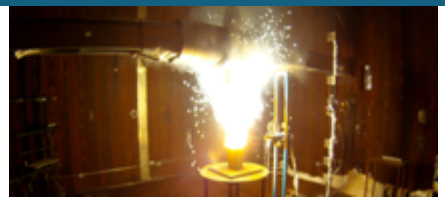
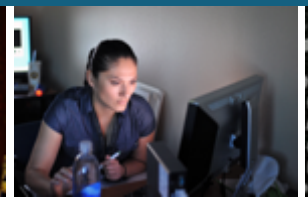
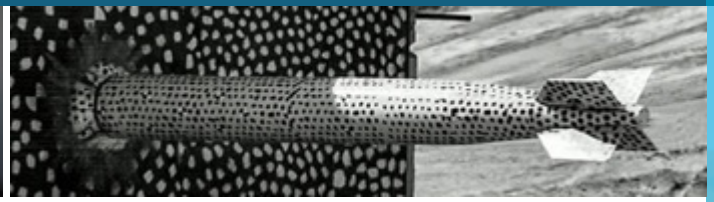
SAND2021-14237PE

Science-Based Advancement of Materials for Hydrogen Technologies (H-Mat: Polymers)







Task P2: Polymer Modeling – Atomistic

Virtual Face-to-Face Meeting
11/9/21 - 11/10/21

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

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

[2]Nanostructure Physics (org 1881)

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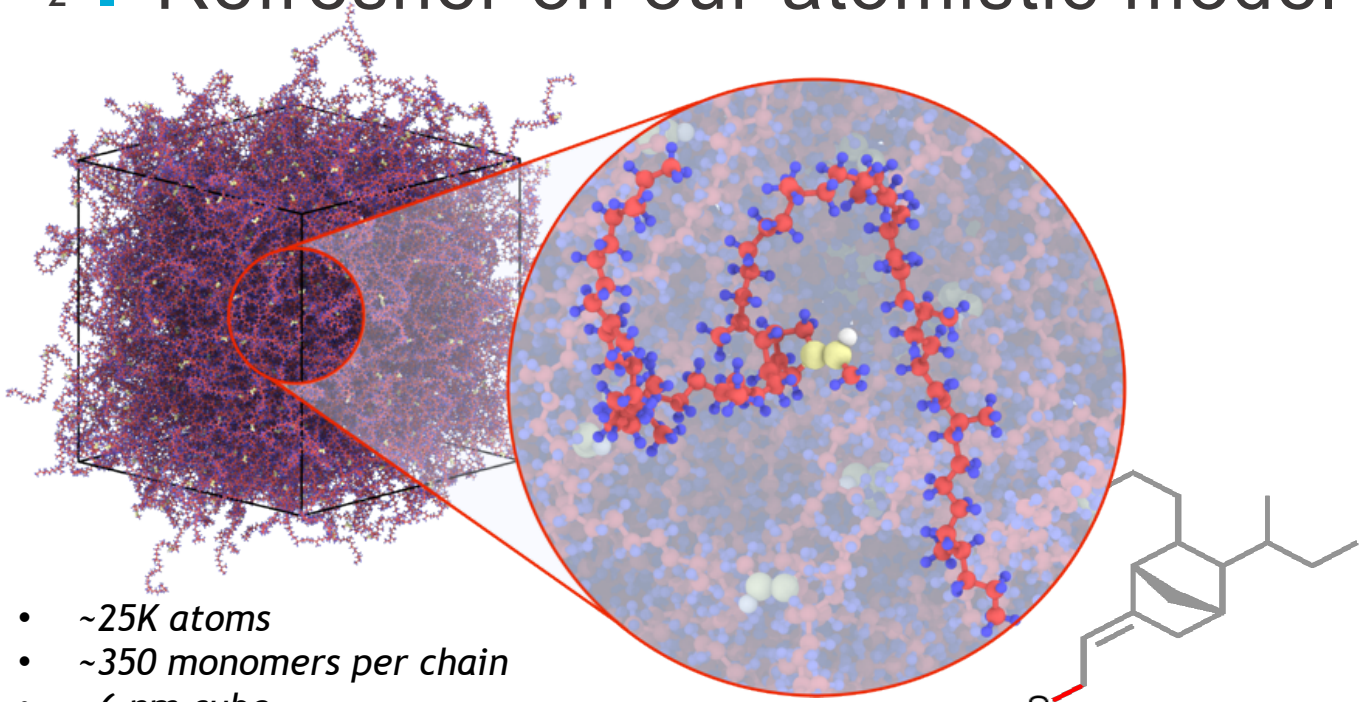
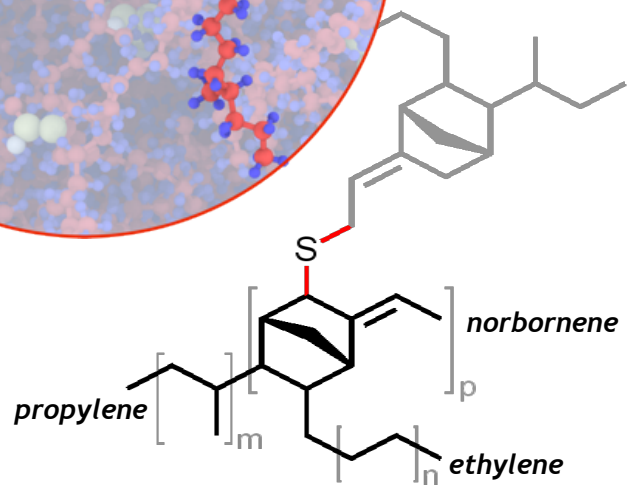
Refresher on our atomistic model



