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Hydrogen transport in metals

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Outline:
review of basic principles of hydrogen transport

- Thermodynamics of high-pressure hydrogen
  - Equation of state for hydrogen
  - Fugacity in gas mixtures containing hydrogen

- Equilibrium hydrogen content in metals (thermodynamics)
  - Sievert’s Law
  - Stress
  - Hydrogen trapping

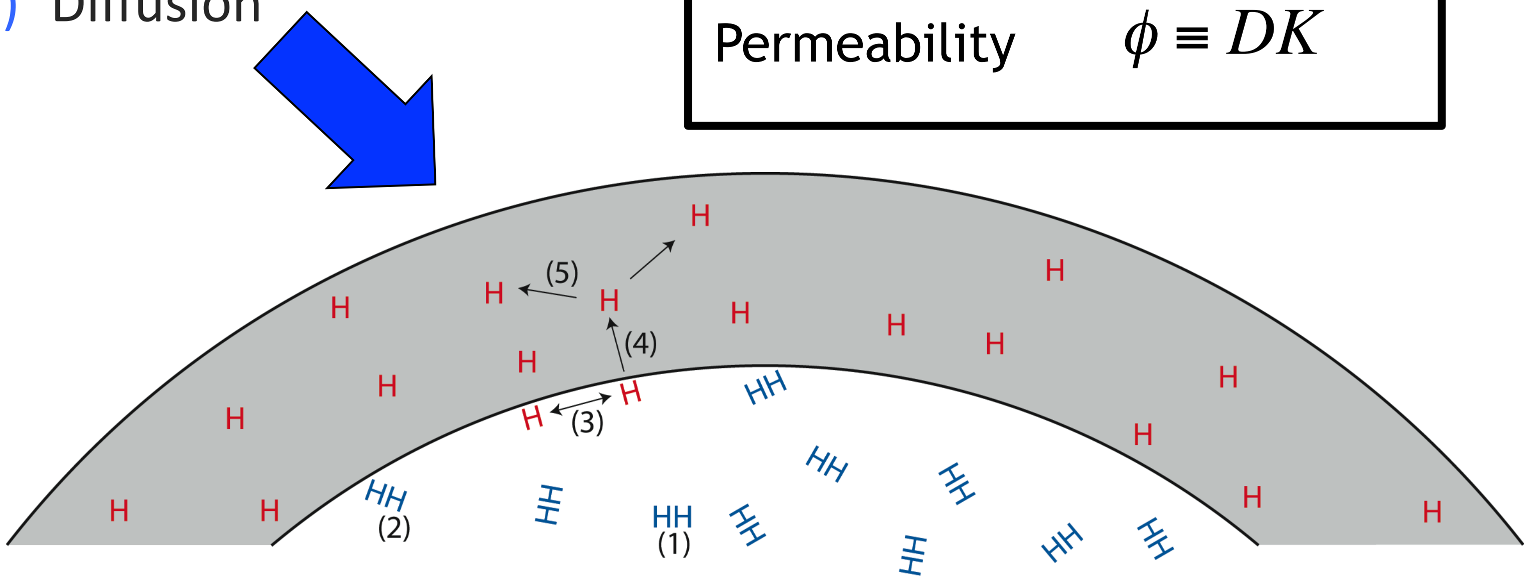
- Hydrogen transport in metals, diffusivity (kinetics)
  - Stress
  - Hydrogen trapping

- Hydrogen transport as a tool to understanding hydrogen-assisted fracture and fatigue

Hydrogen in metals

(1) Hydrogen gas
(2) Physisorption
(3) Dissociation
(4) Dissolution
(5) Diffusion

Solubility	$K = \dfrac{c_o}{\sqrt{f}}$
Diffusivity	$J = -D\dfrac{dc}{dx}$
Permeability	$\phi \equiv DK$

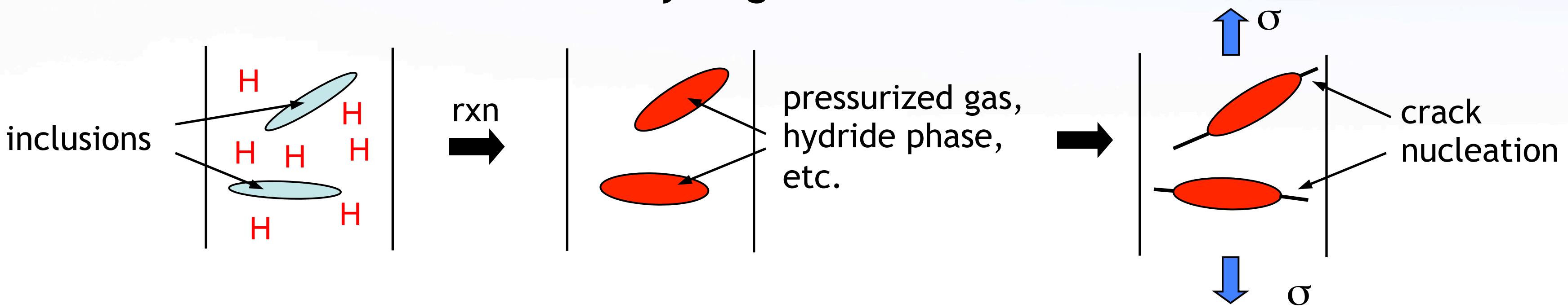


Chemical Equilibrium: $\tfrac{1}{2}H_2 \leftrightarrow \underline{H}$

Hydrogen-assisted fracture mechanisms in metals

Hydrogen attack:

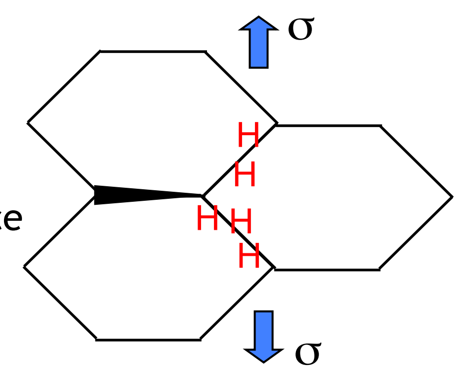
chemical reaction of atomic hydrogen with microstructural features

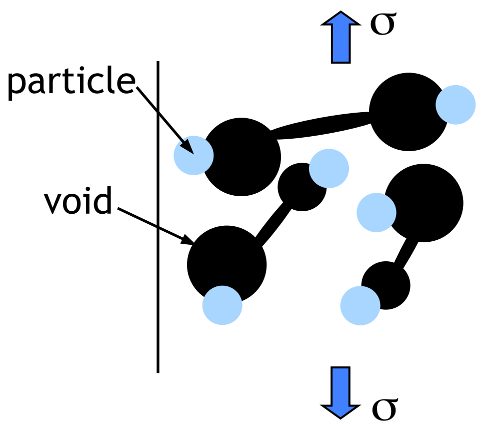


Hydrogen solute effects:

solute hydrogen enhanced failure of interfaces and deformation mechanisms

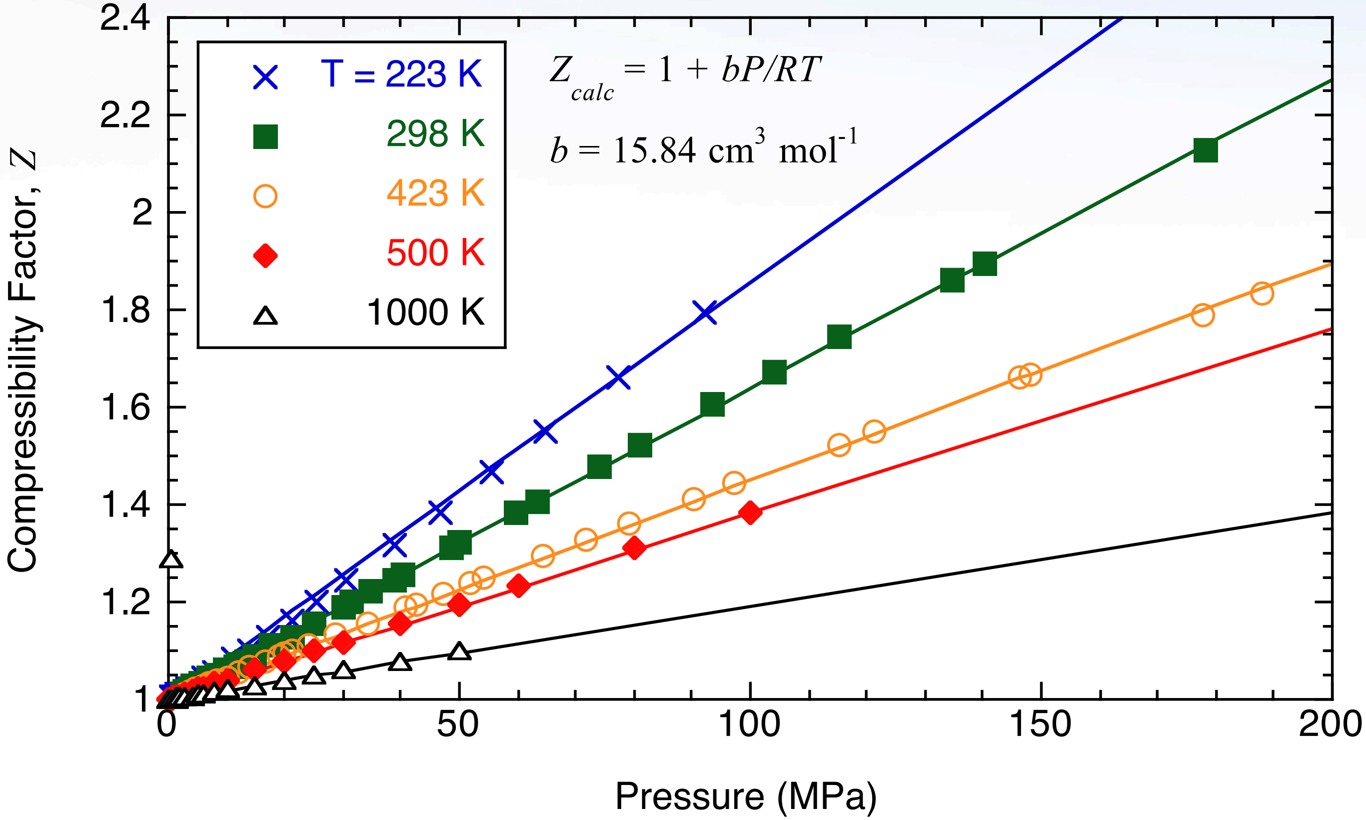
Hydrogen accumulation at interfaces affects strength of interface (grain boundaries, second phases, inclusions)





