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Hydrogen Diffusion In Oversaturated EPDM Rubber: The Effect Of Induced Strain

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H-Mat SM Hydrogen Materials Compatibility Consortium

Controlled by:

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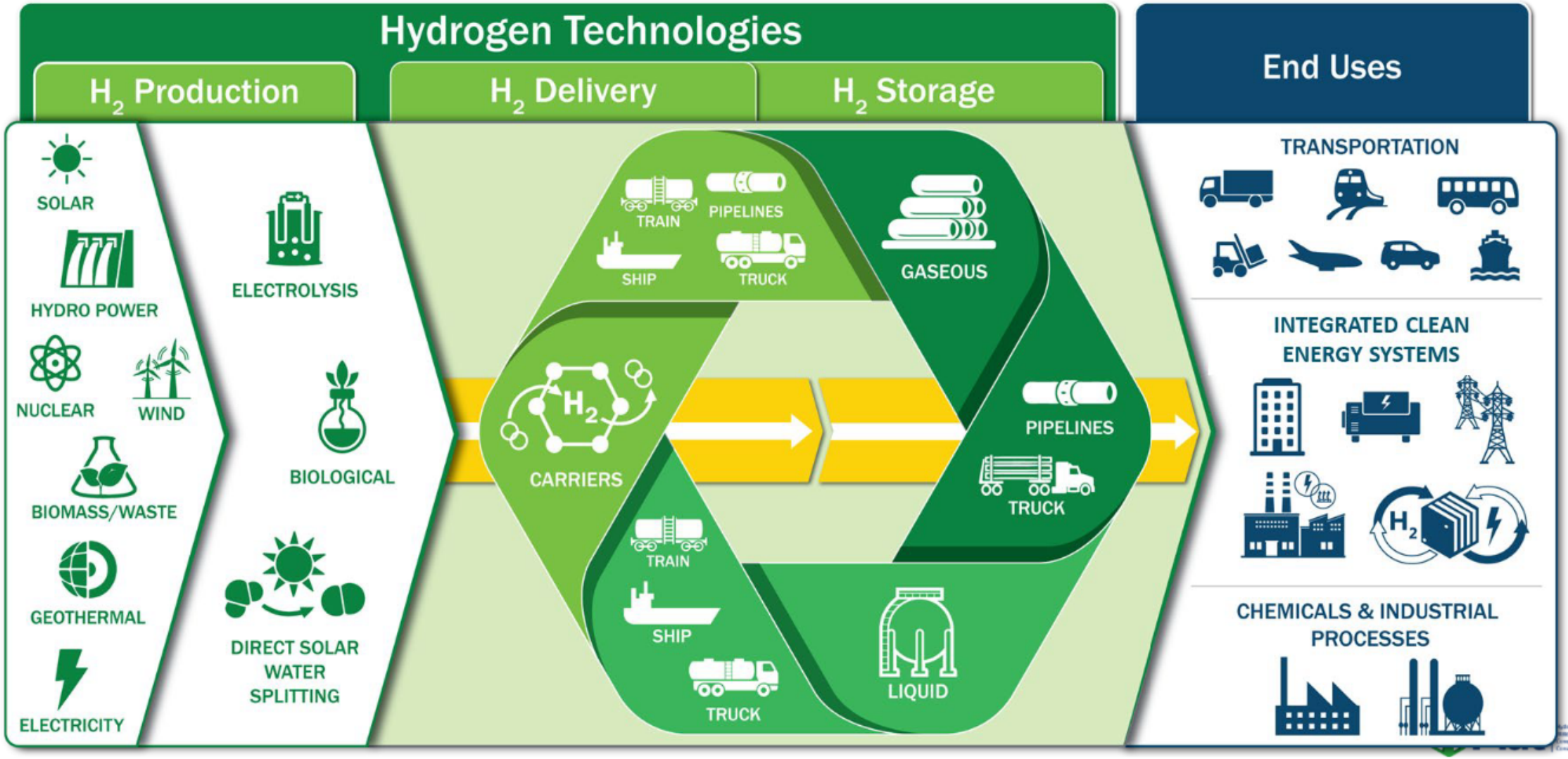
U.S. DEPARTMENT OF ENERGY

NNSA

INFRASTRUCTURE DEPENDENT ON ADVANCED MATERIALS



Source: Ned Stetson 2022 Annual Merit Review HFTO

CYCLIC PRESSURIZATION LEADS TO MATERIAL FAILURE

Polymers do not react with H_2, however diffusion and sudden depressurization of hydrogen through polymers leads to mechanical failure.