- *~25K atoms*
- *~350 monomers per chain*
- *~6 nm cube*
- *Constructed at 1.0 g/cc*
- *NPT ensemble to 1 atm pressure*

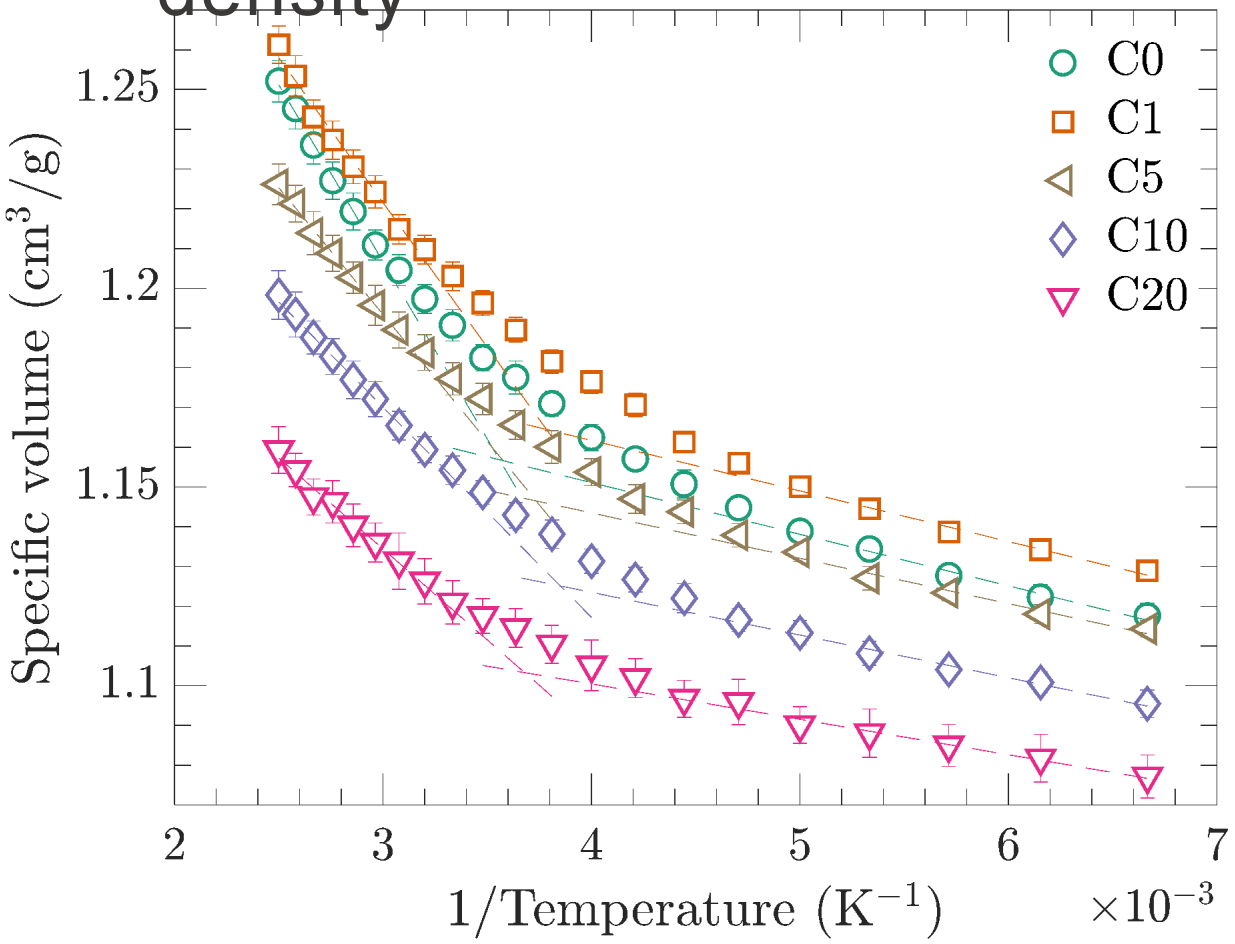


- Utilized an all-atom material representation of crosslinked EPDM.
- Performed classical molecular dynamics with pair-wise interactions defined according to the Jorgensen OPLS interatomic potential [A]
- Entangled configurations at crosslinked consistent to a sulfur vulcanization [B]
- Add hydrogen at various concentrations
- **FY21 direction:** Study role of temperature and crosslink density on gas dynamics in EPDM

[A] *W.L. Jorgensen J. Am. Chem. Soc. (1996)*
[B] *M. Van Duin, Kautschuk Gummi Kunststoffe 55. (2002)*
[C] *Nishimura, Takaishi Model Compound Series Review (2018)*
[D] *S.S. Kulkarni, Int. J. Hydrogen Energy (2021)*

Simulation label	C0	C1	C5	C10	C20	EXP
Number of crosslinked ENB/chain	0	1	5	10	20	5
wt.% ENB	9.76	2.45	11.1	20.1	33.4	10.0 [C,D]

