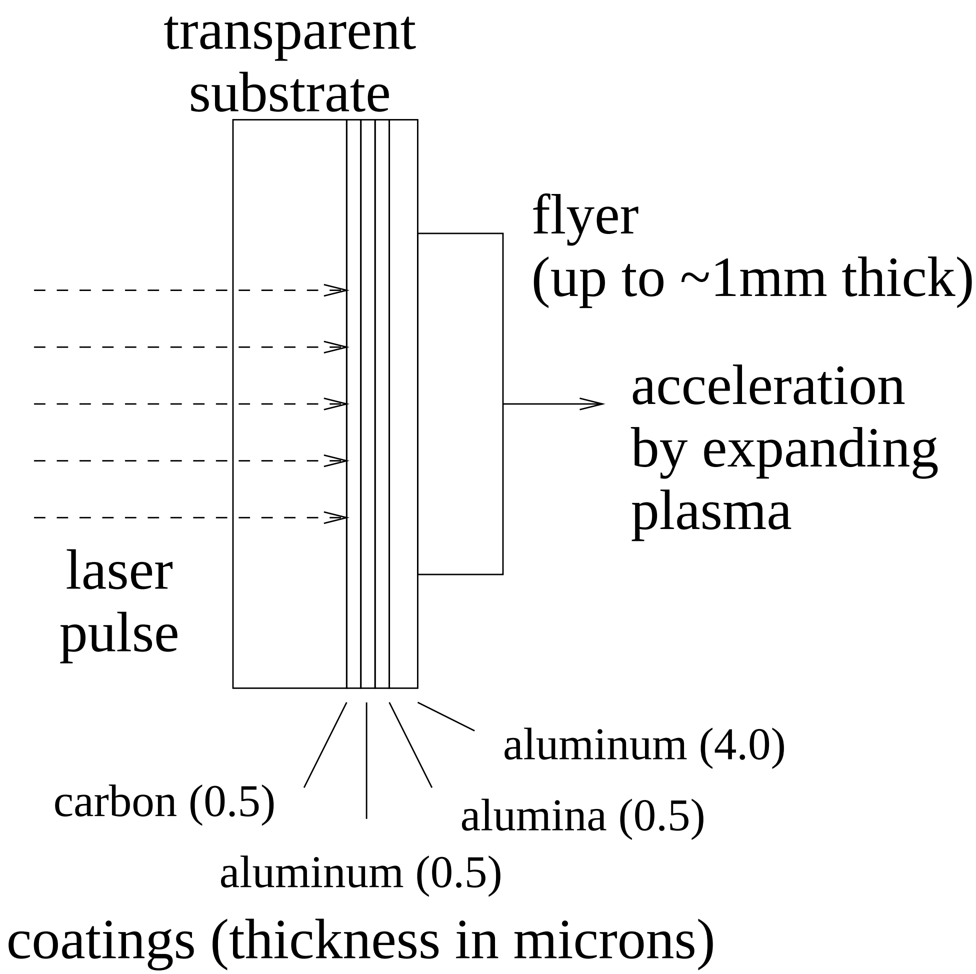


# Electromagnetic launcher

e.g. Z pulsed power machine:

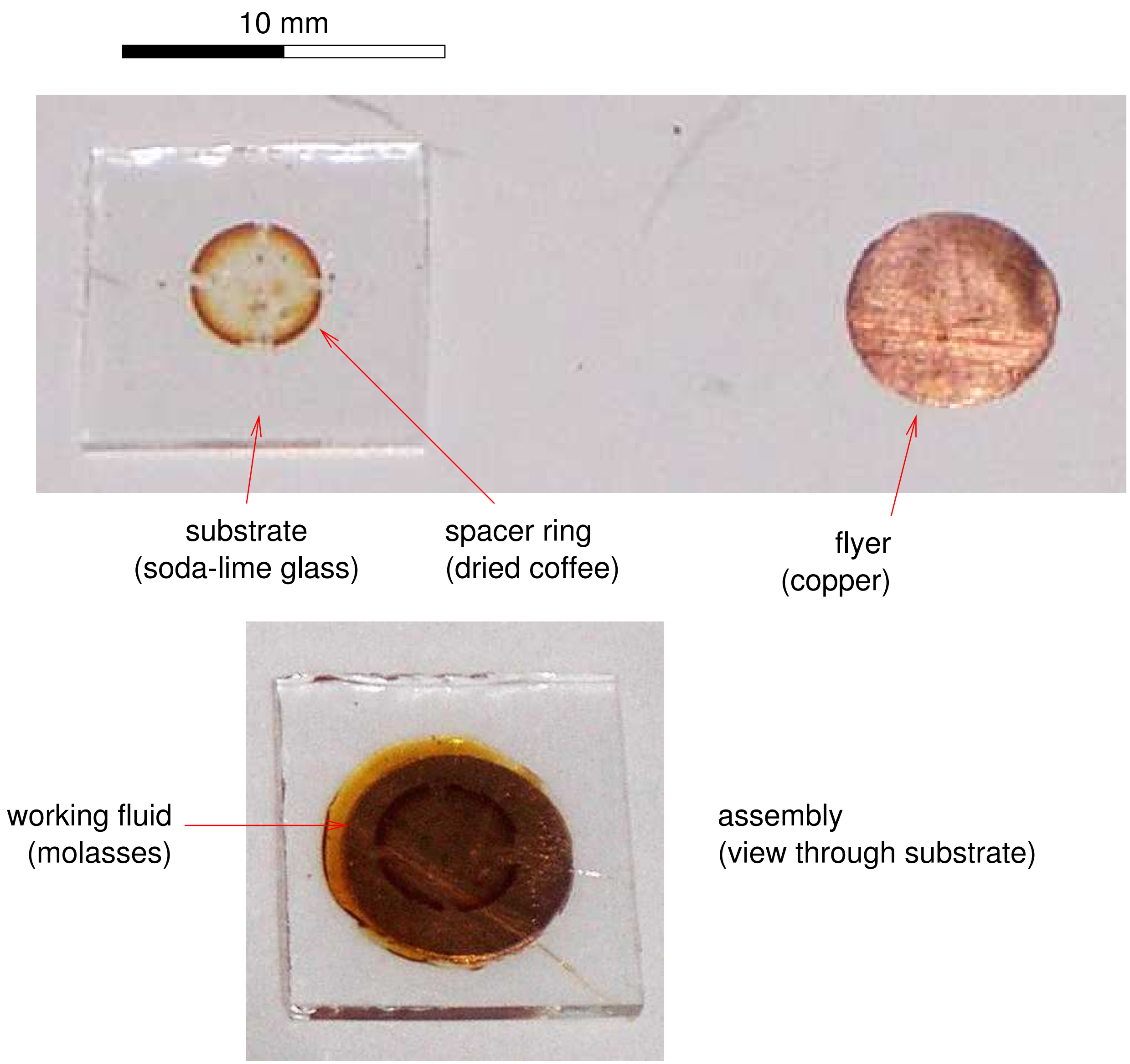


# Laser flyer



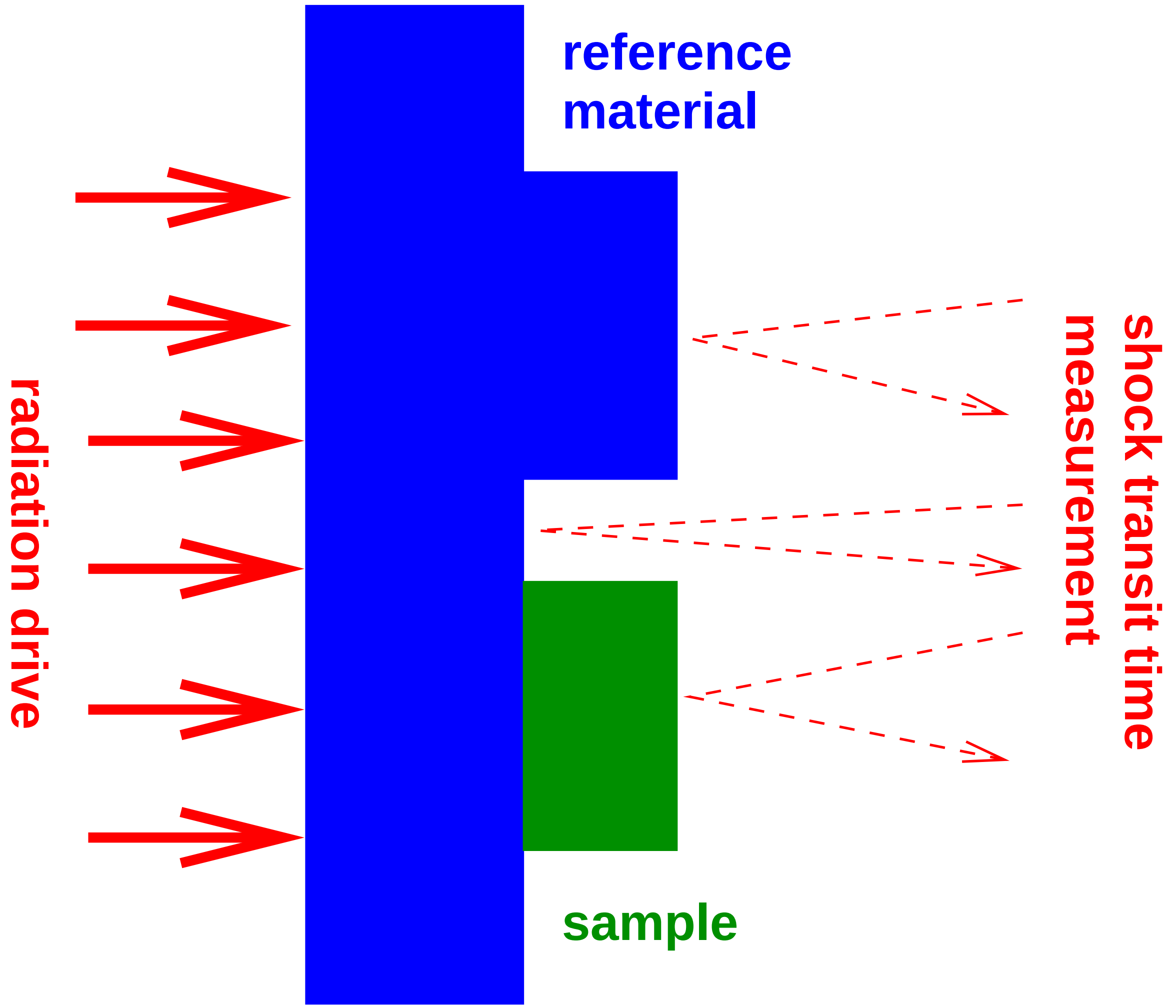

Design: D.L. Paisley, P-24

# Laser flyer


10 mm
substrate
(soda-lime glass)
spacer ring
(dried coffee)
flyer
(copper)
working fluid
(molasses)
assembly
(view through substrate)

# Radiative ablation

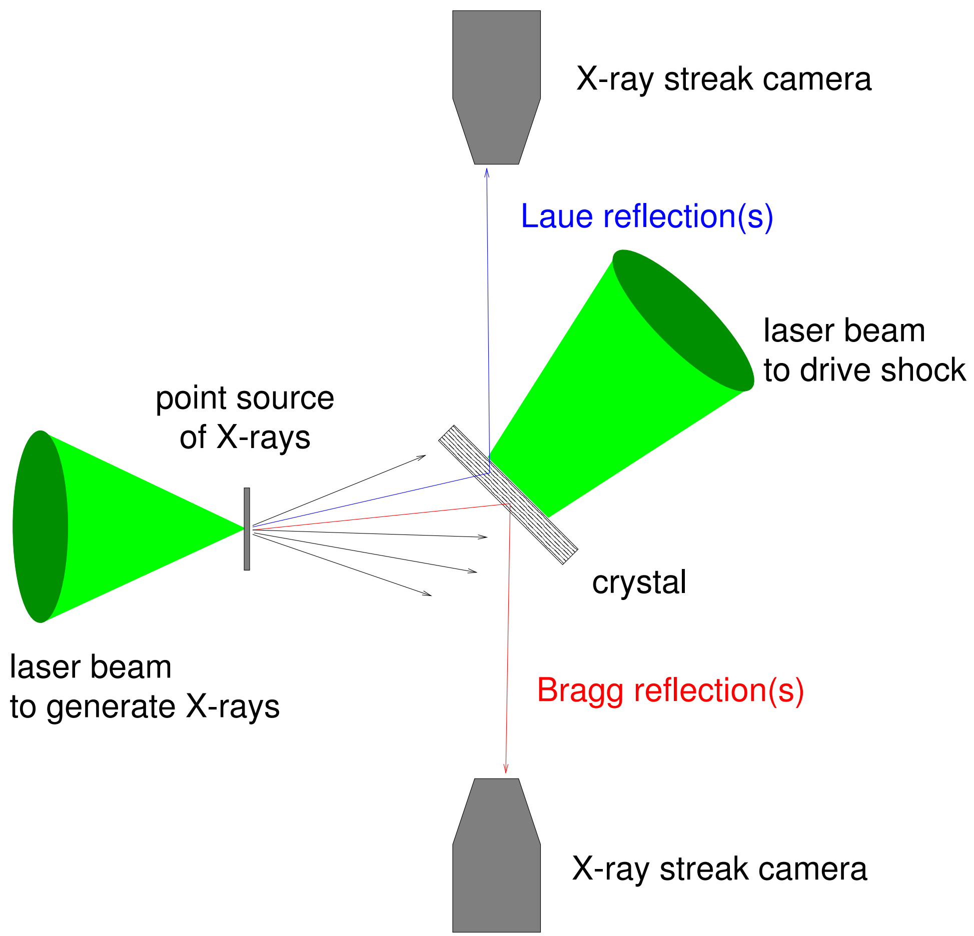
Material ablation drives shock wave by reaction and plasma pressure.