Rapid decompression failure (RDF) is a micro scale phenomena

Mechanism of RDF

(1) Diffusion of hydrogen through the polymer

(2) Deformation of polymer due to hydrogen pressure

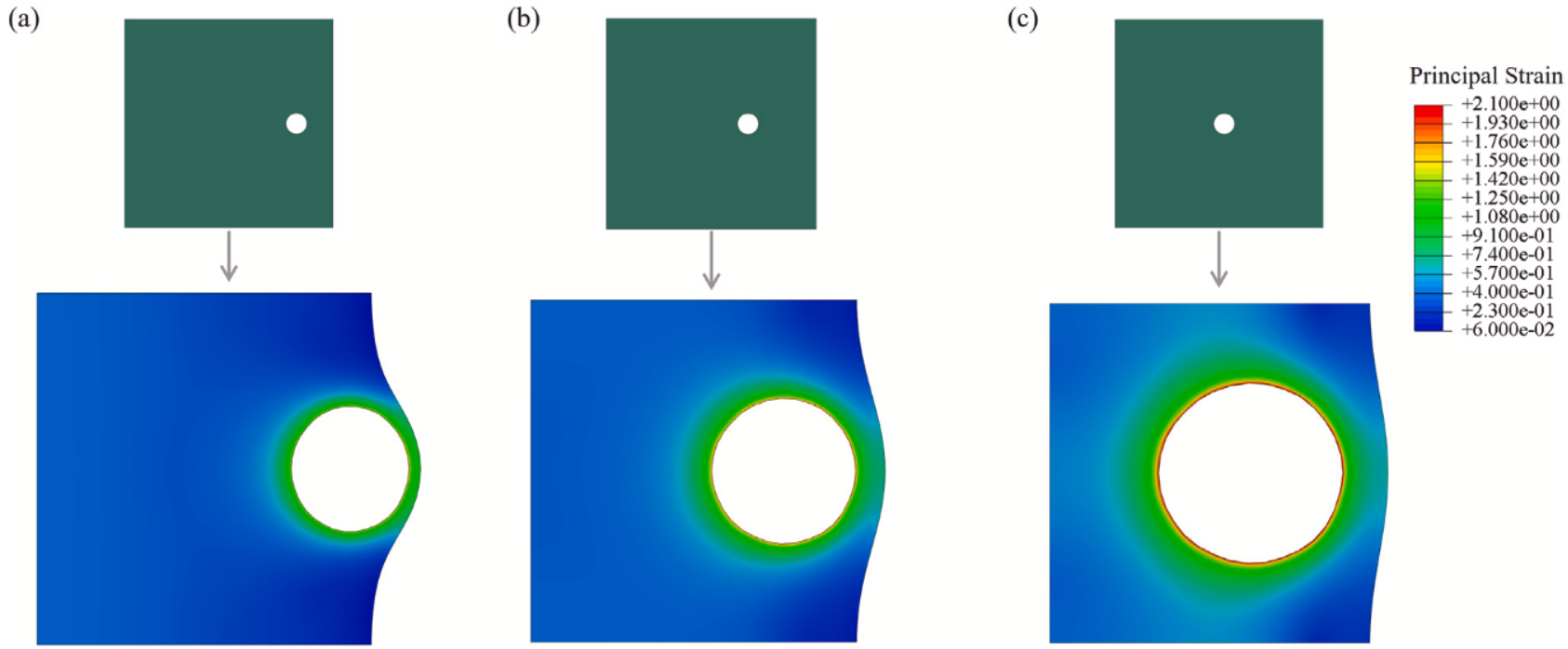
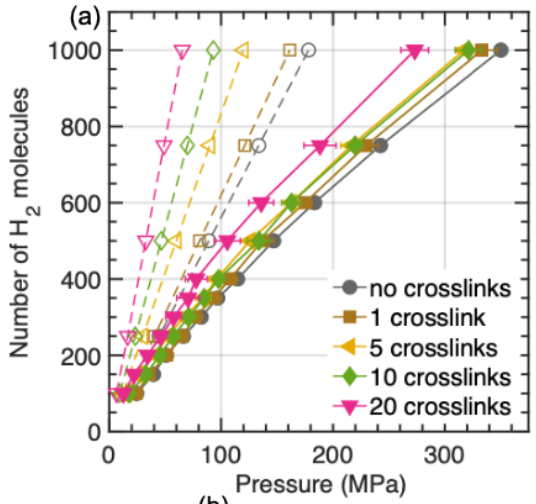


Fig. 14. Spatial principal strain distribution across RVE for cavity located at (a) 0.25 mm, (b) 0.55 mm, and (c) 0.95 mm from the free surface. Plots are shown for pure EPDM material just after depressurization was complete.

Kulkarni et al. J Mechanic and Physics of Solid, 178, 2023

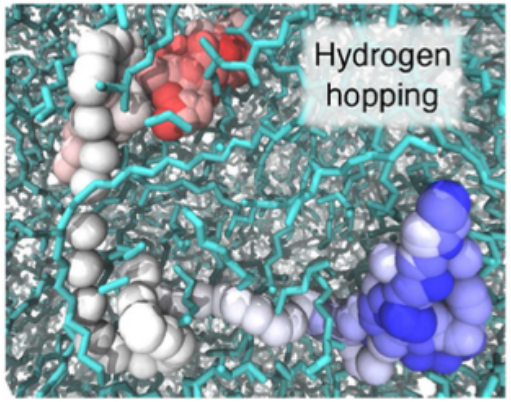
ATOMISTIC MODELING OF EPDM AND H_2[1]



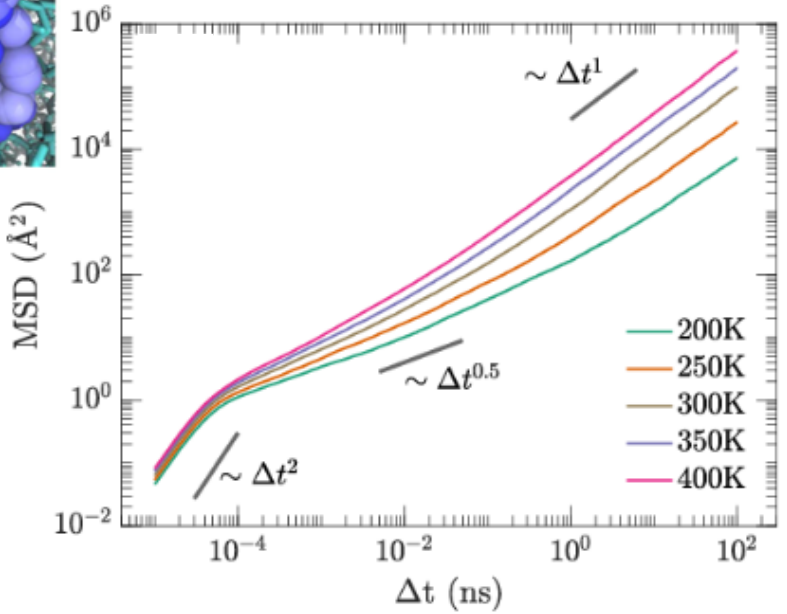
***(a)** Plot of the pressure of each model vs the number of H_2 molecules. Solid lines show our results while dashed lines show Henry's law. **(b)** Hydrogen accessible free volume of the 5 crosslinks EPDM model with 1000 H_2 molecules at pressure and **(c)** after decompression.*

- ✓ Rearrangement of polymer chains is slowed with increased crosslink density.
- ✓ Crosslinks reduce H_2 susceptibility to bubble formation.

SUB-DIFFUSIVE H_2 GAS DYNAMICS[2]



(top) Trace of a single H_2 molecule showing sub-diffusive behavior, and (right) mean squared displacement of EPDM with 1000 H_2 molecules showing sub-diffusive behavior increases as temperature decreases.