Crosslinks increase glass transition temperature and density



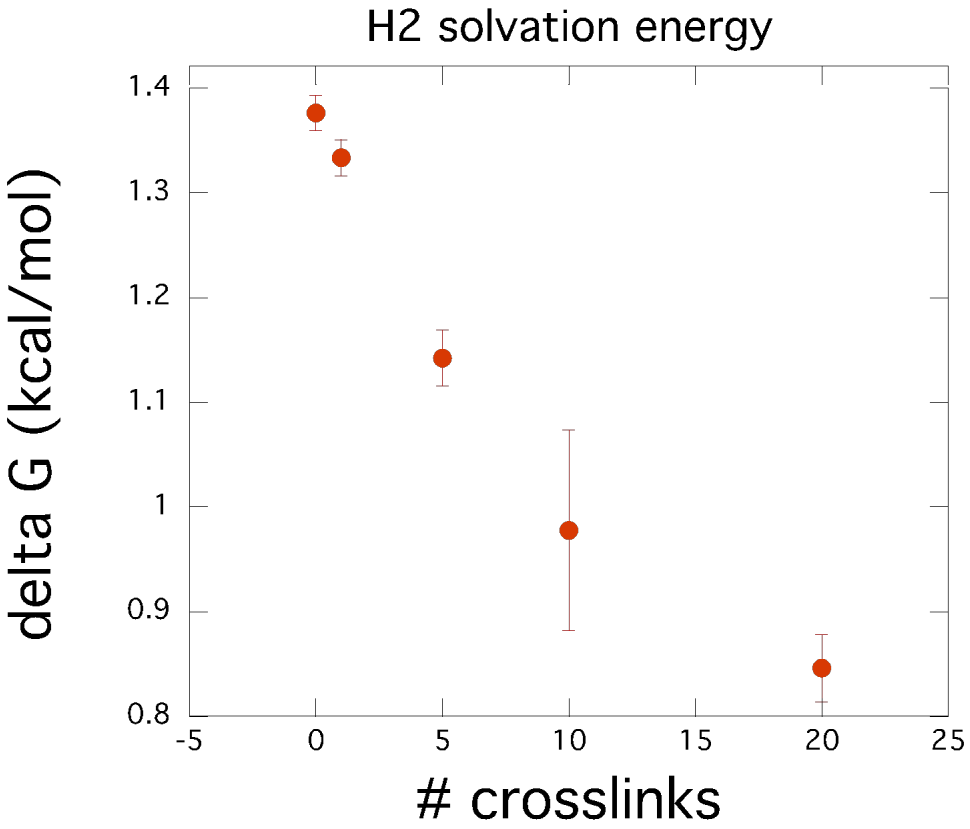
- Assess glass transition temperature using volume-temperature plot
- Run NPT (isothermal-isobaric) dynamics at multiple temperatures and 1 atm of pressure
- **Observations:**
  - Crosslinks increase density at all temperatures
    - Due to addition of sulfur and decrease in volume
  - T_g increases with crosslinks

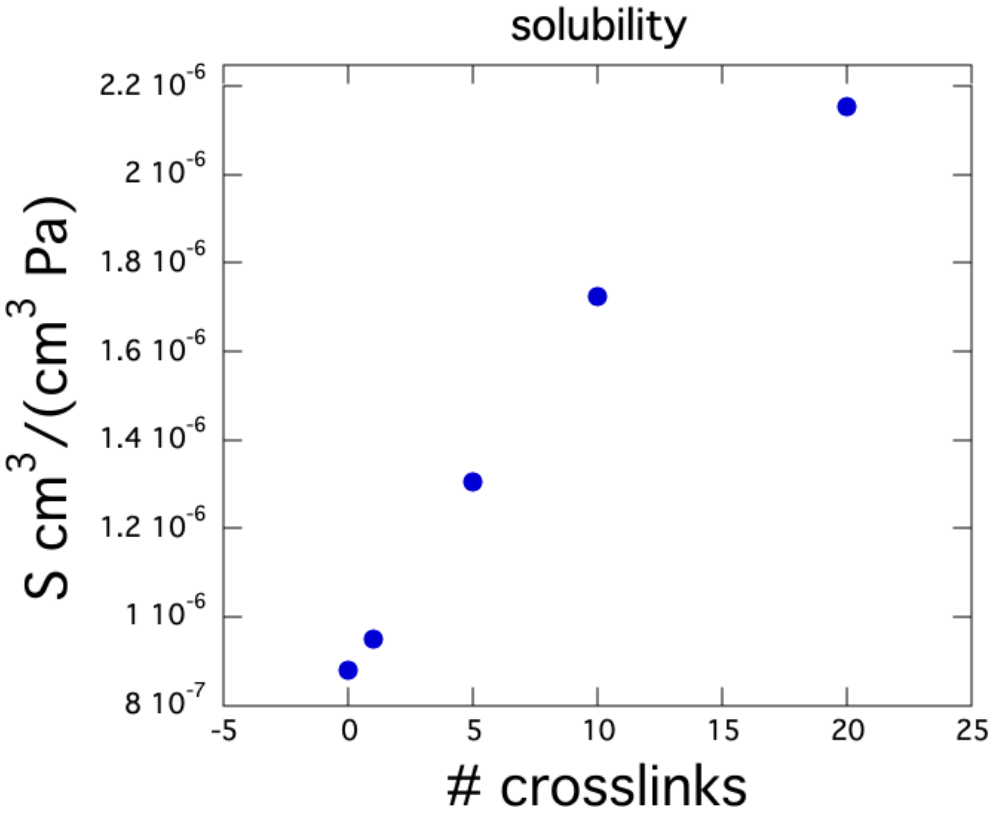
[A] *T. Mokhothu, Polymer testing, 33, 97-106, (2014)*
[B] *Nishimura, Takaishi Model Compound Series Review (2018)*
[C] *S.S. Kulkarni, Int. J. Hydrogen Energy (2021)*