Radiation source: nuclear explosion, laser hohlraum, laser ablation.

# Other shock diagnostics

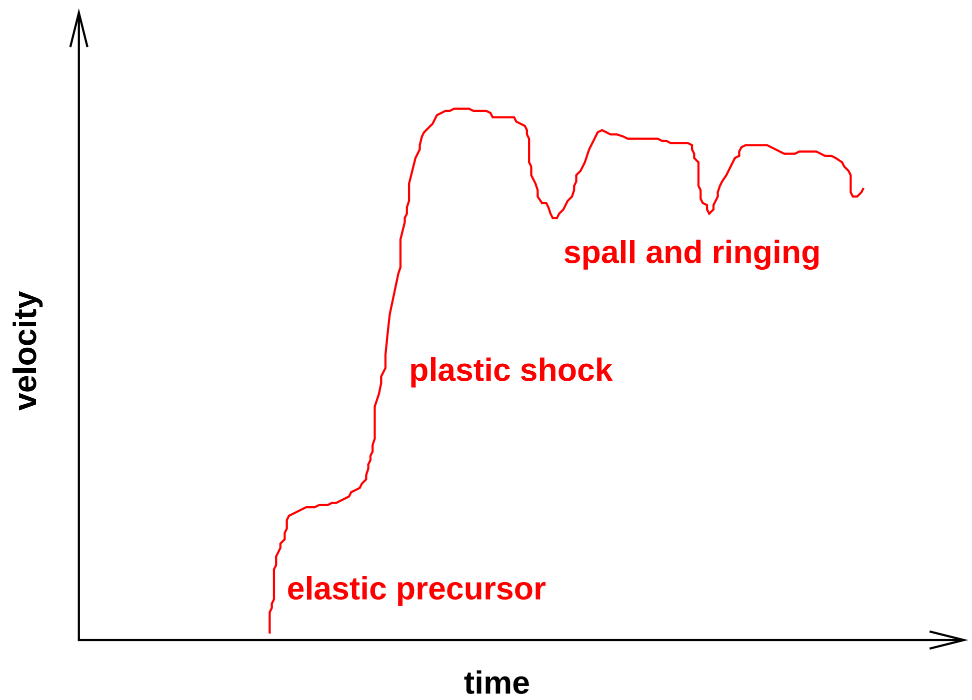
surface velocimetry, radiography, transient x-ray diffraction



# Surface velocimetry

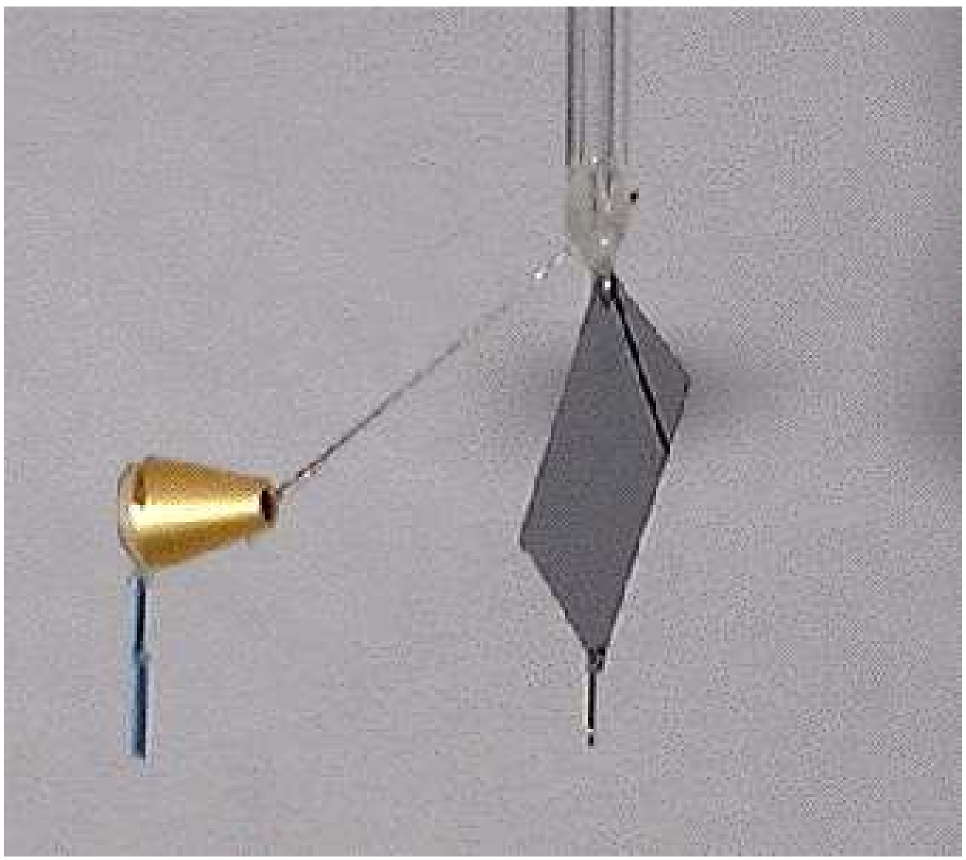
Doppler shift of reflected laser light.