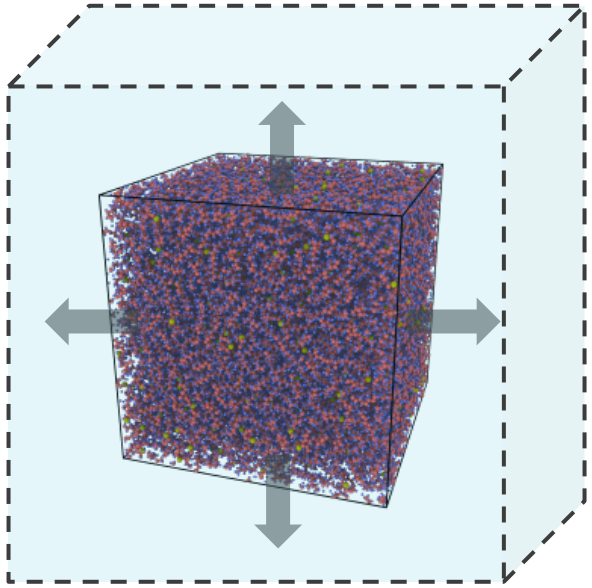


- ✓ Greater H_2 mobility with greater crosslink density, higher temperature, and lower gas concentrations
- ✓ 'Caged' hydrogen having slower dynamics localize forming precursors to cavitation

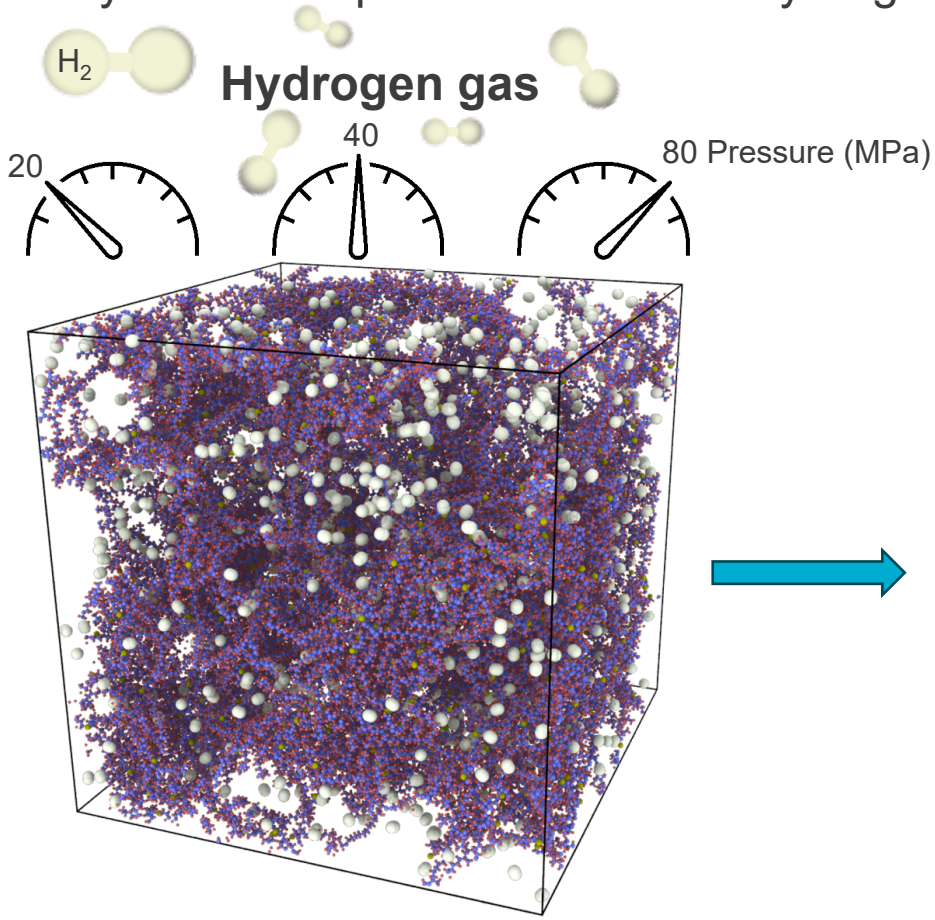
STRAIN INDUCED H_2 GAS DYNAMICS

Goal: Identify changes in diffusion, quantify relationship free volume and hydrogen velocity

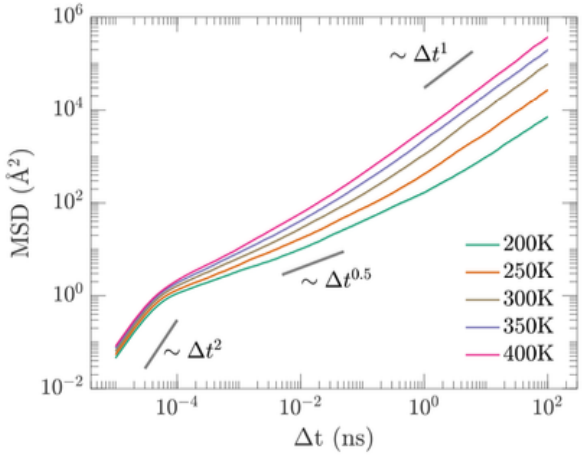
EPDM systems



Isotropic strain



Long diffusion time
(100ns)