Hydrogen enhanced shear localization

Non-ideal behavior of high-pressure hydrogen described by Abel-Noble EOS: $V_m = RT/P + b$



Fitting data of Michels et al (1955) for
$223 < T < 473$ K
$P < 200$ MPa

$b = 15.84\ cm^3\ mol^{-1}$

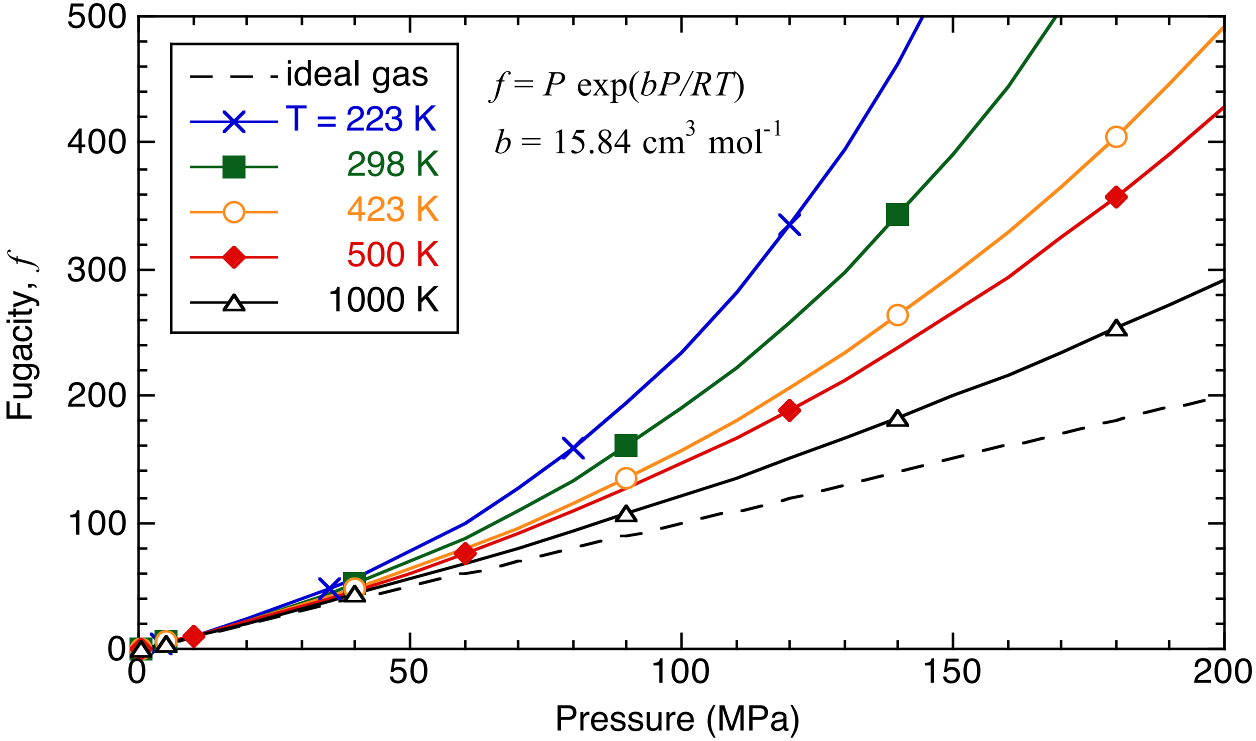
- Compressibility factor $Z = PV_m/RT$
  - for ideal gas $Z = 1$ Ideal gas EOS
  - at high pressure $Z > 1$ Abel-Noble EOS

$$V_m^o = RT/P$$

$$V_m = V_m^o + b$$

Fugacity of gaseous hydrogen
Thermodynamic quantity describing real gas behavior

- Chemical potential of gas: $$\mu = \mu_o + RT \ln\left(\frac{f}{f_o}\right)$$
- Definition of fugacity: $$\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{V_m}{RT} - \frac{1}{P}\right) dP$$