Example velocity history as shock reaches surface:

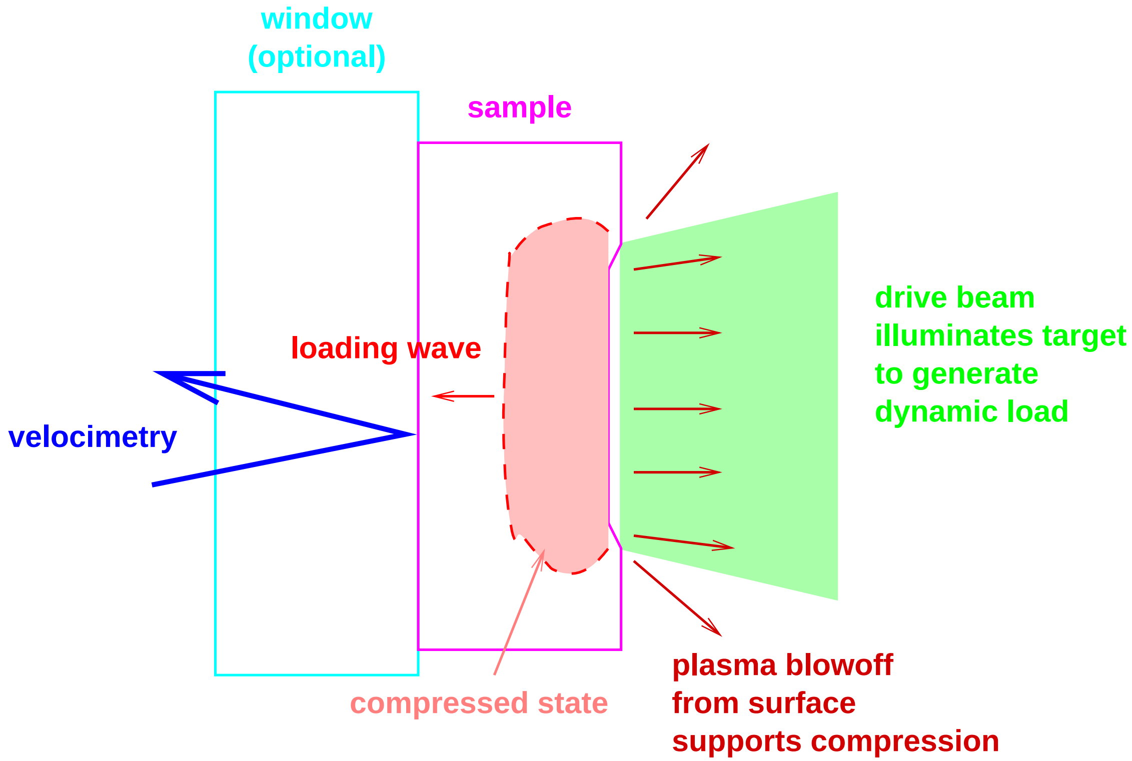


# Transient x-ray diffraction

Si crystal, (100) orientation, 40 $\mu$m thick by 10 mm across:

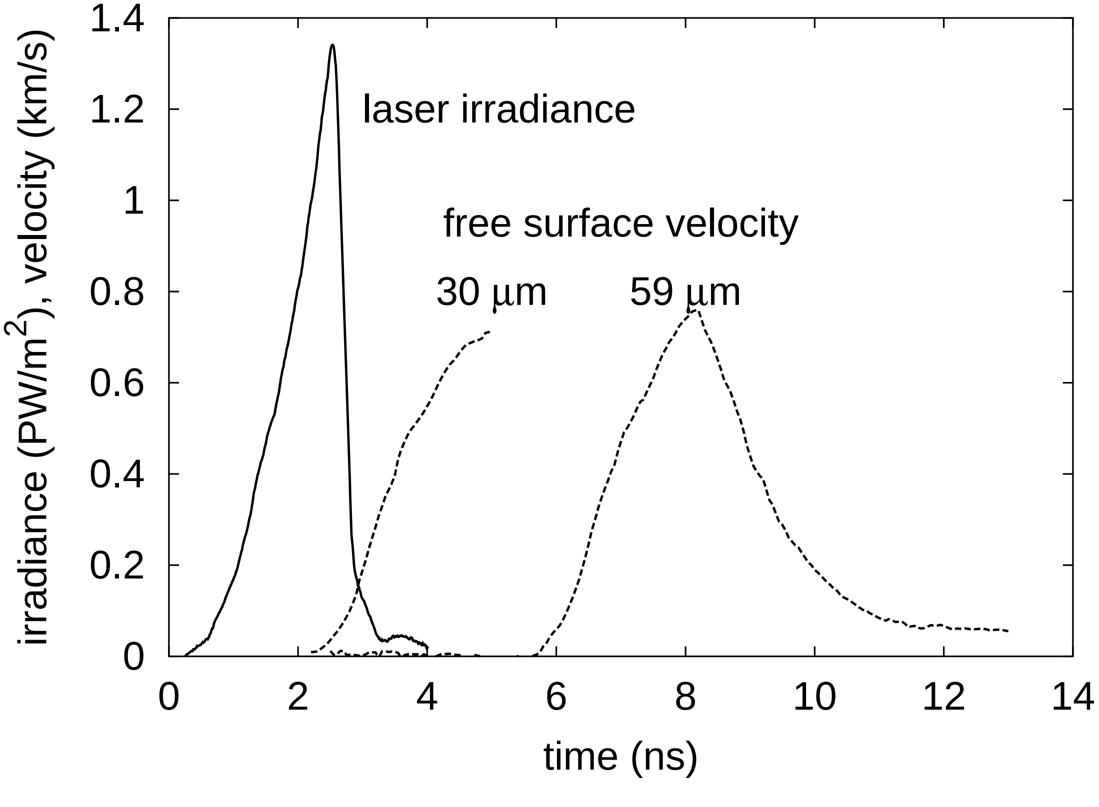


# Quasi-isentropic compression



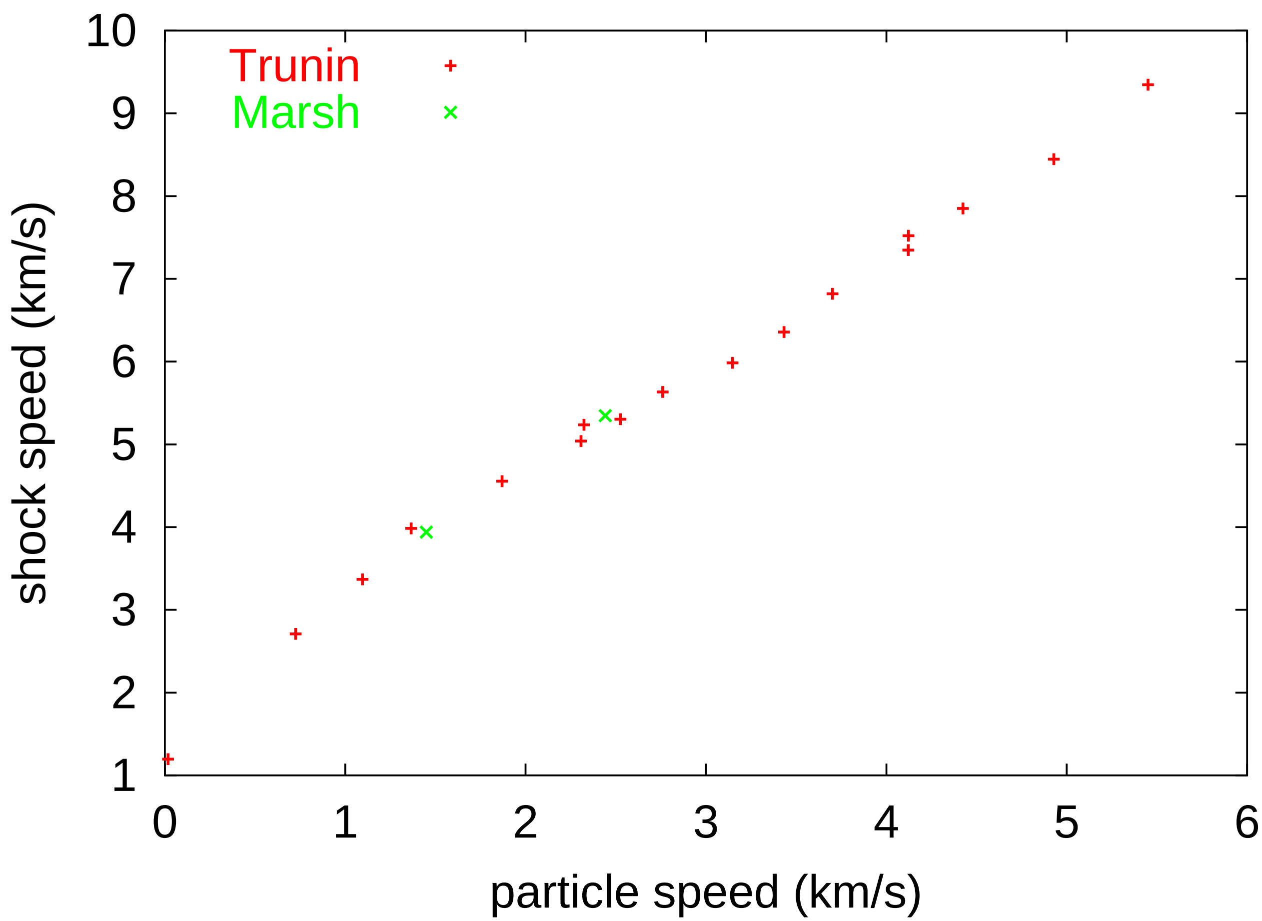
# Quasi-isentropic compression

Si, TRIDENT shot 15018:



# Shock Hugoniot data

Acetone:



# Empirical mechanical EOS

Functional fit to $u_s - u_p$ data, e.g. Steinberg polynomial:

$$u_s = c_0 + \sum_{i=1}^{n} s_i \left(\frac{u_p}{u_s}\right)^{i-1} u_p,$$

R-H relations for states on the Hugoniot. Additional assumption to calculate states off-Hugoniot: Grüneisen approximation,

$$p(\rho, e) = p_{\mathrm{ref}}(\rho) + \Gamma(\rho)\left[e - e_{\mathrm{ref}}(\rho)\right].$$

Thus

$$p(\rho, e) = \frac{F(\rho, e)}{H^2(\rho, e)} + \left[\Gamma_0 + b\mu(\rho)\right]\rho_0 e$$