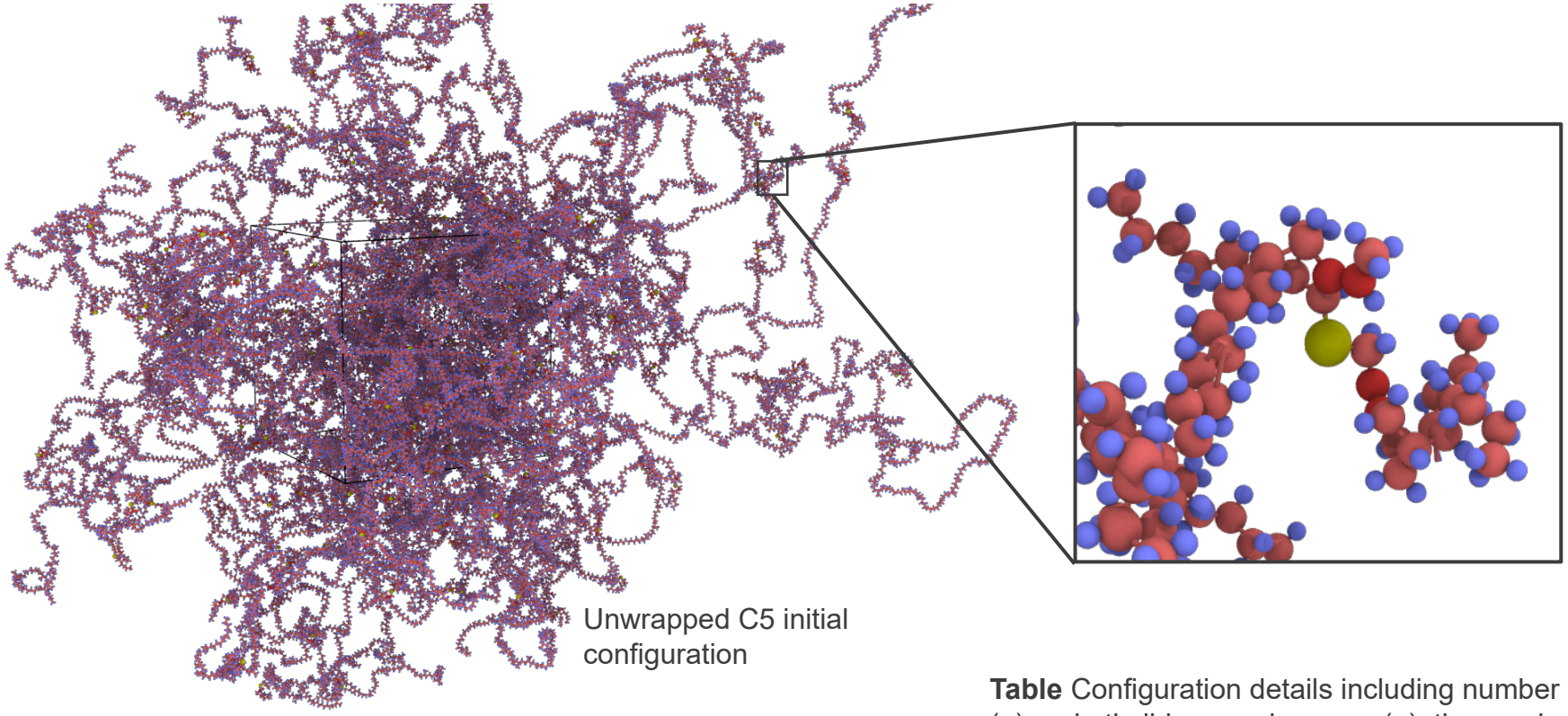


MSD of H_2 in EPDM **(Brownell et al. 2022)**

Output: The effect of nominal strain, matrix cavities, and hydrogen pressure on coefficient of diffusion.

Impact: Inform strain dependent diffusivity, input for higher length scale models (finite models).

BUILDING EPDM CONFIGURATIONS



Unwrapped C5 initial configuration

Cross-link chemistry

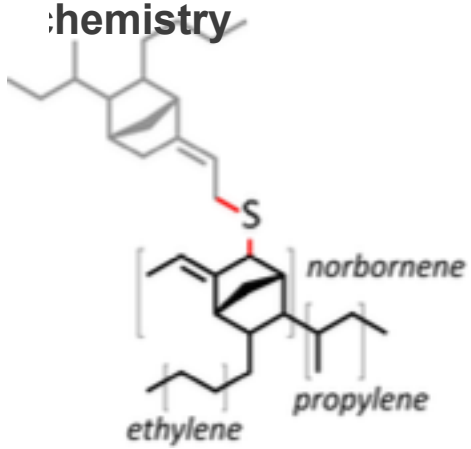


Illustration of sulfur cross-linking of ENB monomers

ethylene-propylene-ethylidene monomer, 5:4:1 ratio

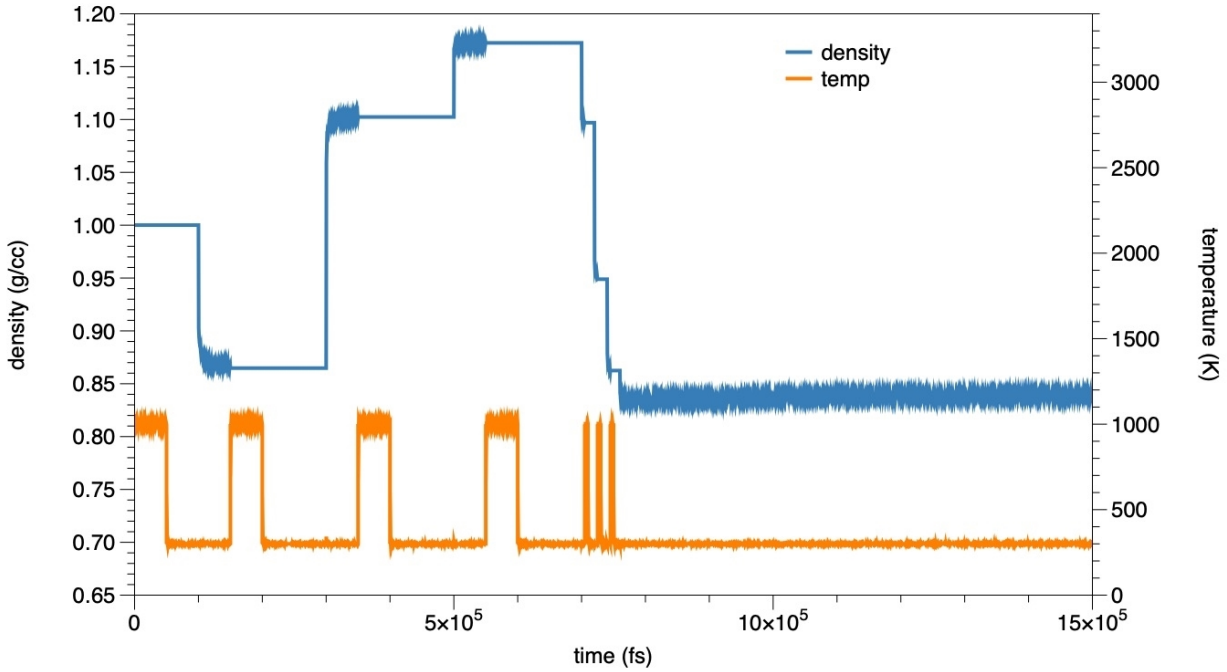
- **C0, uncross-linked**
- **C5, experimental cross-link density**
- **C20, highly cross-linked**