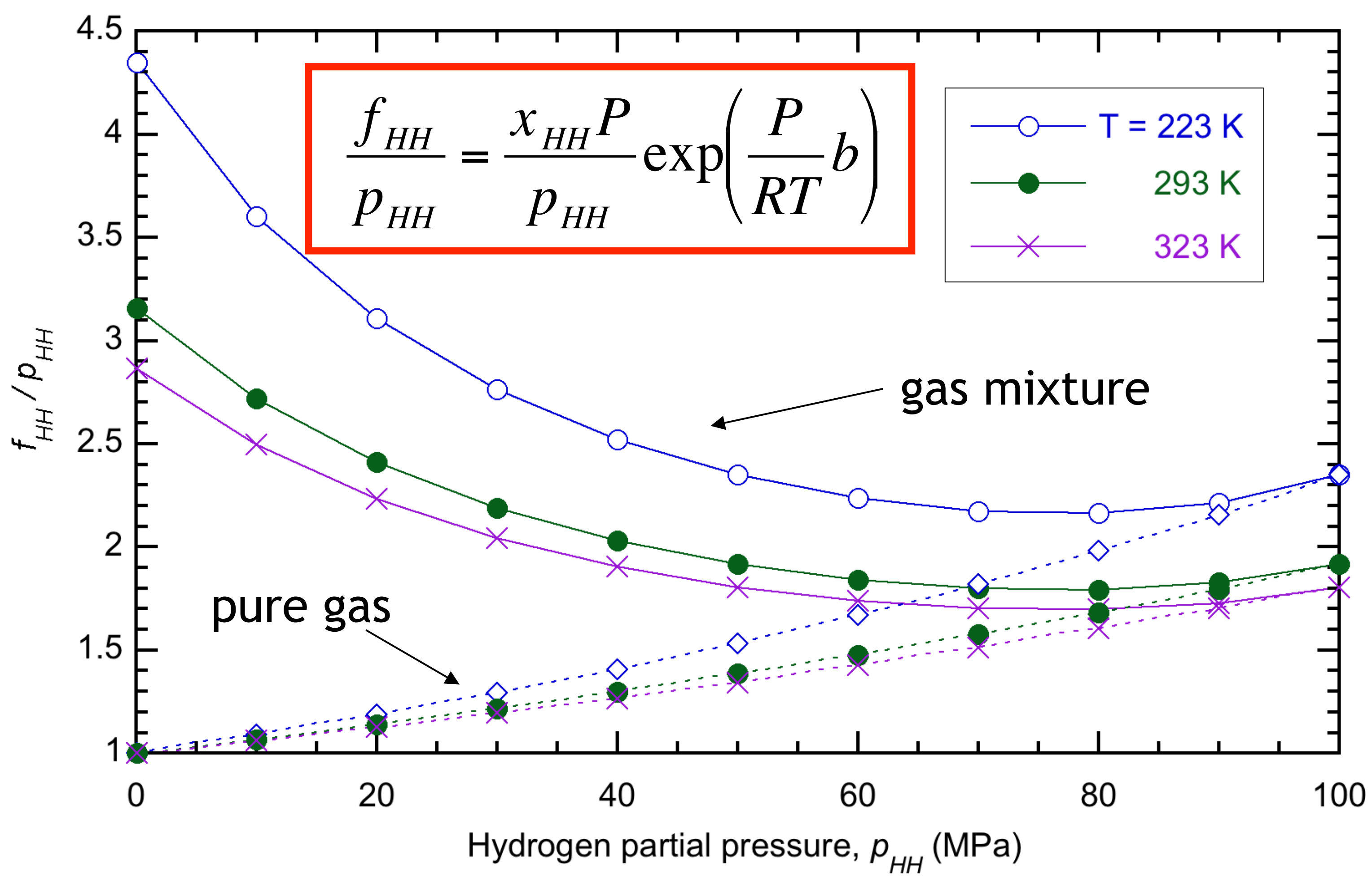


For Abel-Noble equation of state

$$\frac{f}{P} = \exp\left(\frac{P}{RT} b\right)$$

Fugacity of hydrogen in ideal mixtures of gas

Helium-Hydrogen gas mixtures: $P = 100\text{MPa} = p_{HH} + p_{He}$

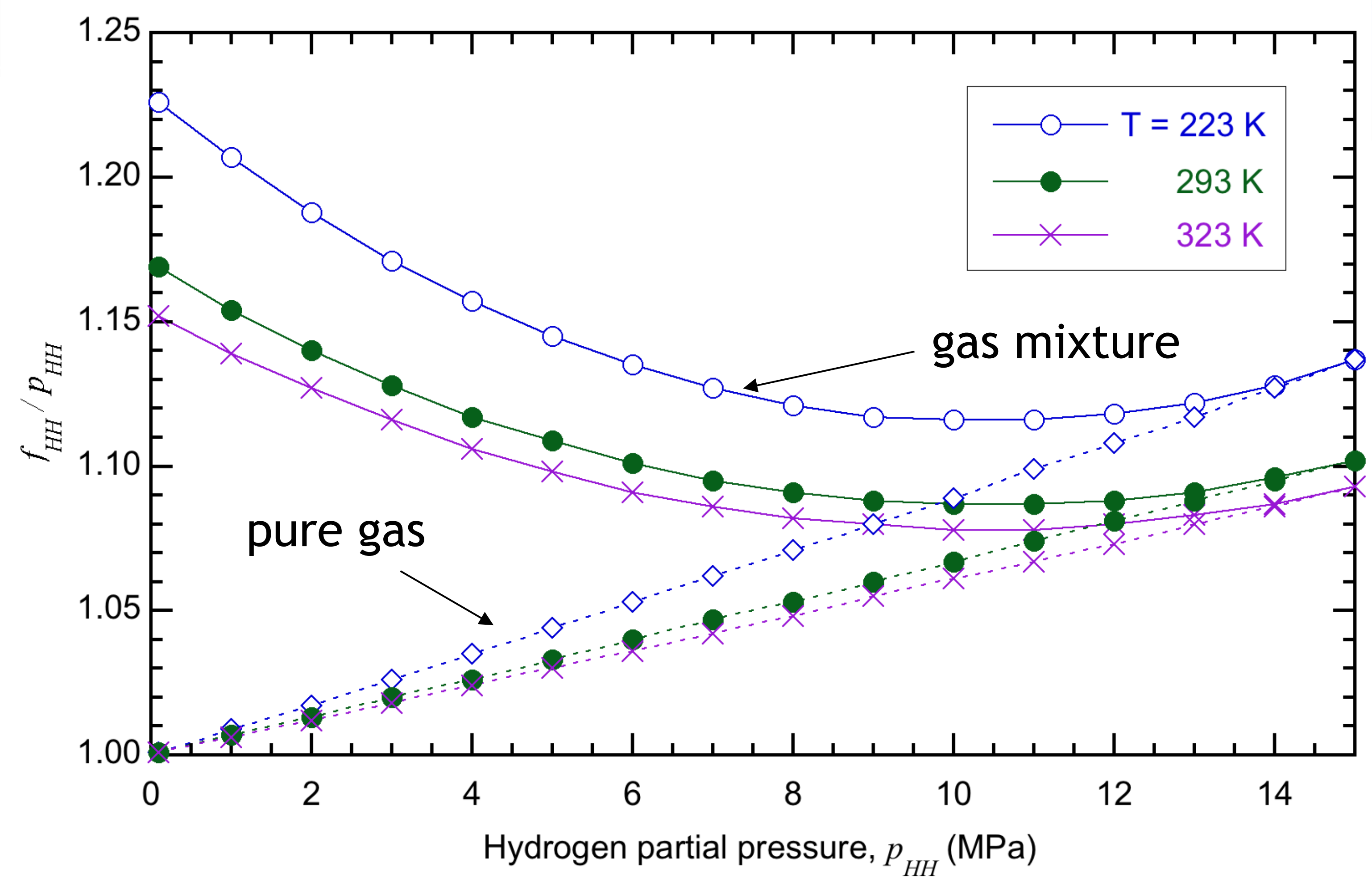


Lewis-Randall rule for ideal mixtures

$$f_i = x_i f$$

Fugacity of hydrogen in ideal mixtures of gas

Helium-Hydrogen gas mixtures: $P = 15\text{MPa} = p_{HH} + p_{He}$



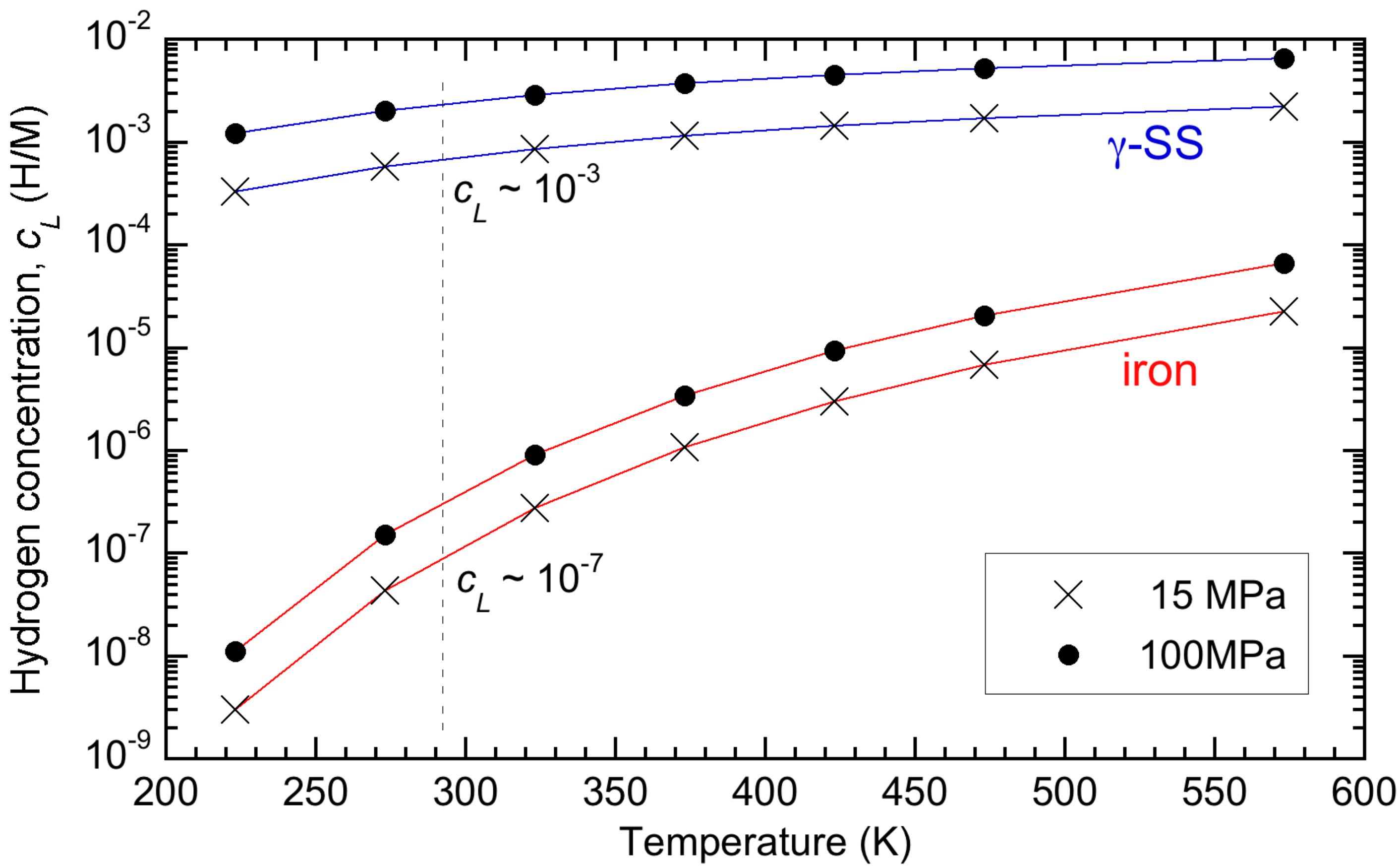
Concentration of hydrogen in metals

$$\tfrac{1}{2}H_2 \leftrightarrow \underline{H}$$

$$\tfrac{1}{2}\mu_{HH} = \mu_H$$