Simulation label	C0	C1	C5	C10	C20	EXP
T_g(K)	280.9 ± 1.1	264.3 ± 11.5	267.8 ± 10.6	259.7 ± 10.0	271.8 ± 14.4	231.5 [A]
ρ (g/cm³) at 300K	0.841 ± 0.003	0.833 ± 0.001	0.849 ± 0.002	0.867 ± 0.002	0.889 ± 0.002	0.921 [B,C]

Hydrogen solubility

calculated by thermodynamic integration
averaged over 3 configs for each system

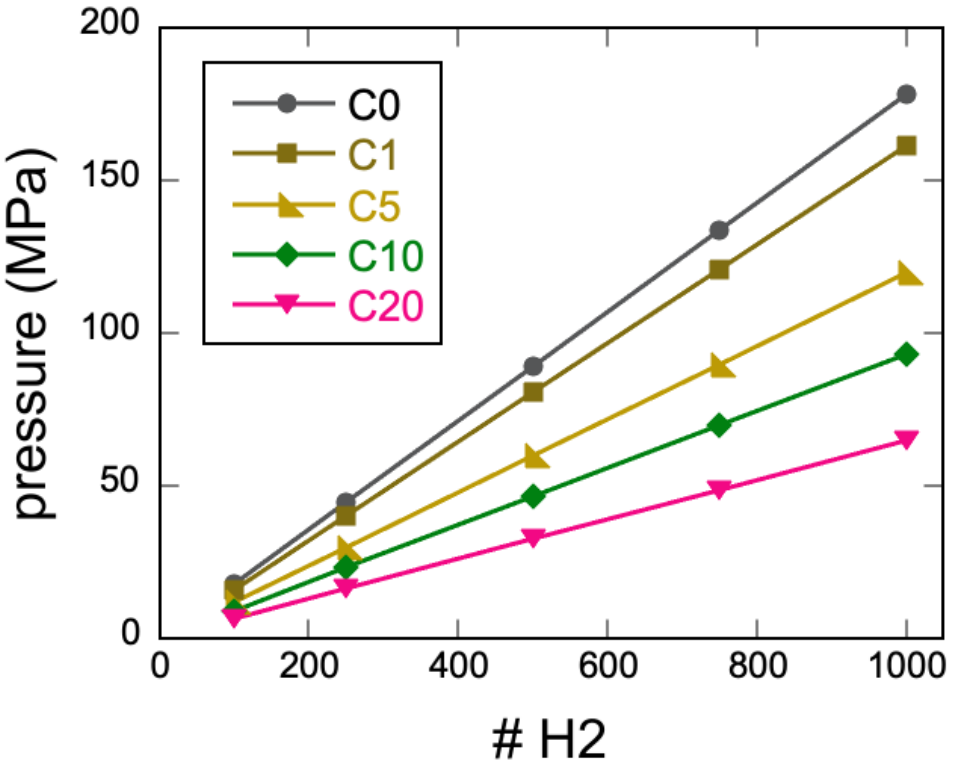




previous sims for H2 in EPDM: S = 0.68e-6 $cm^3/(cm^3\ Pa)$
experiment for H2 in EPDM: S = 0.394e-6 $cm^3/(cm^3\ Pa)$