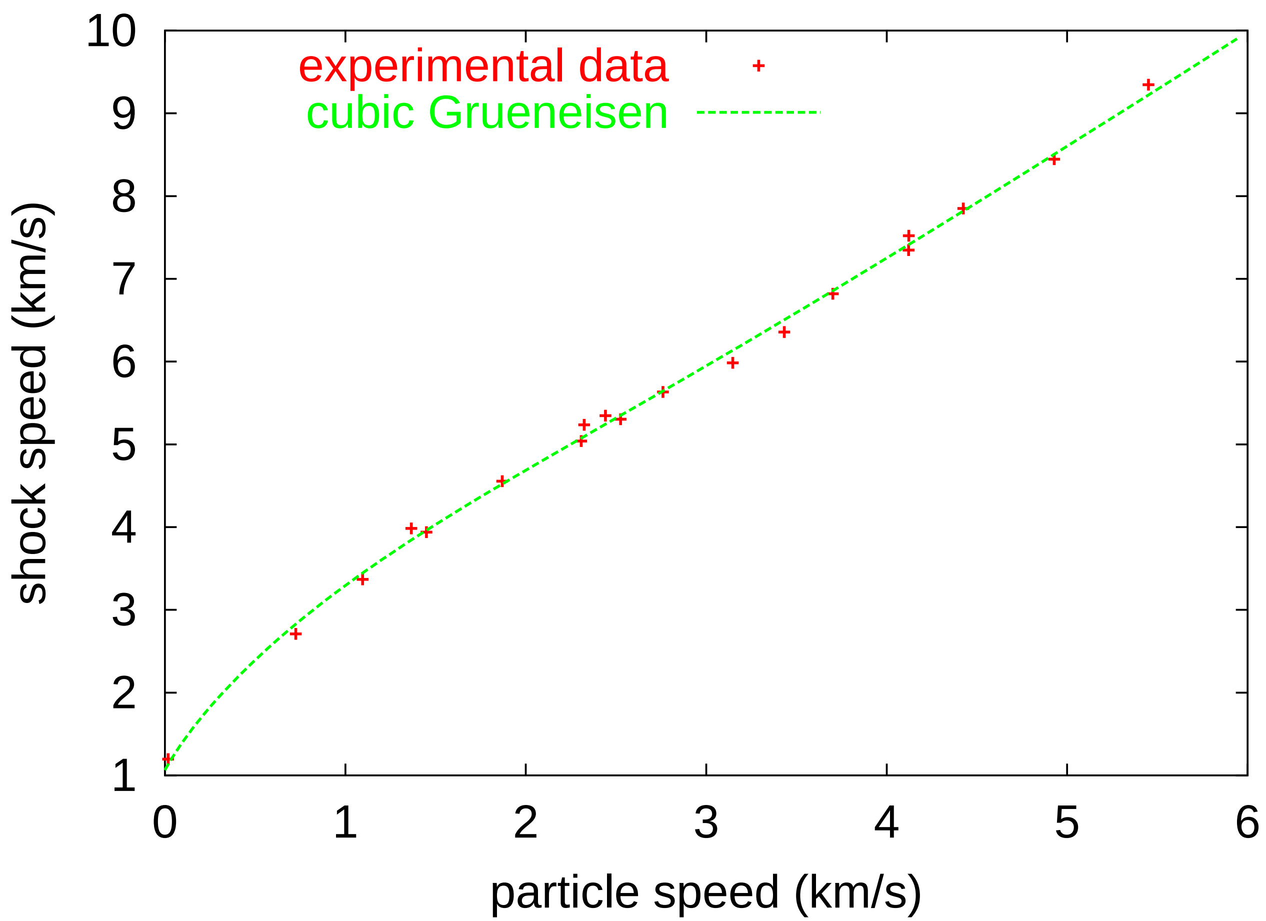
where $\mu(\rho) = \rho/\rho_0 - 1$,

$$\begin{aligned} F(\rho, e) &= \rho_0 c_0^2 \mu \left\{1 + \mu\left[(1 - \Gamma_0/2) - \mu b/2\right]\right\} \\ H(\rho, e) &= 1 + \mu - \mu\left[\sum_{i=1}^{n} s_i \left(\frac{\mu}{\mu + 1}\right)^{i-1}\right] \end{aligned}$$

(thermodynamically incomplete).

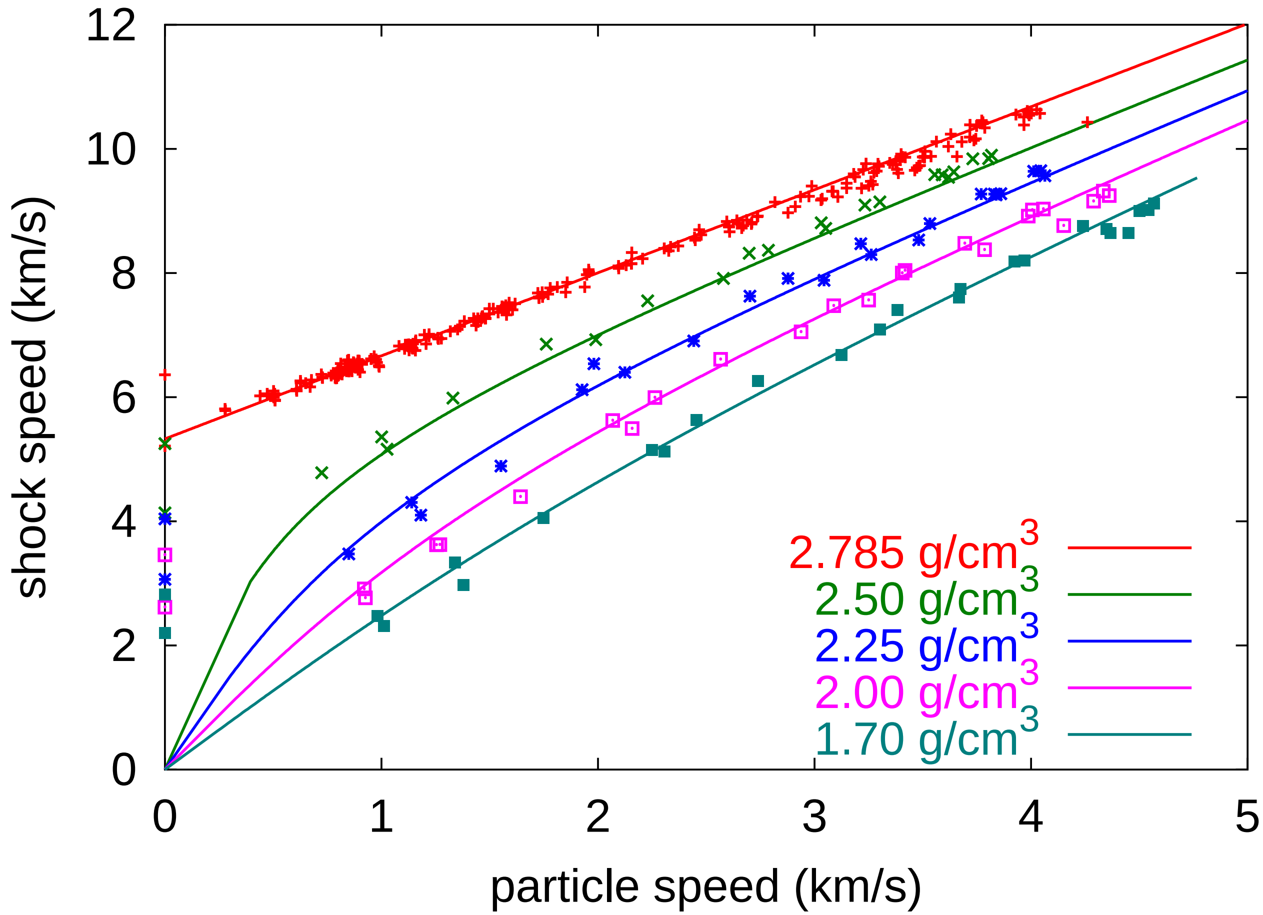
# Shock Hugoniot fit

Acetone:



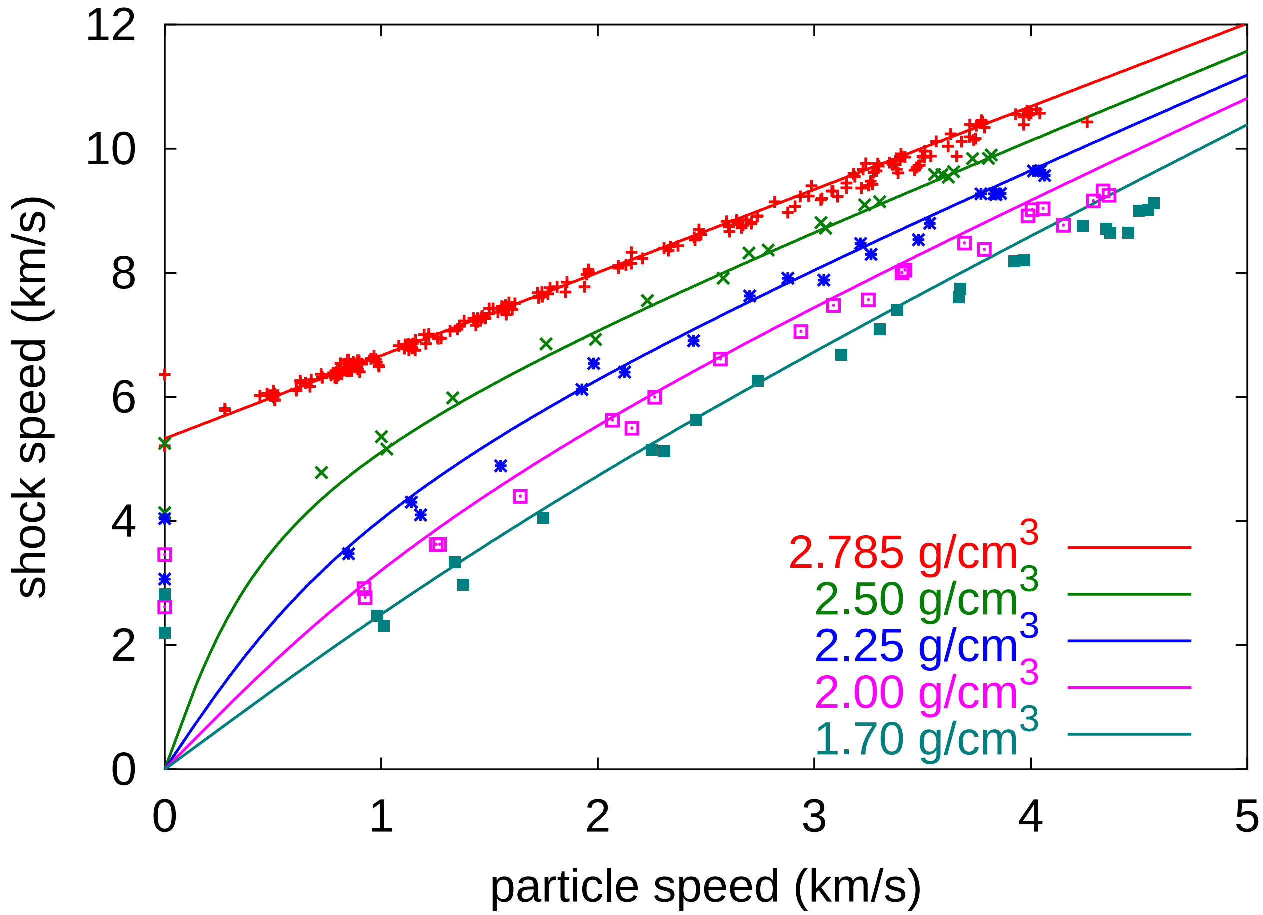
# Accuracy of empirical EOS

Shock Hugoniot for solid and porous Al; empirical EOS fitted to $u_s - u_p$; $\Gamma(\rho)$ estimated from slope of $u_s - u_p$:



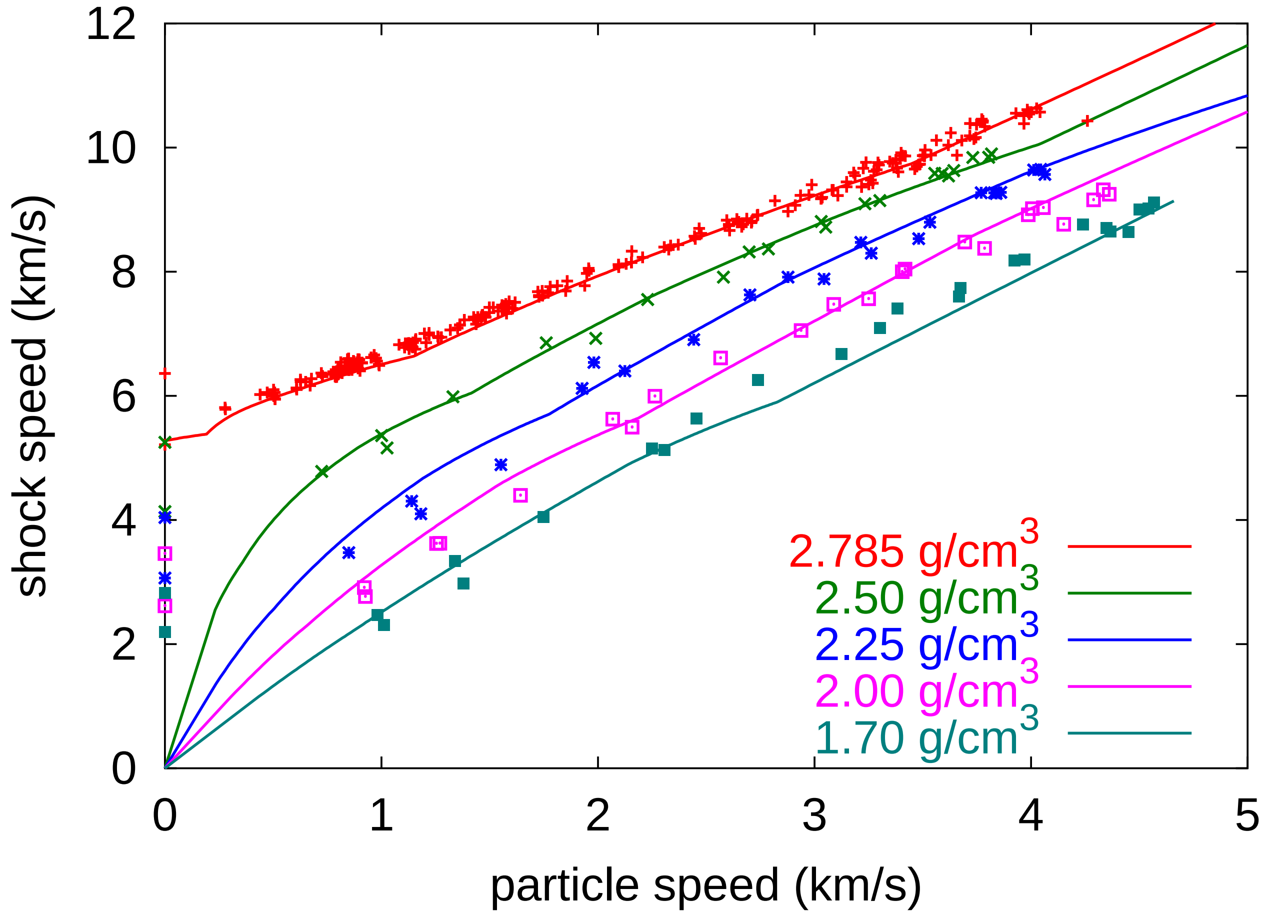
# Accuracy of empirical EOS

Shock Hugoniot for solid and porous Al; empirical EOS fitted to $u_s - u_p$; $\Gamma(\rho)$ adjusted to reproduce porous Hugoniot points:



# Accuracy of theoretical EOS

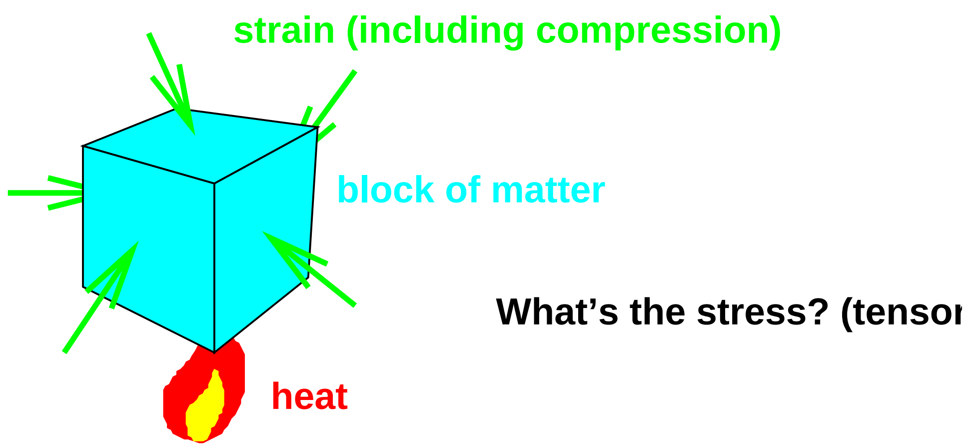
Shock Hugoniot for solid and porous Al; theoretical EOS uses *ab initio* quantum mechanics:



# Limitations and current research

- Thermodynamic equilibrium
  - electronic states: 'non-LTE effects' (below ns)
  - atomic configuration: phase change dynamics (ps to Myr)
- Stress tensor: decomposition into EOS and stress deviator not always valid.
- Measurement of temperatures in shock experiments is difficult – how to test theoretical EOS?
- Accuracy of quantum mechanical EOS predictions, especially for $f$-electron materials (lanthanides and actinides).

# Stress in continuum mechanics




Strain tensor $e(\vec{r})$, stress tensor $\tau(\rho, T, e)$ – generalized EOS.

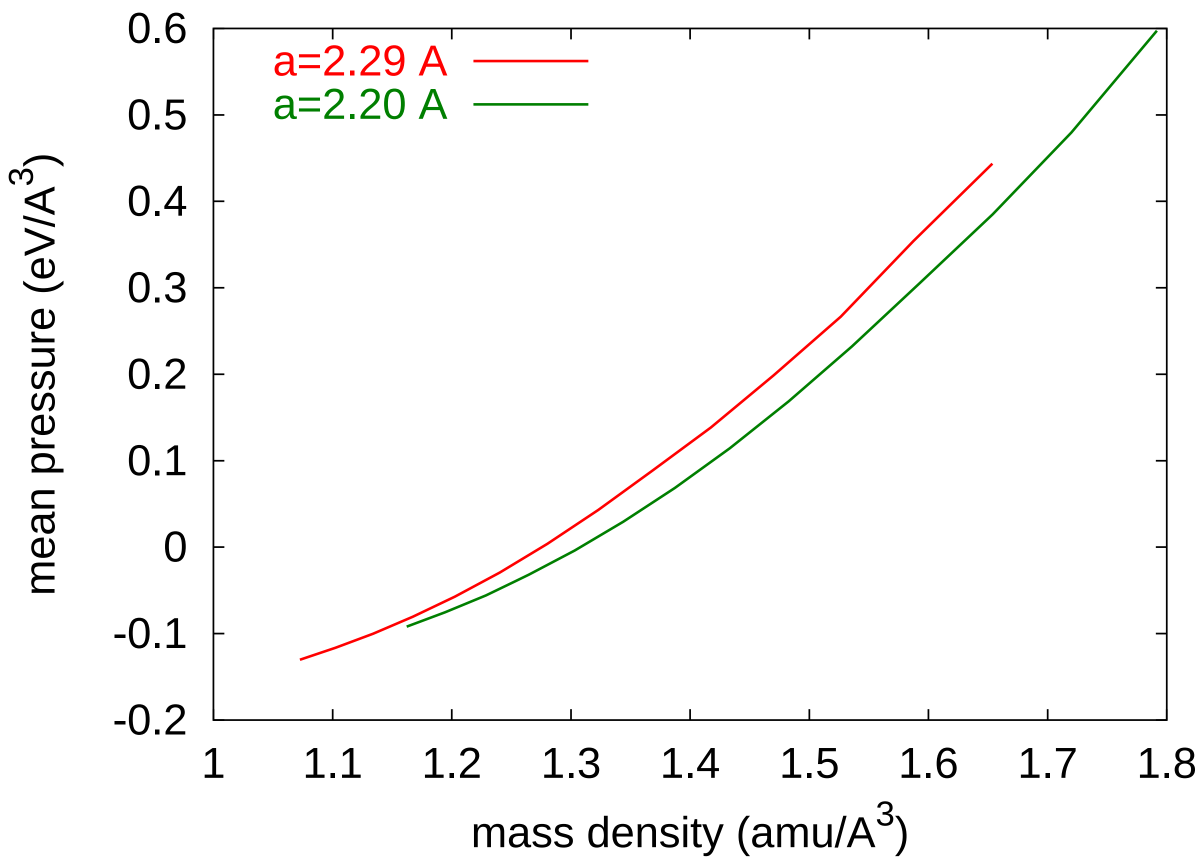
Deviatoric decomposition:

$$e = \mu I + \epsilon, \quad \tau = -pI + \sigma; \quad \mu \equiv \frac{1}{3}\mathrm{Tr}\, e, \quad p \equiv -\frac{1}{3}\mathrm{Tr}\, \tau$$

Assumption that scalar properties are independent: $p(\mu, T)$, $\sigma(\mu, T, \epsilon)$.

# Uniqueness of the EOS

QM prediction of stress tensor in Be for different elastic strains:




D.C. Swift and G.J. Ackland, Appl. Phys. Lett. **86**, 6 (2003).

– at the end of the day, the EOS may not really exist!