$$c_o = \left[K_o \exp\left(-\Delta H / RT\right)\right] f_{HH}^{1/2}$$

Sievert's Law



γ-SS

K_o = 0.00192 H/M

ΔH = 5.9 kJ/mol

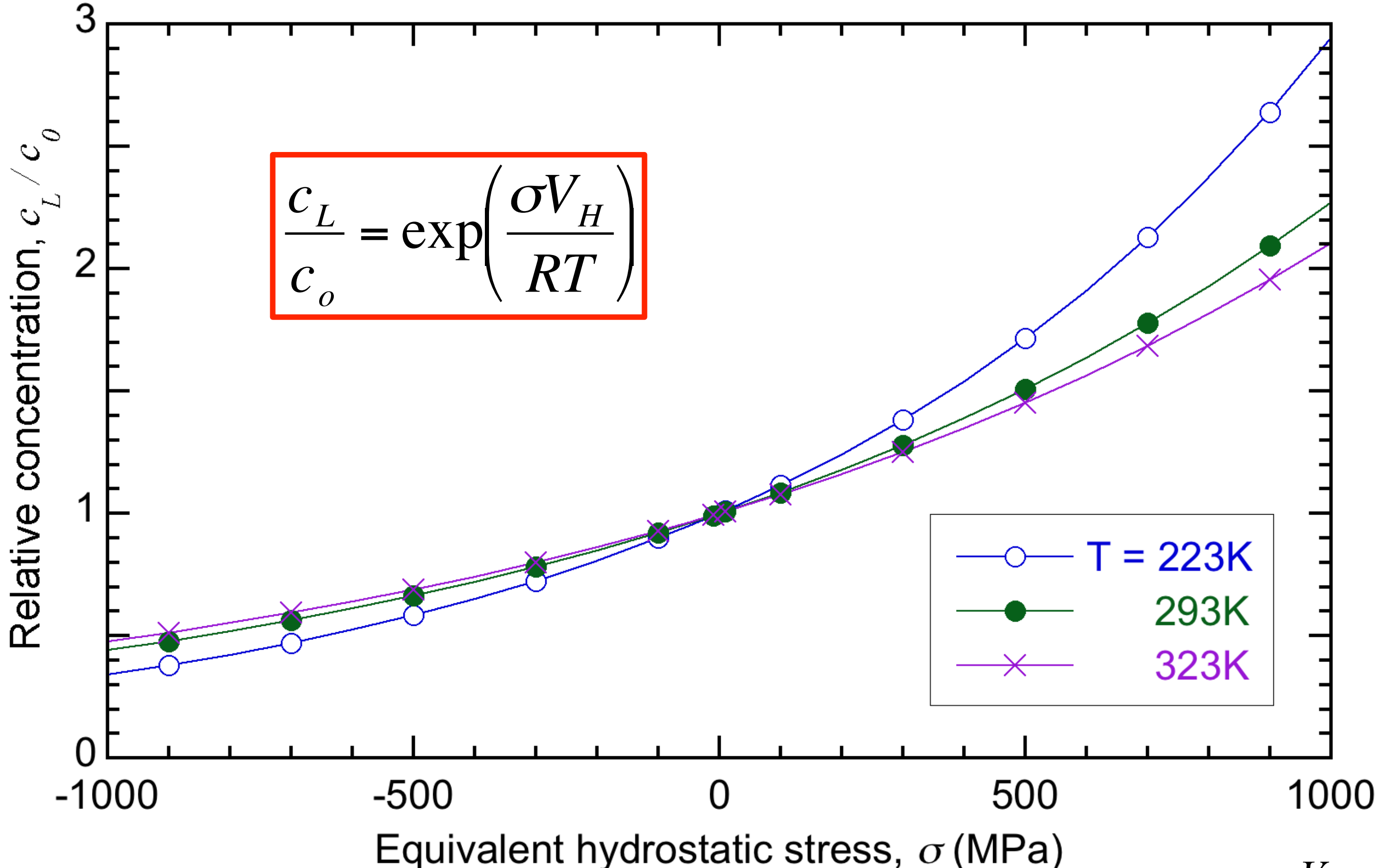
Iron

K_o = 0.00171 H/M

ΔH = 27.2 kJ/mol

Stress affects hydrogen content in metals

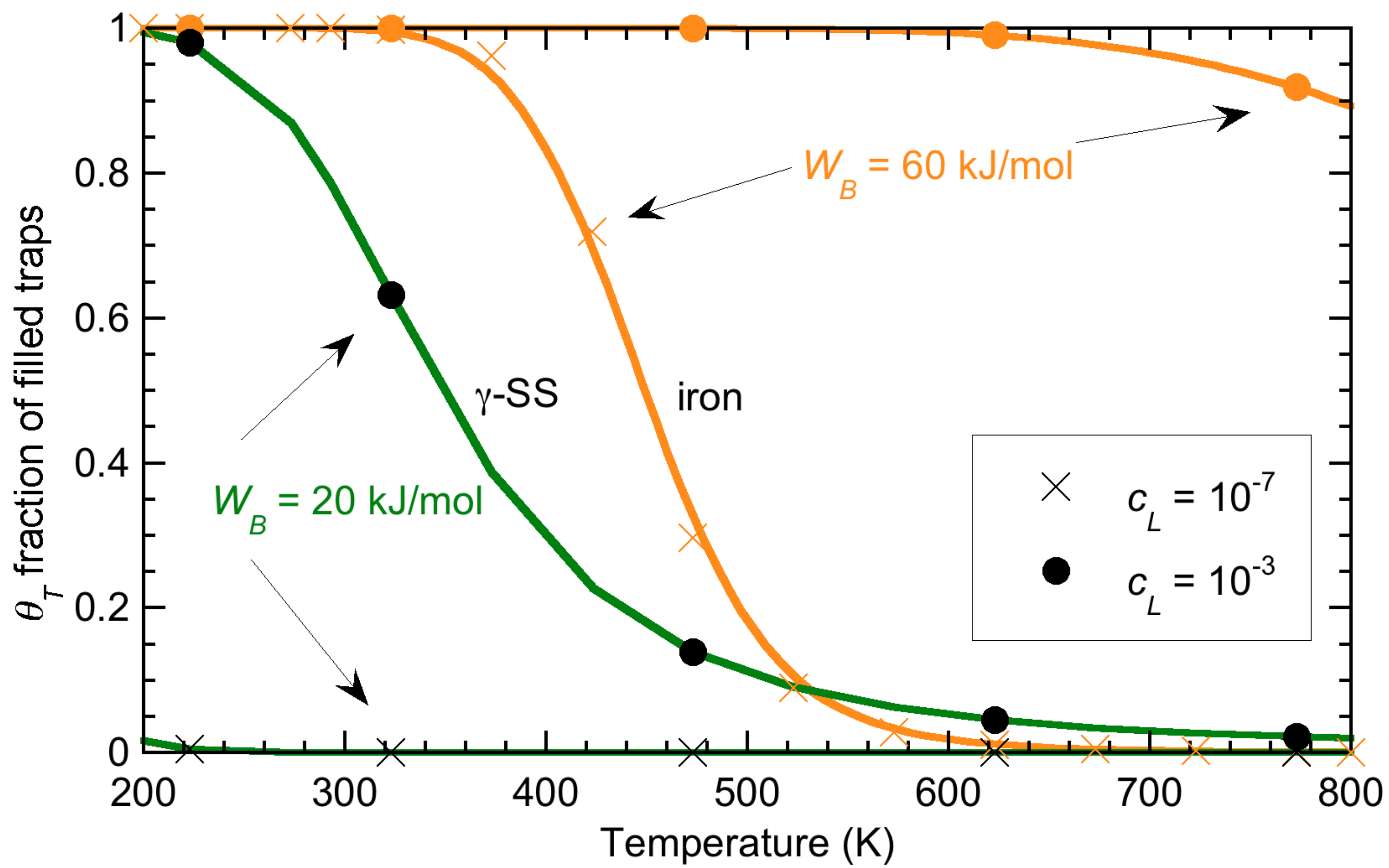
- Tensile stress increases hydrogen content
- Compressive stress decreases hydrogen content



V_H = 2 cm^3/mol

Trapping is characterized by trap energy and lattice hydrogen concentration

Equilibrium between lattice hydrogen and traps $\frac{\theta_T}{(1-\theta_T)} = \theta_L \exp\left(\frac{W_B}{RT}\right)$