Implications of H_2 solubility

If Henry's law holds: p = c/S

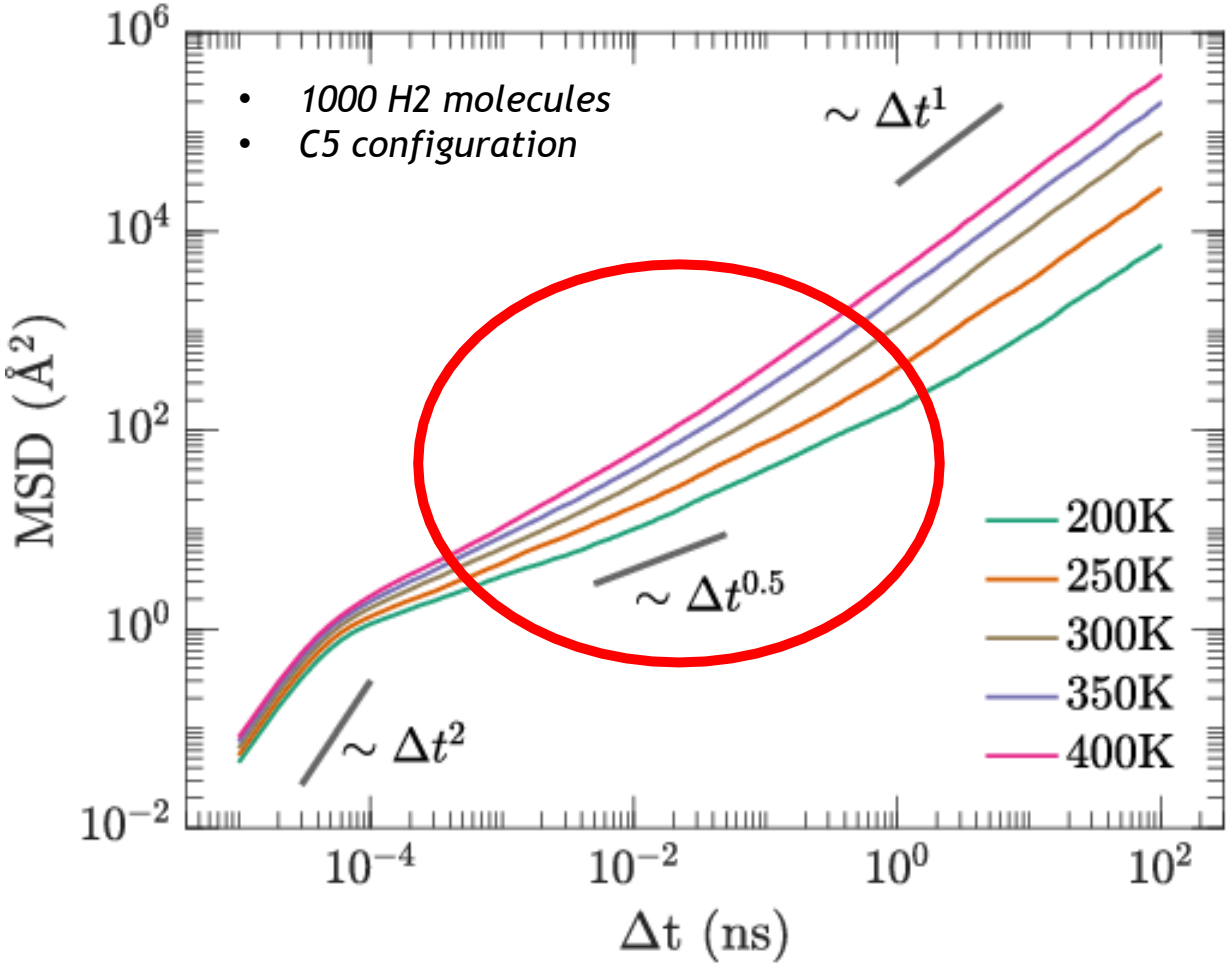


lower crosslink systems are at higher pressure for same H2 concentration

at high pressure:

- indications that Henry's law does not hold
- free energy to insert H_2 goes up
- extracting pressure vs concentration requires different simulations