Built via Enhanced Monte Carlo [int'Veld, 2001]
@ 1.0g/cc
~125K atoms
OPLS-aa

Table Configuration details including number of repeat units per chain of ethylene (m), propylene (n) and ethylidene norbornene (p), the number of native crosslinks per chain (x-links)

	m	n	p	x-links	monomers per chain	chains	total atoms
C0	110	55	5	0	170	97	124,451
C5	220	110	5	5	340	49	123,627
C20	220	110	20	20	370	39	122,382

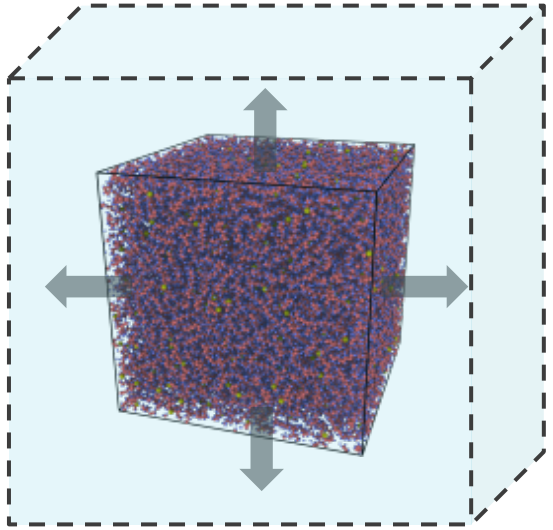
EQUILIBRATION PROTOCOL

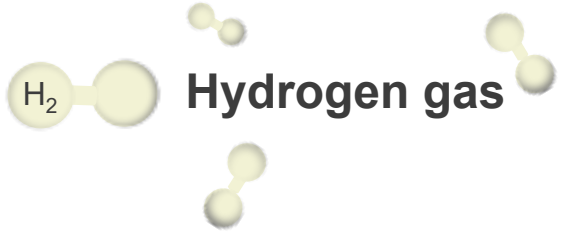


	density (g/cc)	dimensions (Å^3)
C0	0.837 ± 0.004	105.389 ± 0.149
C5	0.844 ± 0.002	105.503 ± 0.087
C20	0.891 ± 0.001	105.677 ± 0.038
exp.	0.850-0.88 [1]	-

ISOTROPIC STRAIN

11 nominal strain values (0.0 – 0.5, 0.05 increments)