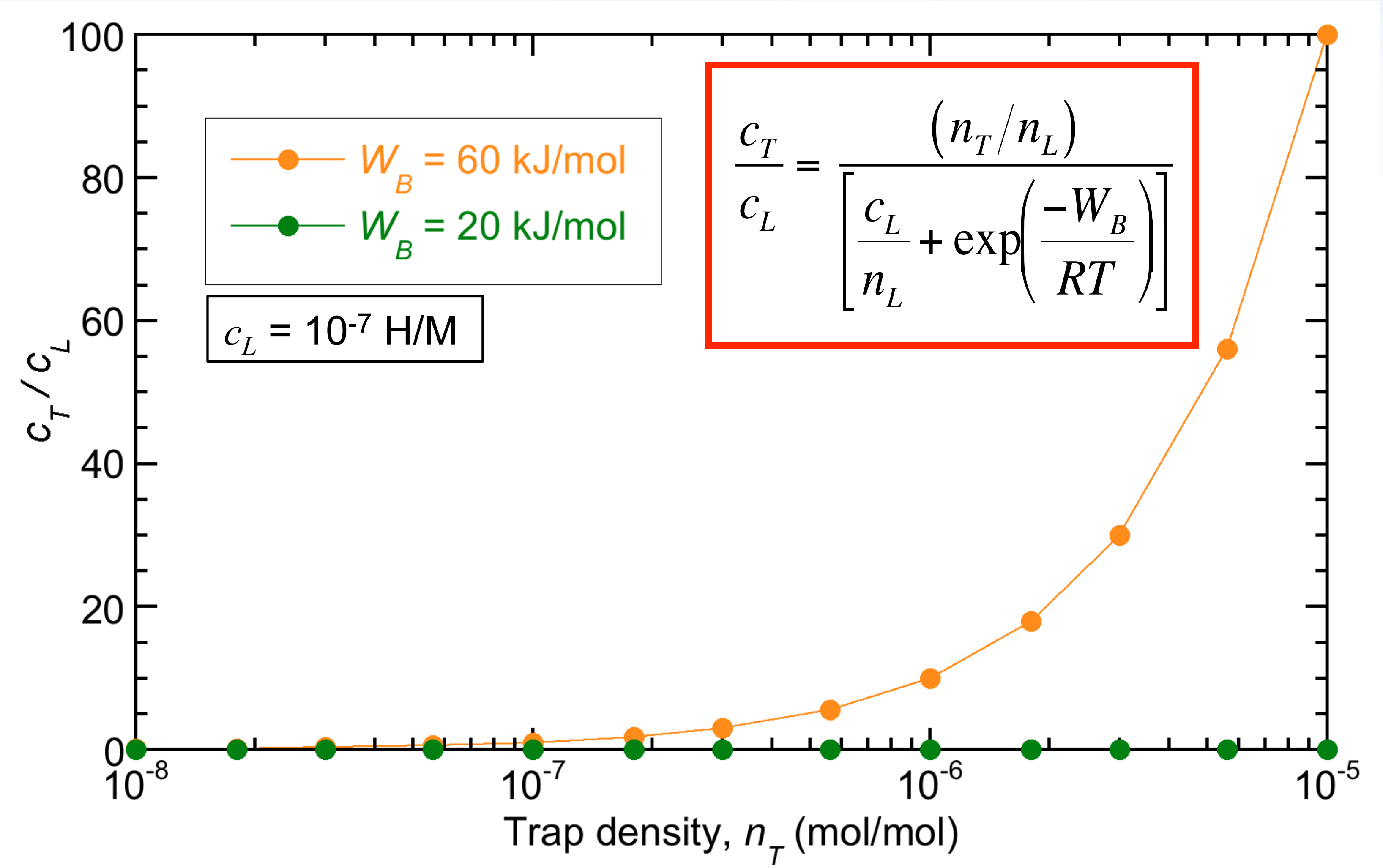
$\theta_T = \frac{c_T}{n_T}$

$\theta_L = \frac{c_L}{n_L}$

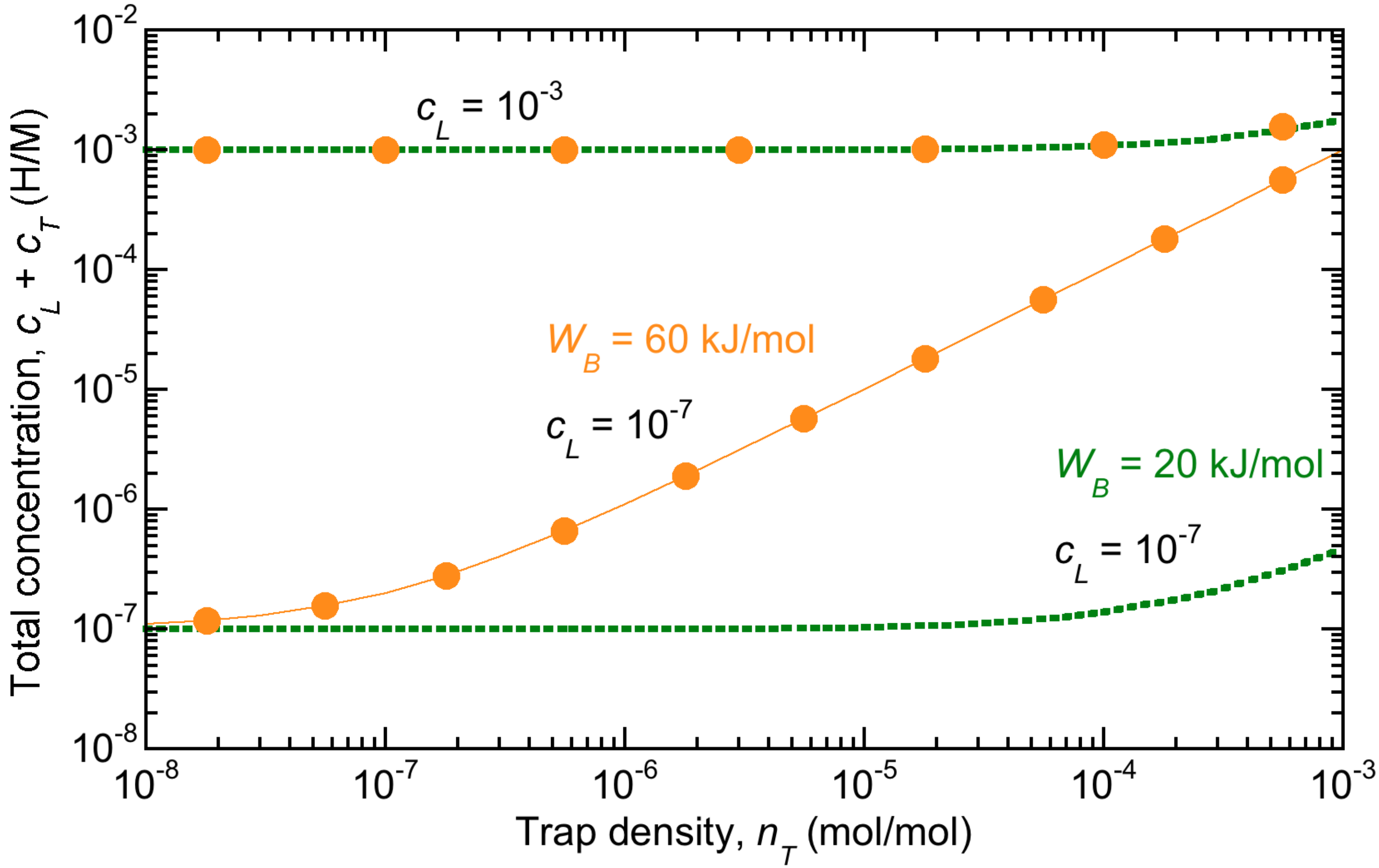
n_T = number of trap sites

n_L = 1 = number of lattice sites

Trapped hydrogen can be much larger than lattice hydrogen

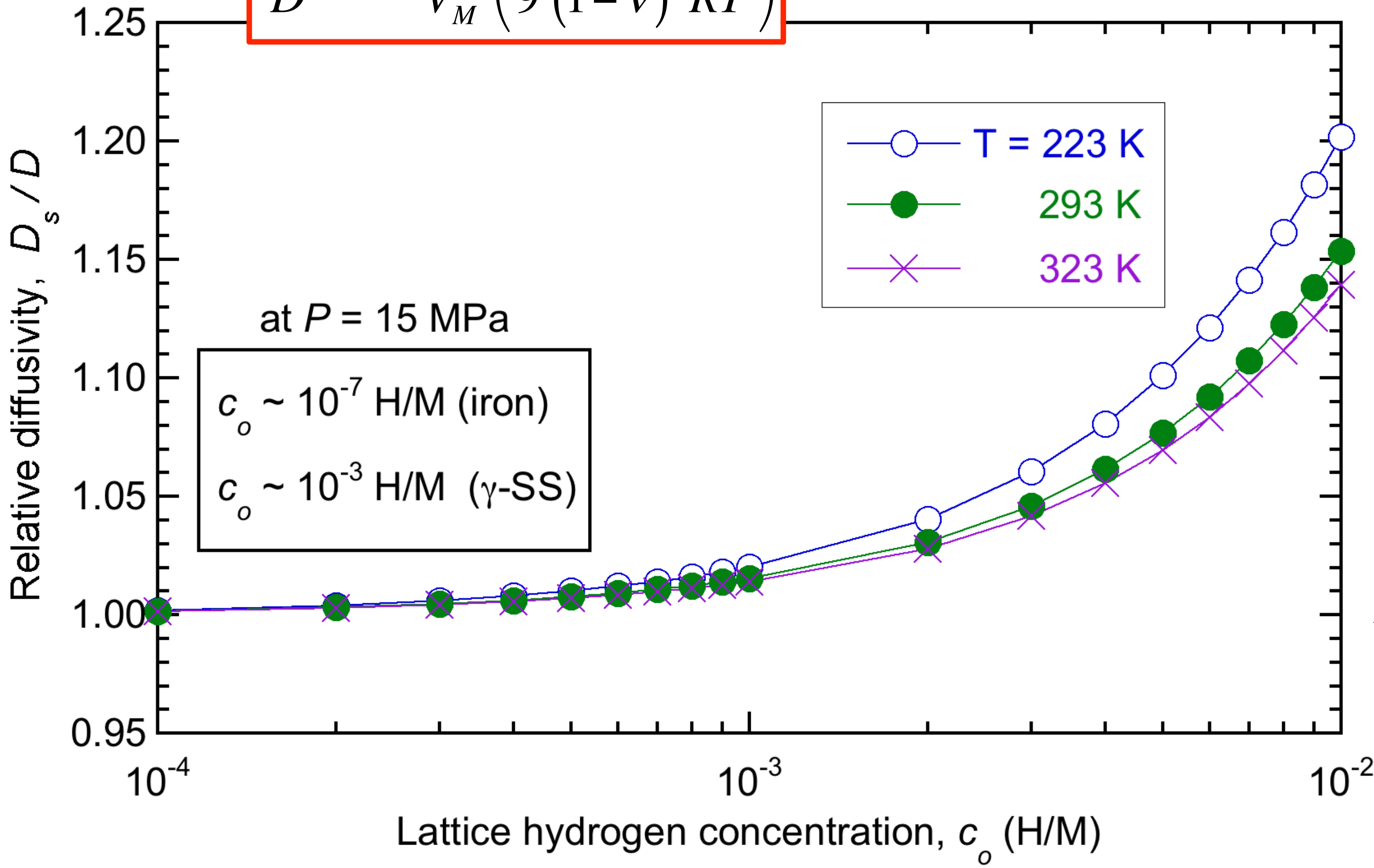


Hydrogen trapping is most significant at high energy and low lattice concentration



Stress has minimal effect on hydrogen diffusivity