Mean squared displacement highlights anomalous gas diffusion

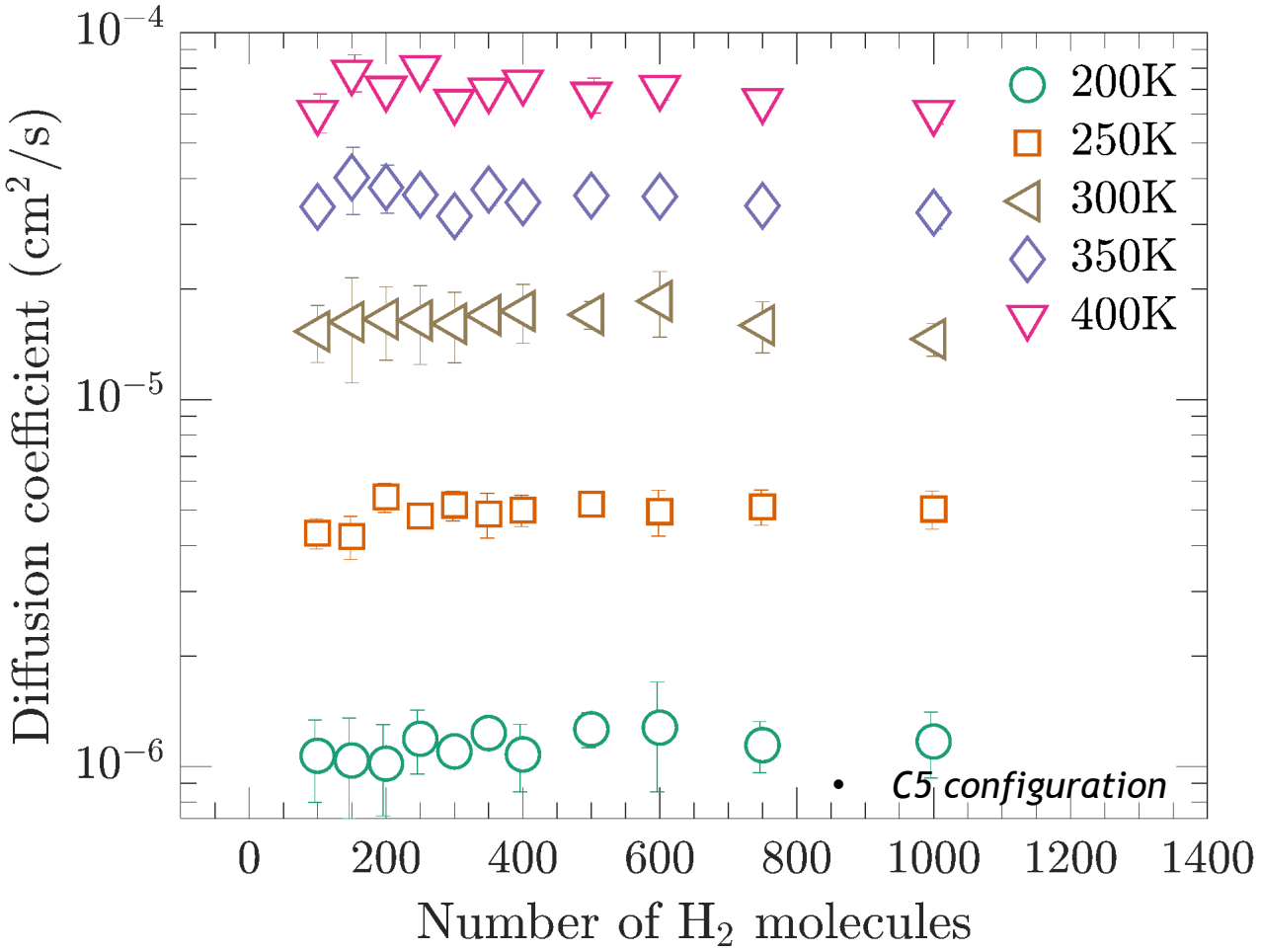


- Mean squared displacement (MSD) shows pressurized gas dynamics in the polymer

$$\text{MSD} = \langle \Delta r^2(t) \rangle = \langle |\boldsymbol{r}(t_0 + t) - \boldsymbol{r}(t_0)|^2 \rangle$$

- Ensemble average behavior
- **Observations:**
  - Multiple regimes: ballistic ($\sim \Delta t^2$) diffusive ($\sim \Delta t^1$) and sub-diffusive ($\sim \Delta t^{0.5}$)
  - Intermediate timescales show anomalous sub-diffusive diffusional properties exaggerated at low-temperatures

Diffusion coefficient invariant with gas concentration

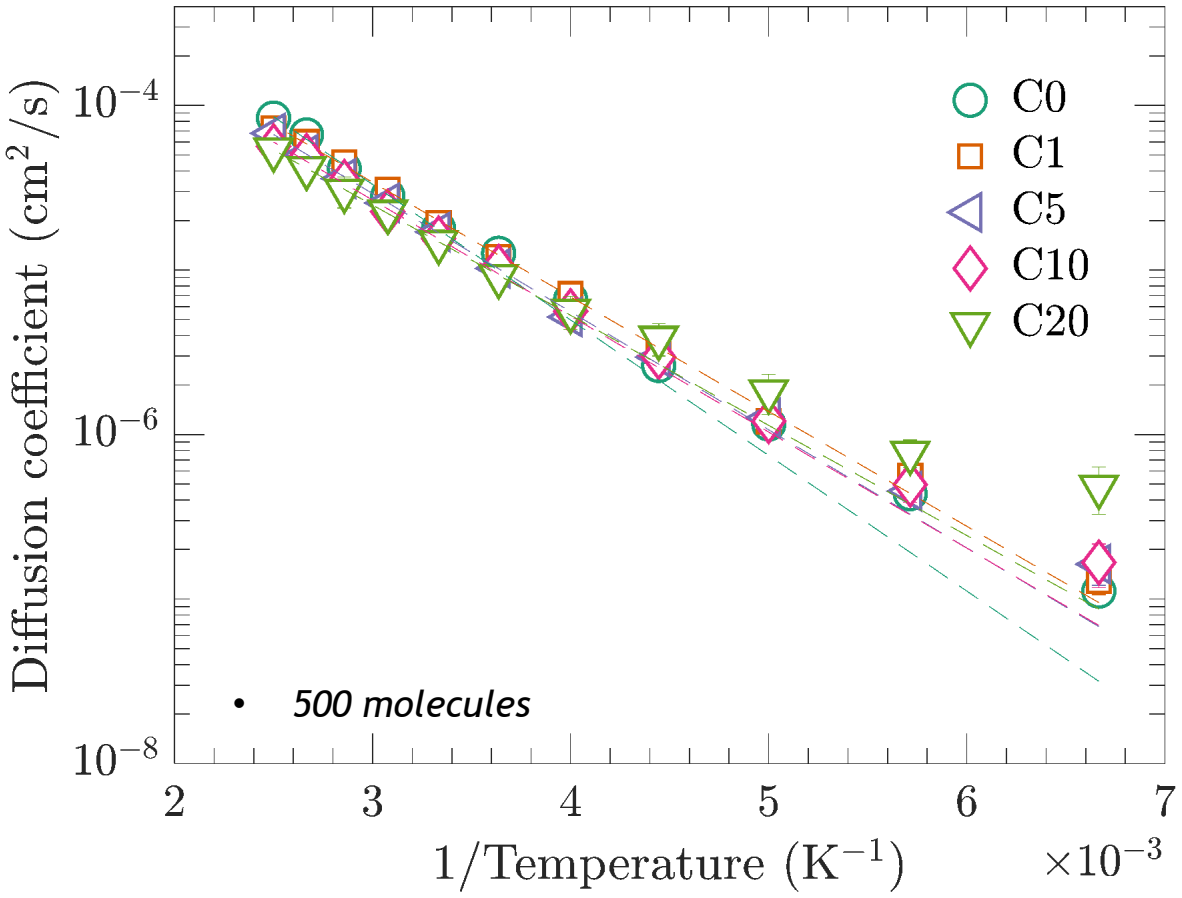


- Calculate the diffusion coefficient from the slope of the MSD in the diffusive regime