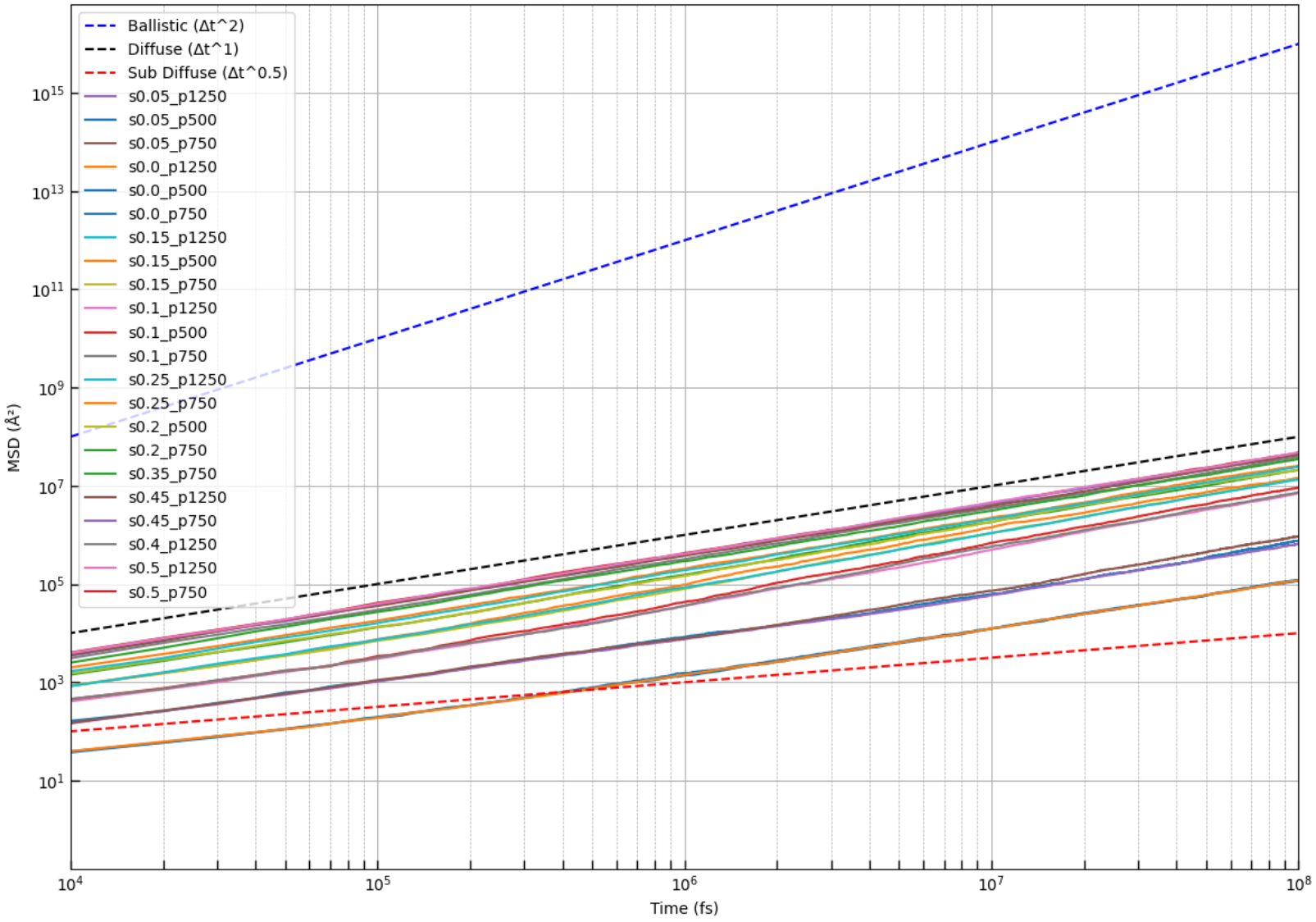
Concentration ∝ partial pressure

HYDROGEN PRESSURIZATION

# of H_2 molecules	wt. ppm	approx. P (MPa)
500	1700	20
750	2555	40
1250	4258	80

1 DuPont, Nordel IP-4725P, Nordel IP-4750P

SIMULATION OUTPUT: DIFFUSION COEFFICIENTS



Mean Square Displacement

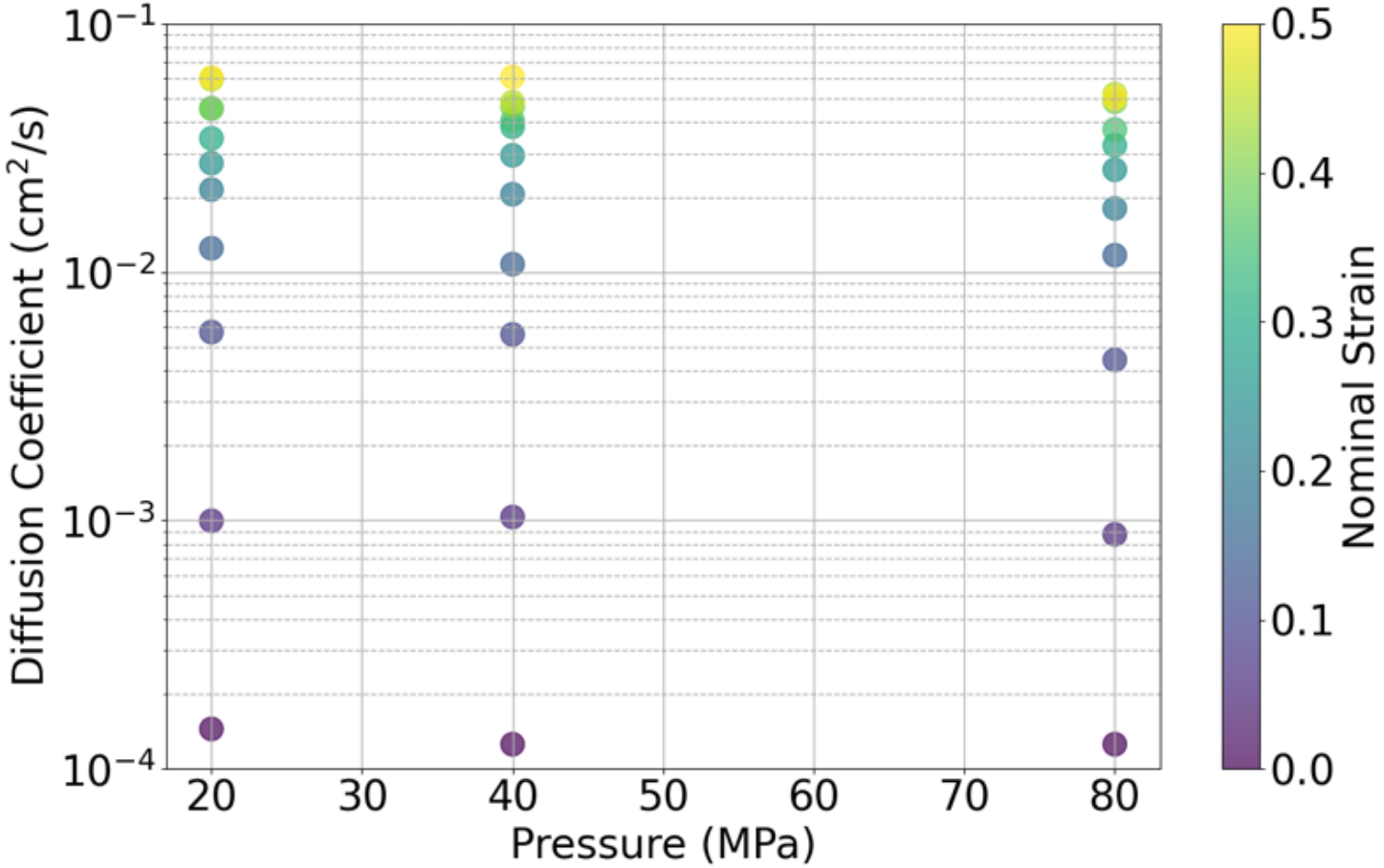
$$MSD = \langle \Delta r^2(t) \rangle = \left\langle \left| r(t_0 + t) - r(t_0) \right|^2 \right\rangle$$