$$\frac{D_s}{D} = 1 + \frac{c_o}{V_M}\left(\frac{2}{9}\frac{E}{(1-\nu)}\frac{{V_H}^2}{RT}\right)$$



V_M = 7.1 cm³/mol
V_H = 2 cm³/mol
E = 200 GPa
ν = 0.33

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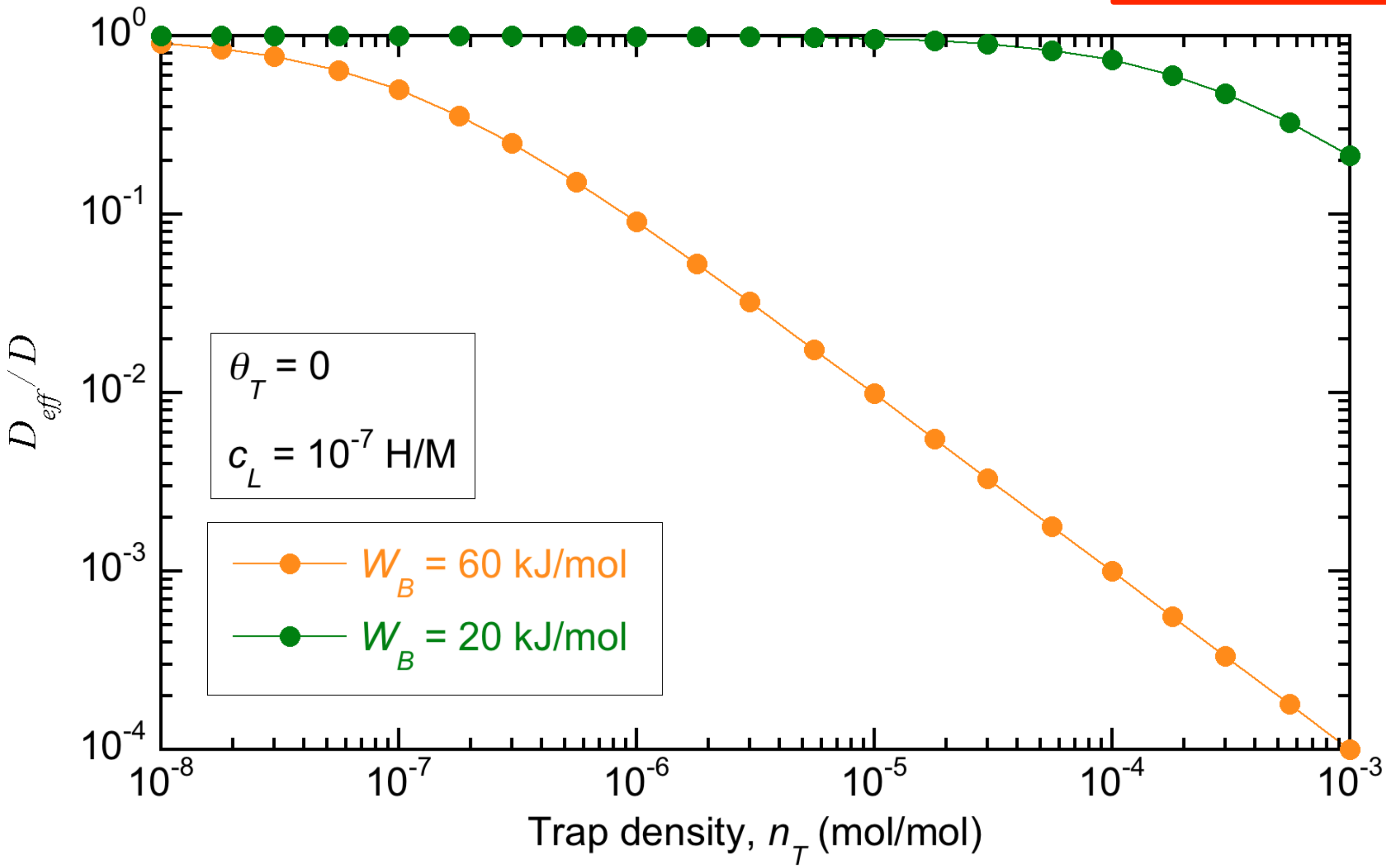
Diffusivity is decreased by trapping

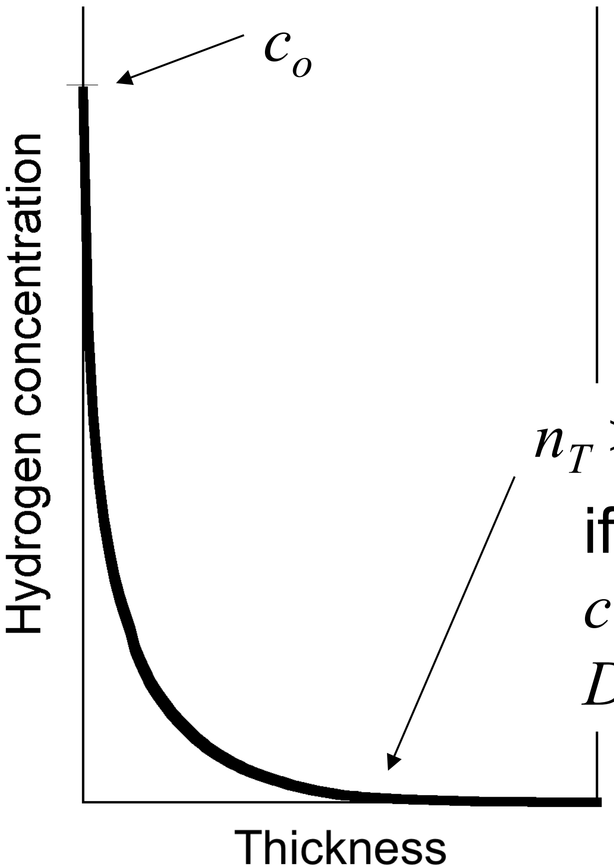
The effective diffusivity (D_{eff}) is a function of lattice hydrogen as well as trapped hydrogen:

$$\frac{D_{eff}}{D} = \frac{c_L}{c_L + c_T(1-\theta_T)}$$



Diffusivity measured near ambient temperature is difficult to interpret

Consider concentration gradient across membrane or wall at room temperature

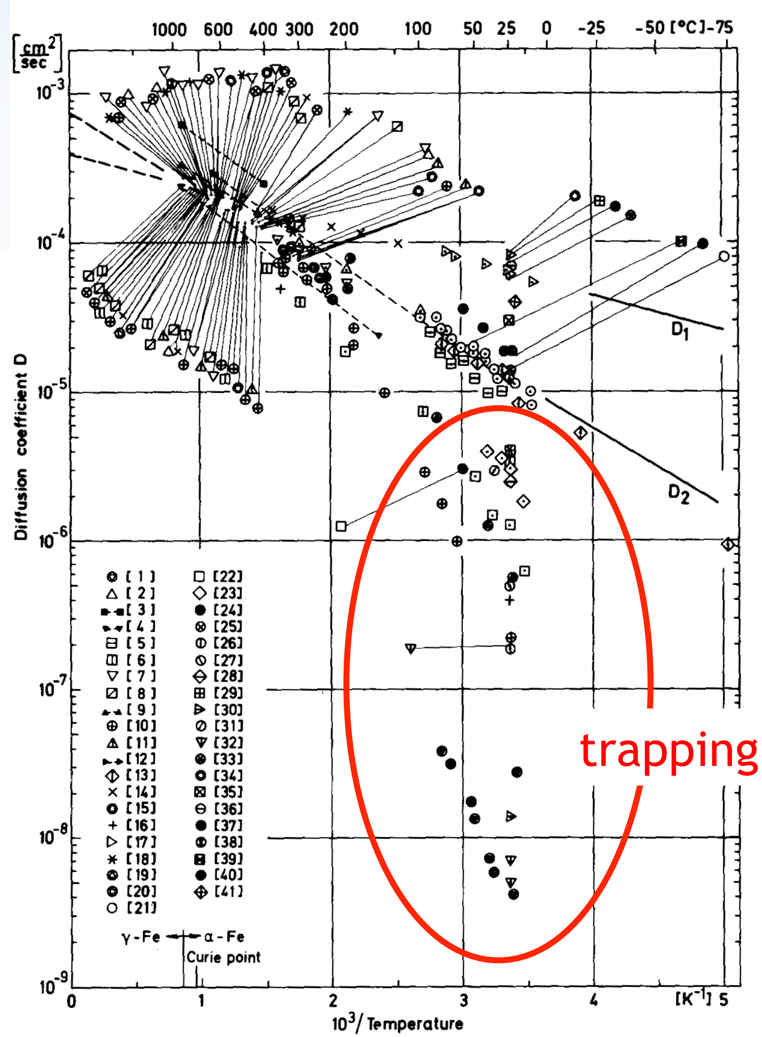


$n_T >> c_L$

if W_B is large

$c_T >> c_L$

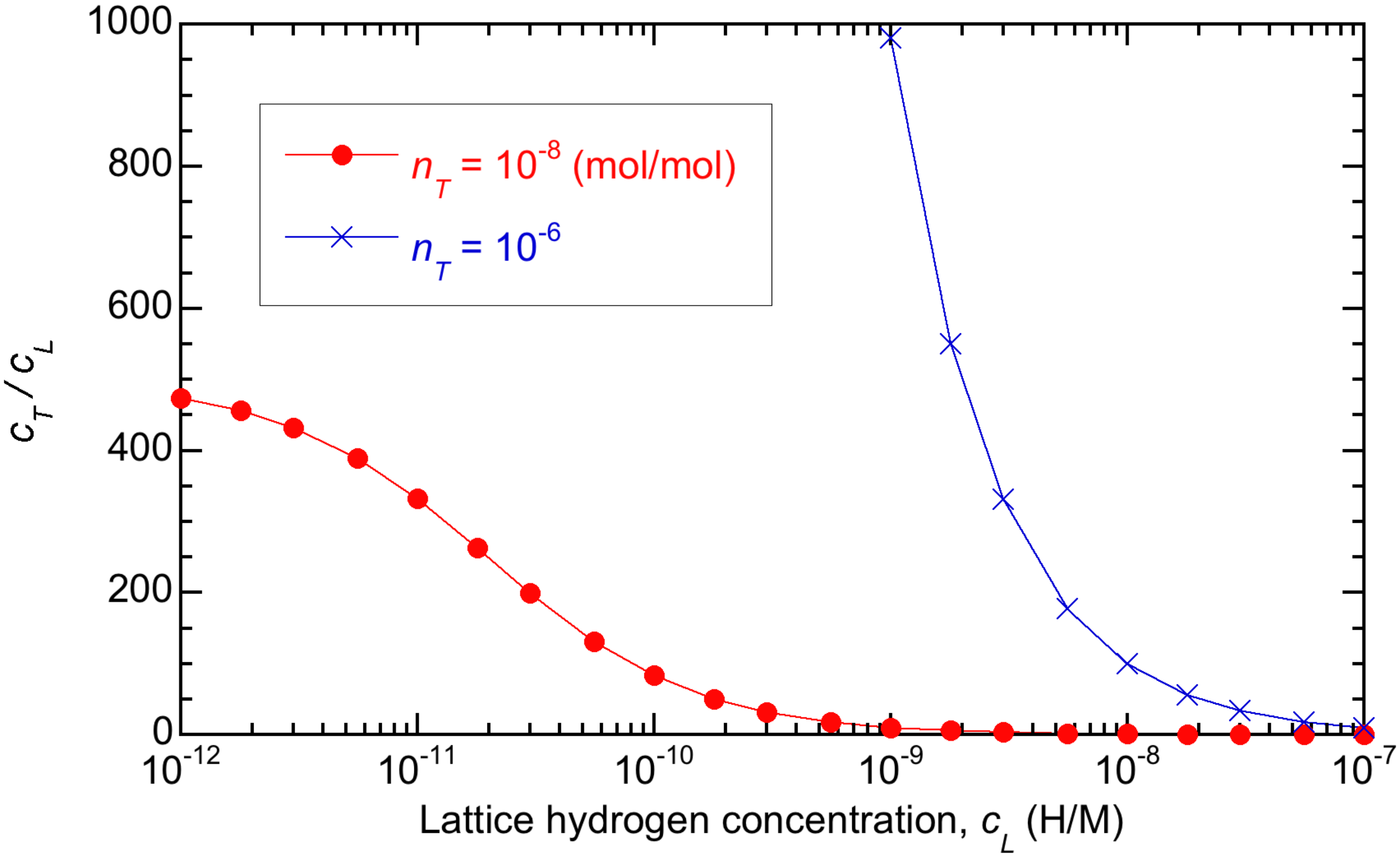
$D_{eff} << D$



From: Diffusion in Solids, Nowick and Burton, eds., 1975

At low hydrogen concentrations, traps are hydrogen sinks $c_T >> c_L$

When c_L is very small $\frac{D_{eff}}{D} \sim \frac{1}{c_T/c_L}$



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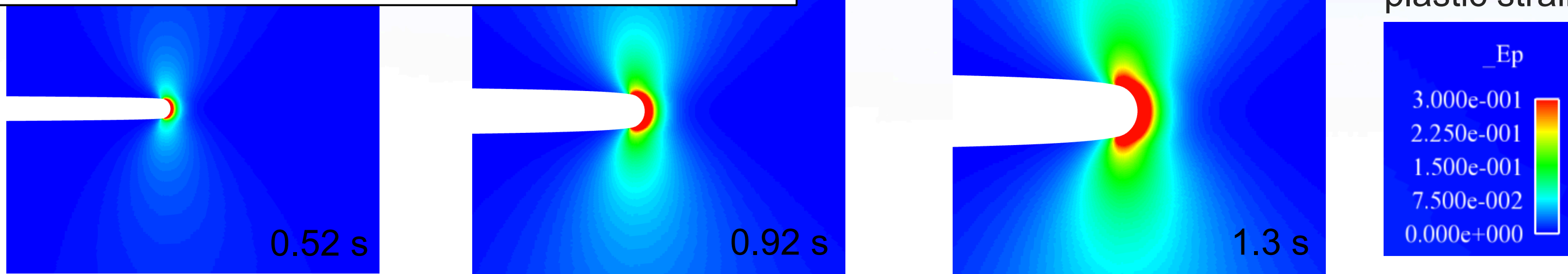
Hydrogen transport laws can be coupled with stress analysis to inform physics