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

- Ensemble average behavior
- **Observations:**
  - Lower temperatures result in slower gas dynamics
  - Increased gas concentrations have consistent values, suggesting steric effects are not important in gas diffusion

Crosslinks promote low-temperature gas diffusion

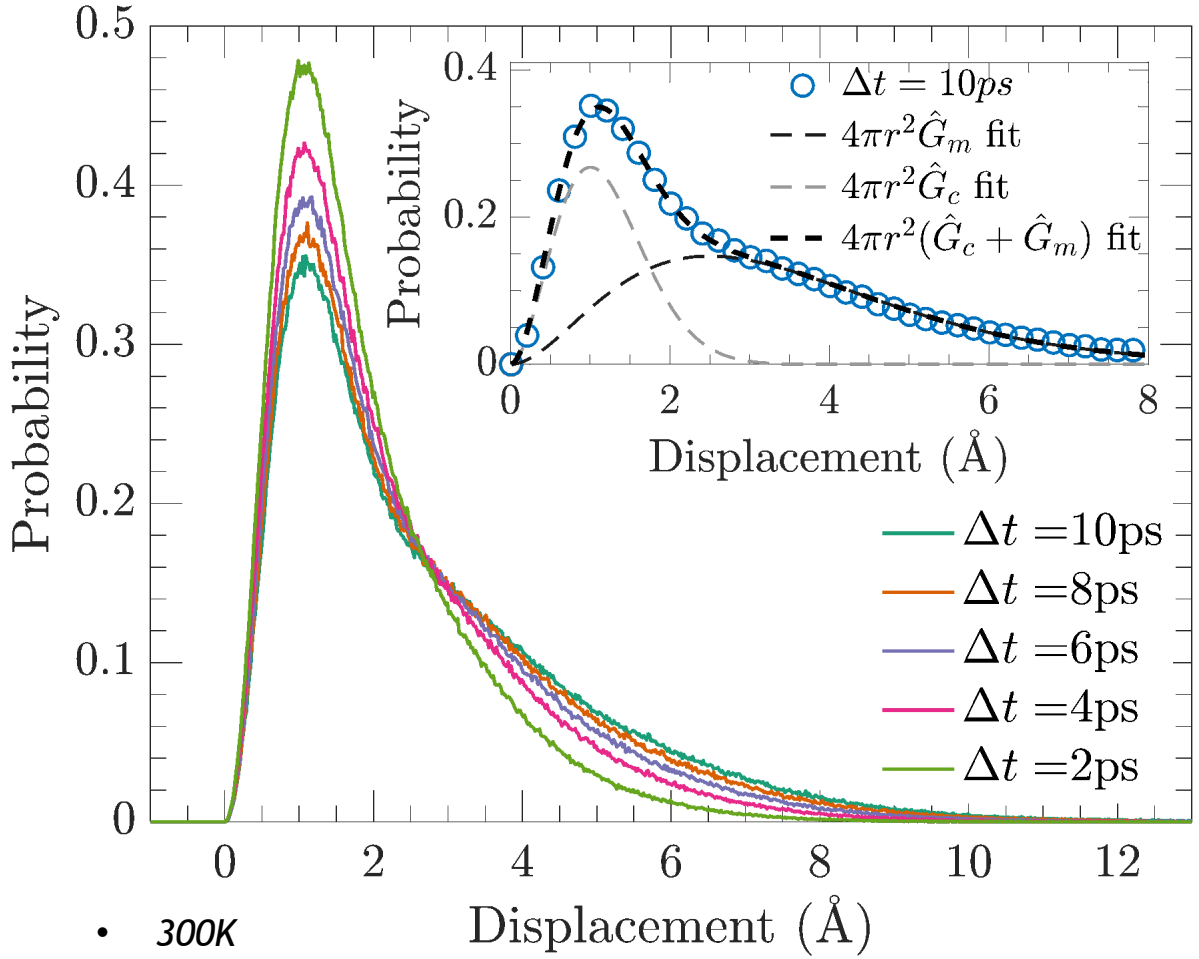


- **Observations:**
  - Decreases in diffusion with decreased temperature
  - Low-temperature values overestimate Arrhenius behavior $D = D_0 \exp(-E_A/RT)$
    - Suggests mobility-limited polymer improved diffusional properties of dissolved gas
  - High-temperature diffusivity decreases with increased crosslinks
    - Indicative of a more dense material impeding diffusion
  - Increased crosslinks result in greater low-temperature diffusion

[A] *S.W. Rutherford, Polymer (2007)*
[B] *J.Tan, RSC Adv. (2020)*
[C] *G.J. Van Amerongen, J. Appl. Phys., (1946)*

Simulation label	C0	C1	C5	C10	C20	EXP, SIM
$D(\mathrm{cm^2/s}) \times 10^{-6}$	17.9 ± 1.8	19.3 ± 2.2	17.0 ± 0.2	15.6 ± 1.1	14.7 ± 3.4	8.0 [A] , 87.4 [B]
$D_0(\mathrm{cm^2/s}) \times 10^{-3}$	5.9 ± 0.8	4.6 ± 1.5	4.5 ± 2.0	3.1 ± 0.9	2.6 ± 0.2	
E_A (kJ/mol)	14.3 ± 0.3	13.5 ± 0.9	13.7 ± 1.1	13.0 ± 0.9	12.9 ± 0.5	~20.0 [C], ---

