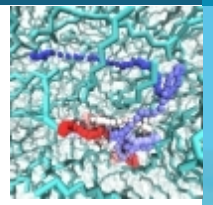
SAND2022-2396R

Sandia National Laboratories

H-Mat: Task P2 (SNL) Computationa Polymer modeling Accomplishments



Matthew Brownell[1] Amalie Frischknecht[2] and Mark Wilson[1]

[1]Computational Materials and Data Science (org 1864)

[2]Nanostructure Physics (org 1881)

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FY21 Accomplishments

Two classes of hydrogen gas are observed in pressurized EPDM

The H_2 gas with slower diffusional dynamics localizes away from crosslinks

Increasing crosslinks can:

- Slow the structural rearrangement of EPDM after decompression
- Increases gas mobility in the EPDM

Publications / presentations:

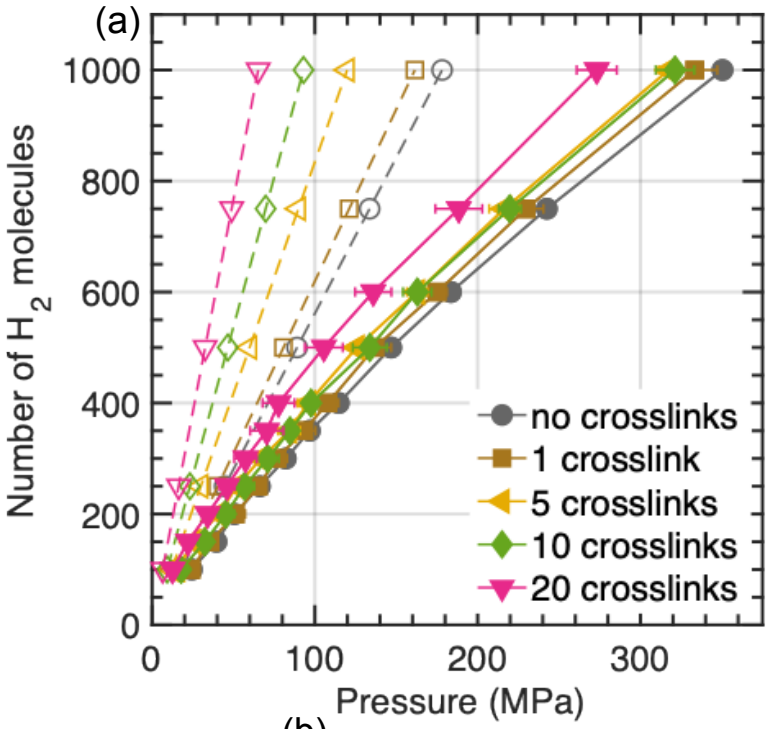
- *High-Pressure Hydrogen Decompression in Sulfur Crosslinked Elastomers;* Wilson M., Frischknecht, A. (In technical review)
- *Sub-diffusive High-Pressure Hydrogen Gas Dynamics in Elastomers;* Brownell M., Frischknecht A., Wilson M. (in technical review)
- *MRS Fall Meeting 2021: Atomistic modeling of elastomer performance during exposure to high-pressure hydrogen,* Brownell M., Frischknecht A., Wilson M.

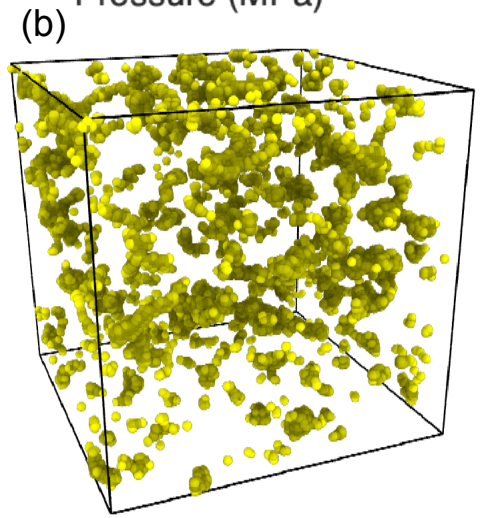
Atomistic modeling of EPDM and H_2

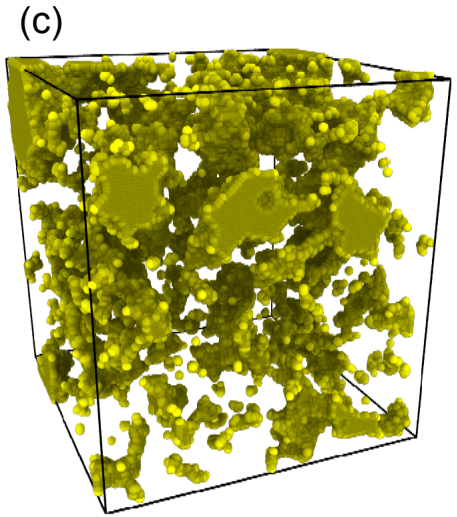
SUCCESSES:
- Calculated gas solubility-pressure relationships in dilute limit.
- Free volume is calculated before and after decompression and found to corelate to crosslink density.