The number of dislocation trap sites scales with the equivalent plastic strain

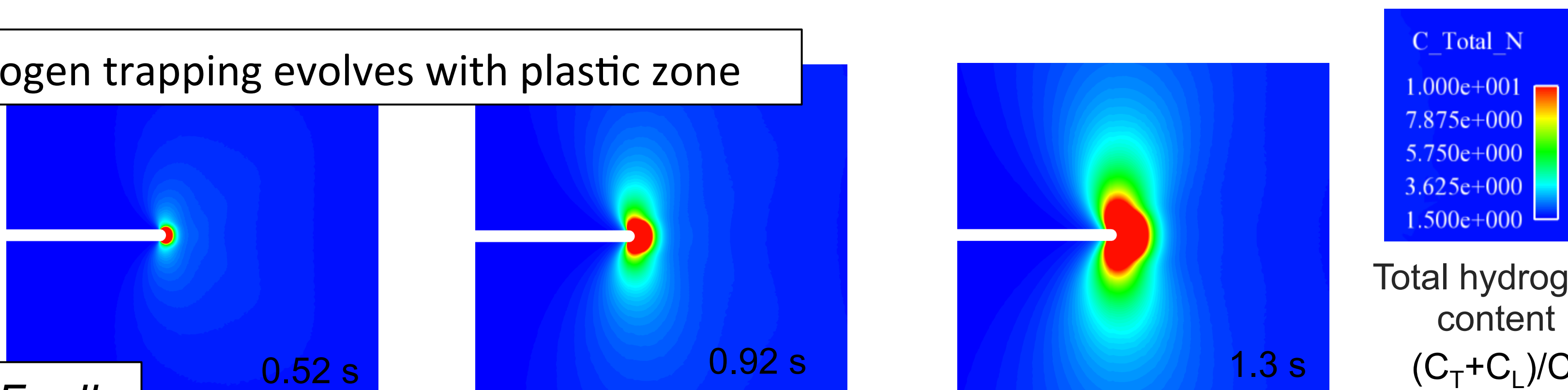


mechanical → *diffusion*

Transport rules coupled with mechanics

$$D^*\dot{C}_L - \nabla_{\mathbf{X}} \cdot \mathbf{D}_L \nabla_{\mathbf{X}} C_L + \nabla_{\mathbf{X}} \cdot \frac{V_H}{RT} C_L \mathbf{D}_L \nabla_{\mathbf{X}} S_H + \theta_T \frac{dN_T}{d\epsilon_p}\dot{\epsilon}_p = 0$$

Hydrogen trapping evolves with plastic zone

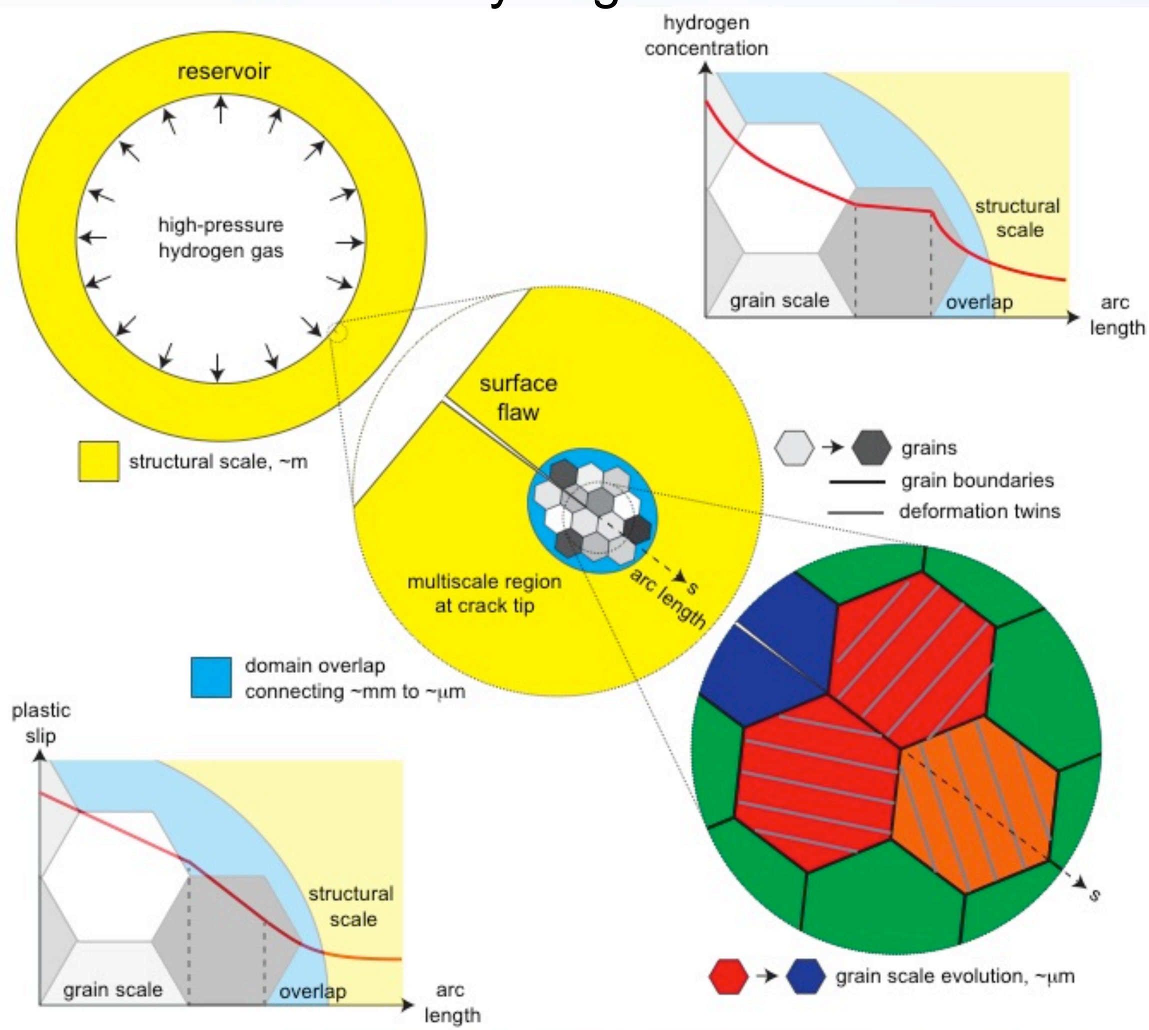


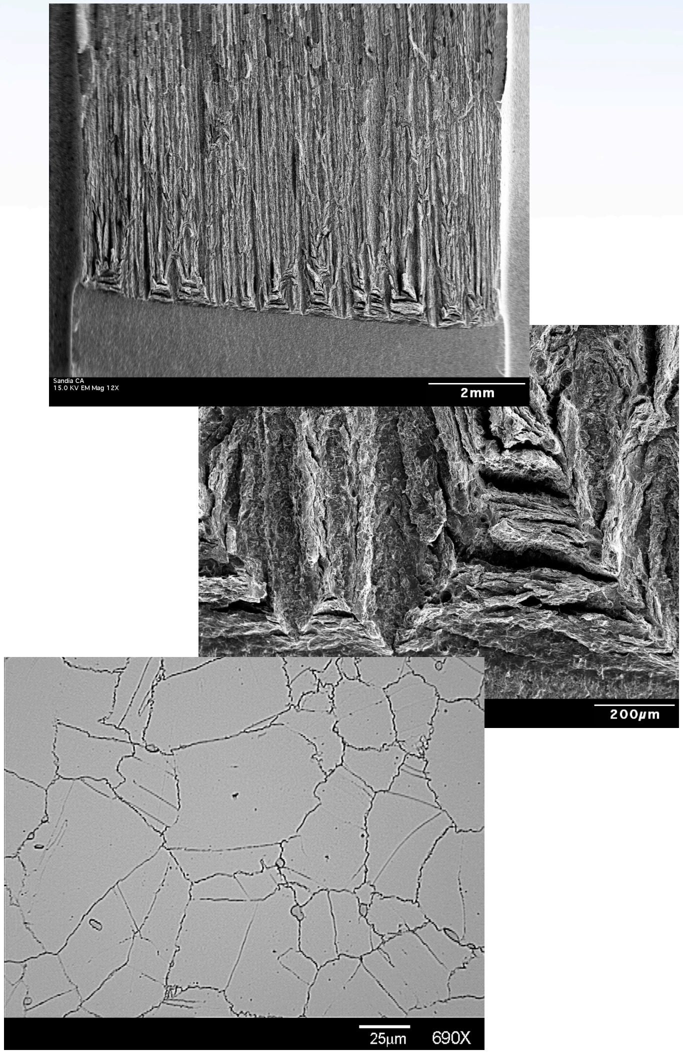
Total hydrogen content $(C_T+C_L)/C_0$

PI: J. Foulk

Multiscale/multiphysics models provide insight to mechanisms at the microstructural scale

Transport is a key component of interpreting fracture and fatigue measurements in hydrogen





Summary

- Hydrogen fugacity
  - Abel-Noble EOS works well for gaseous hydrogen
  - Gas mixtures increase fugacity
- Stress
  - Tensile stress increases hydrogen dissolved in metals (compressive stress decreases hydrogen content)
  - Stress has minimal effect on hydrogen diffusivity
- Hydrogen trapping
  - Low trap energy (γ-SS): essentially no effect on hydrogen and hydrogen transport
  - High trap energy (iron and steels):
    - Substantial increases in dissolved hydrogen content
    - Large decreases in apparent hydrogen diffusivity
- Coupled hydrogen transport and mechanics models are necessary to enhance physical understanding of hydrogen-assisted fracture and fatigue