Diffusion Coefficient

$$D = \frac{1}{6t} \langle \Delta r^2(t) \rangle$$

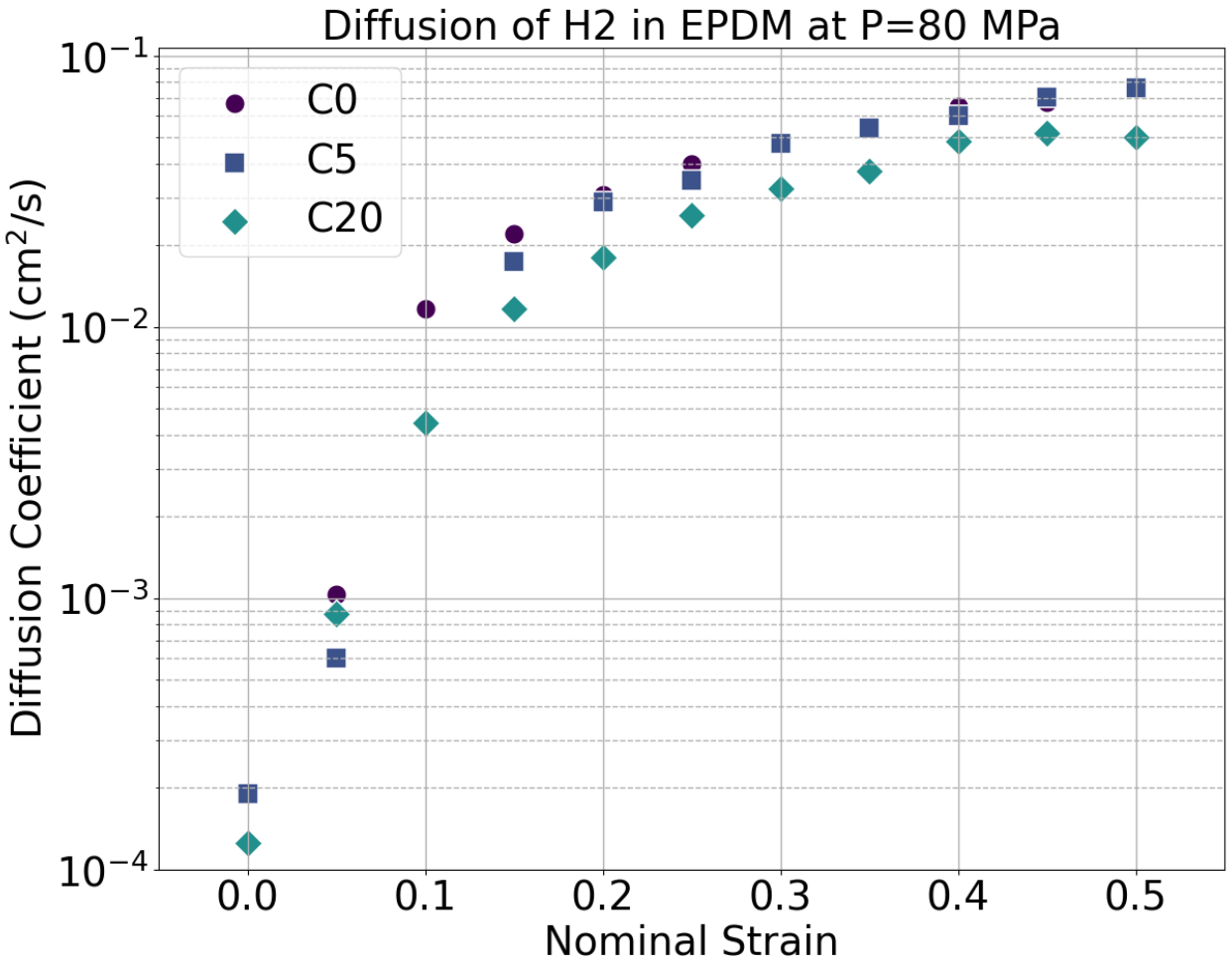
MSD of hydrogen in uncross-linked EPDM at 300 K for 100 ns of simulation time. Dotted reference lines given for ballistic, sub-diffuse and **diffuse** behavior.

DIFFUSION INDEPENDENT OF HYDROGEN PRESSURE



Diffusion coefficients of H2 molecules at three pressure levels in highly crosslinked EPDM (C20, 20 crosslinks per chain) with various nominal strain values

DIFFUSION IS HEAVILY STRAIN DEPENDENT

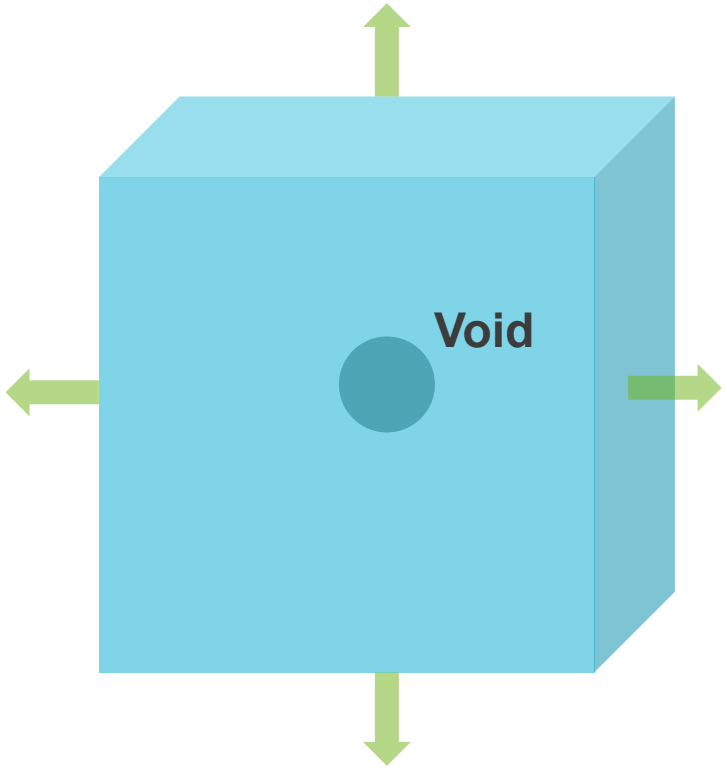


Strain dependent diffusion coefficients of H2 for uncross-linked (C0), moderately cross-linked (C5) and highly cross-linked (C20) systems