METHOD:
- Molecular dynamics simulations are performed for all-atom representations of EPDM
- Various degrees of crosslinking are imposed in initial configurations
- H_2 gas is inserted into EPDM configurations at various pressures
- Simulations model rapid decompression to 1 atm

SIGNIFICANCE:
- Structural rearrangement of polymer chains is slowed with increased content of crosslinks
- Suggests a composition with increased percentage of crosslinks could reduce H2 susceptibility to bubble formation







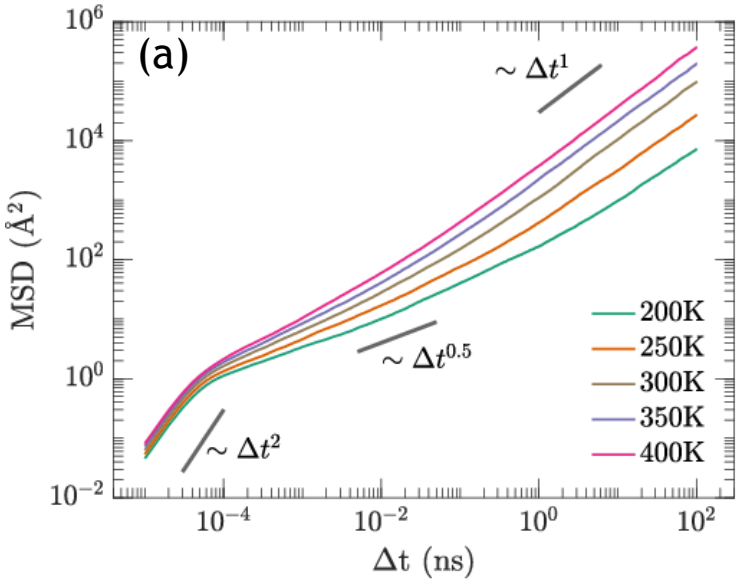
***(a)** Plot of the pressure of each model vs the number of H_2 molecules. Solid lines show our results while dashed lines show Henry's law. **(b)** Hydrogen accessible free volume of the 5 crosslinks EPDM model with 1000 H_2 molecules at pressure and **(c)** after decompression.*

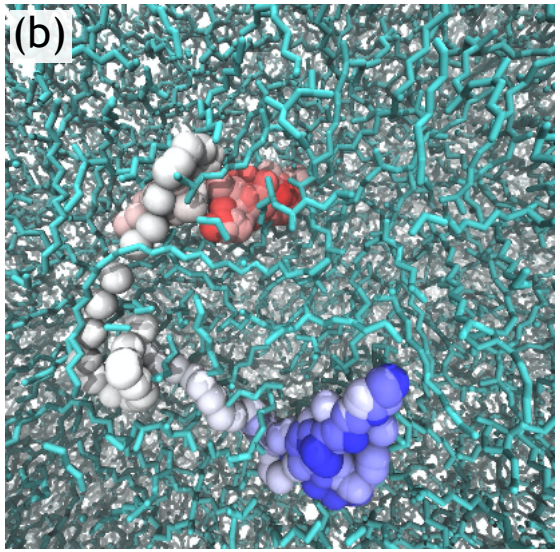
Sub-diffusive high pressure H_2 gas dynamics

SUCCESSES:
- Identified sub-diffusive behavior of H_2 which was larger at temperatures below glass transition temperature.
- Showed that the slower moving H_2 atoms were localizing away from sulfur on the crosslinks.

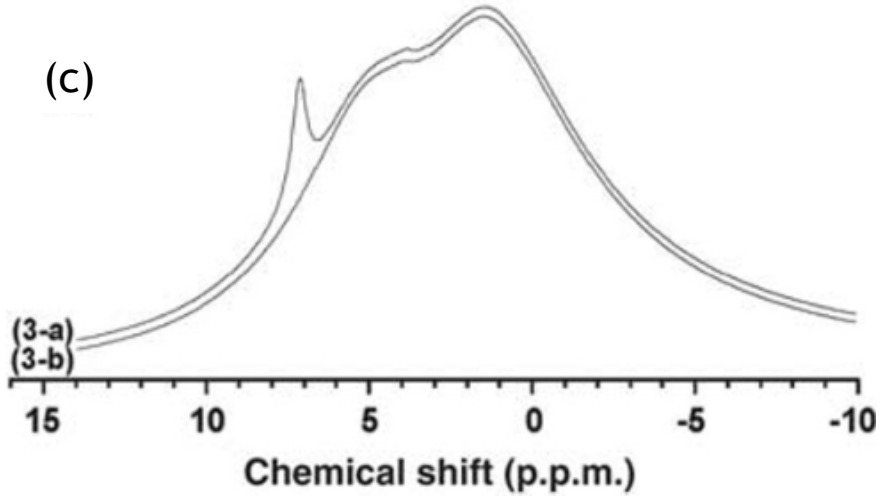
METHOD:
- Movement of H_2 gas is measured and analyzed over 2 ns of simulations time.
- Displacement of H_2 gas is measured to classify caged/mobile hydrogen.
- RDF is used to measure distribution of hydrogen throughout EPDM.

SIGNIFICANCE:
- Greater gas mobility occurs with greater crosslinks, higher temperatures, and lower gas concentrations.
- Caged hydrogen exhibits slow dynamics and localization, possible precursors to cavitation.





***(a)** Mean squared displacement of EPDM with 1000 H_2 molecules showing sub-diffusive behavior increases as temperature decreases. **(b)** Trace of a single H_2 molecule moving from one caged cite to another. Time is represented by the colors starting on red and moving to white then blue. **(c)** ¹H NMR spectra of NBR exposed to 100 MPa of hydrogen gas indicating two types of dissolved hydrogen in NBR.**



* Fujiwara and Nishimura DOI:10.1038/pj.2012.111

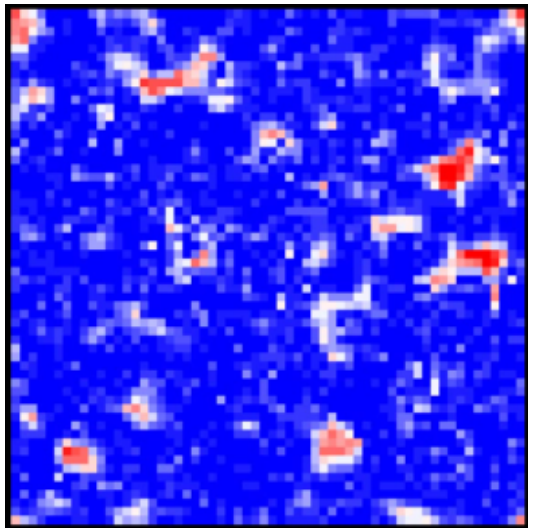
Analysis of dynamic free volume

SUCCESSES:
- Developed postprocessing method to analyze free volume much faster than previously
- Observed dynamic behavior of free volume and identified persistent areas of free volume
- Identified a correlation between free volume before and after decompression which increases with greater crosslinking

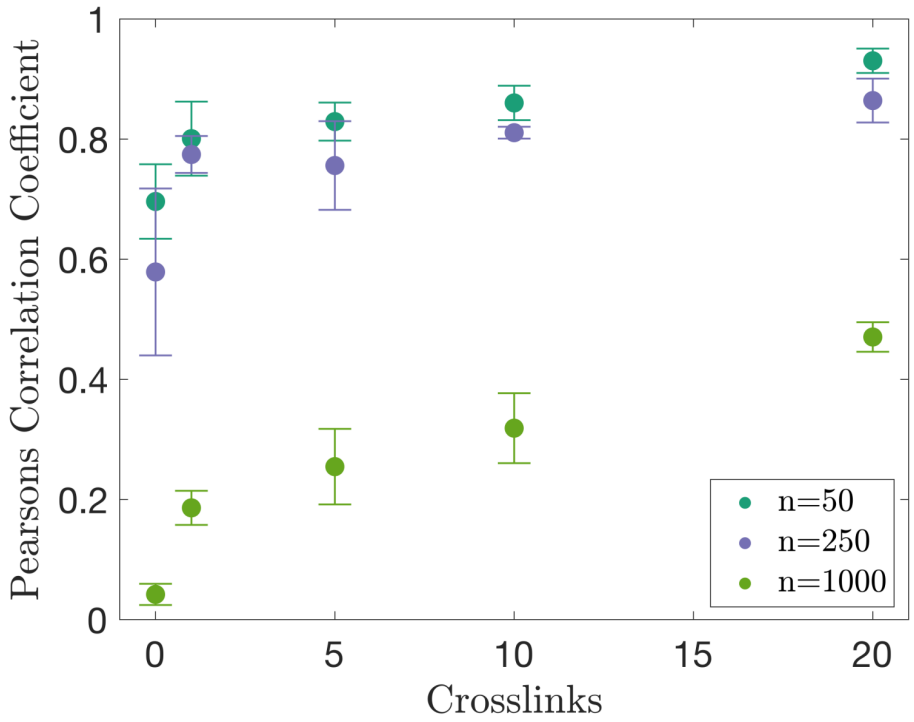
METHOD:
- A new tool was created to analyze the free volume of a system and to compare the free volume with atom displacements and locations.

SIGNIFICANCE:
- Increasing crosslinks increases the correlation of free volume before and after decompression.
- Now able to know how free volume is created during decompression

(a)



(b)



***(a)** Video of a 2D slice of free volume movement with time. The color map indicates the average time a pixel is free volume. **(b)** Pearson's correlation coefficient of the free volume before and after decompression, showing increased correlation with increased crosslinks.*