CONSIDERING OTHER STRAINED CONFIGURATIONS

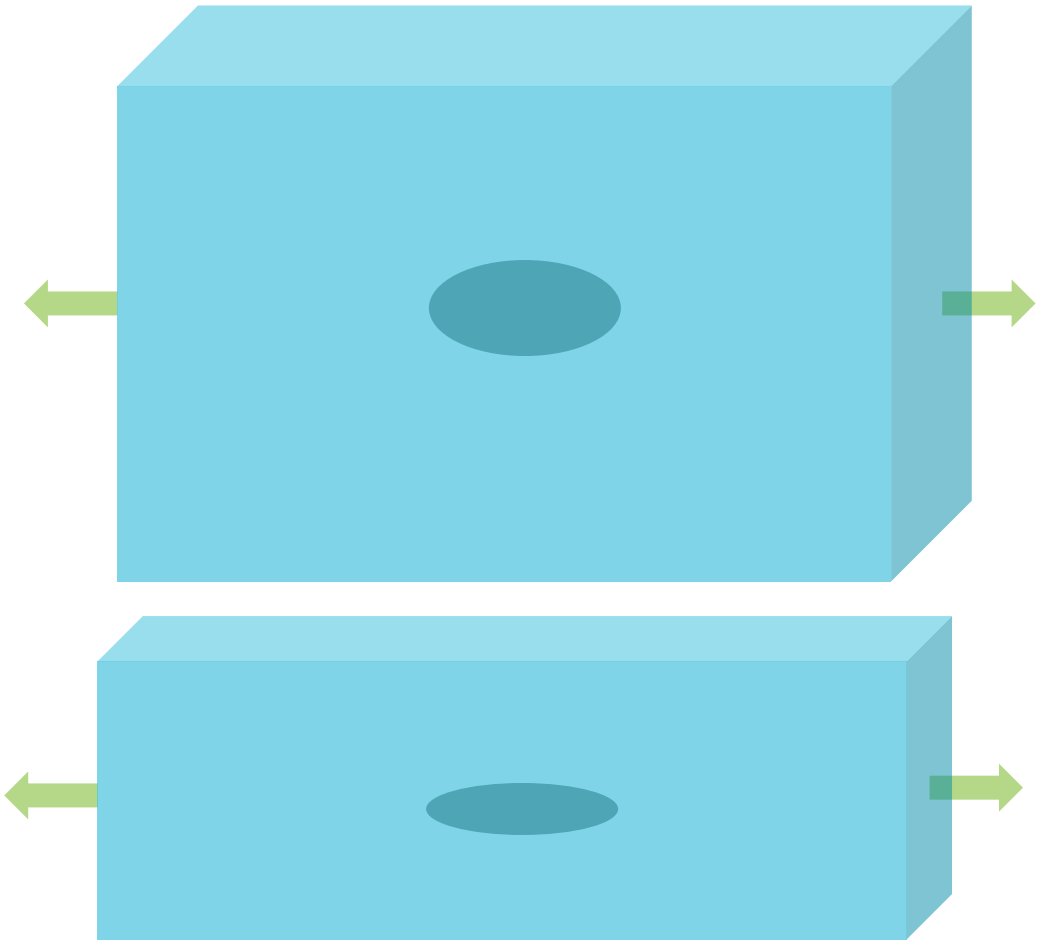
Isotropic strain

- Scaled equally in x, y and z directions
- Increase in void dimension but no change in void shape



Anisotropic strain

- Strain in x
- Account for Poisson's ratio



ONGOING WORK

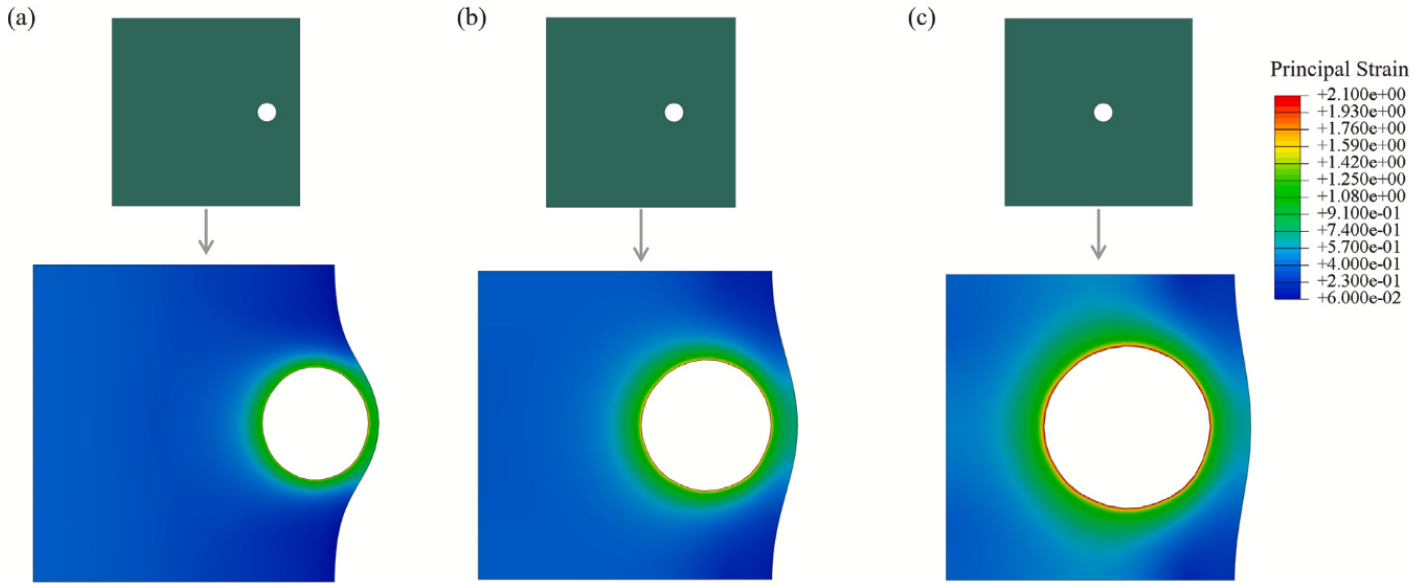
- Diffusion study of hydrogen in multiple strained configurations
- Consider RDF/PCF of hydrogen in the system
- Free volume analysis

OUTPUT

- Effect of nominal strain D_{coeff}
- Effect of hydrogen pressure on D_{coeff}
- Matrix cavities/free volume
  - RDF
  - free volume analysis

IMPACT

- Inform strain dependent diffusivity, input for higher length scale models (finite models).



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THANK YOU!
QUESTIONS?

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EXTRA SLIDES