Atomistic detail shows origin of sub-diffusive behavior



- *300K*
- *C5 configuration*
- *500 molecules*

- Calculate average displacement from simulation trajectories

$$G_s(r,t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta(r - |r_i(t) - r_i(t_0)|) \right\rangle$$

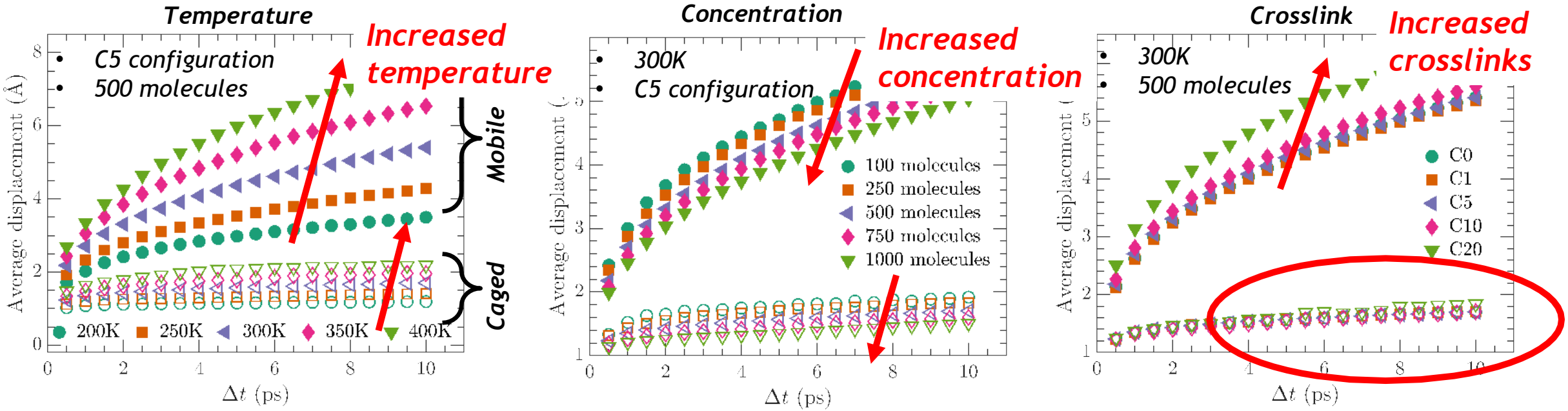
- Bimodal distribution is suggestive of two groups of gas in polymer

$$G_s(r,t) \approx 4\pi r^2 \left(\hat{G}_1(r,t) + \hat{G}_2(r,t)\right)$$

- Two groups with differing diffusional dynamics has been characterized in NBR via ^{1}H NMR [A, B]
- We curve fit the distributions
- **Observations:**
  - Low-displacement peak remains at constant value with time
  - Higher-displacement tail increases with time

[A] *S. Nishimura, Chem. Phys. Lett. (2012)*
[B] *H. Fujiwara, Polym. J. (2012)*

Statistical analysis of curve fits show behavior of both groups



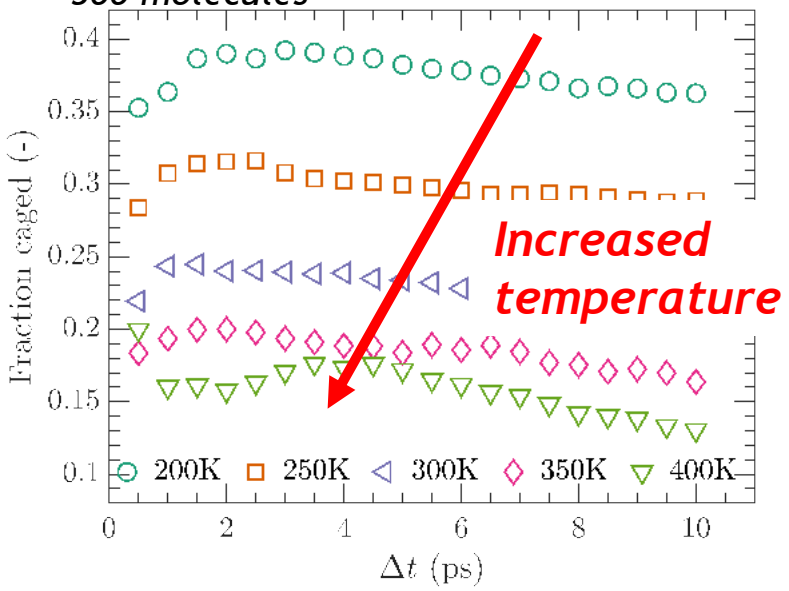
- Calculate expectation value of displacement from the fit distributions

- **Observations:**
  - Increased temperatures results in increased displacements for both groups
  - Increased concentrations decrease displacements. Suggestive of steric effects impacting diffusional properties. Counter to bulk response
  - Increased crosslinks increases diffusion in mobile group. Displacement of caged group is consistent, suggestive that caging structure is the same from one crosslink density to next

Statistical analysis of curve fits show behavior of both groups

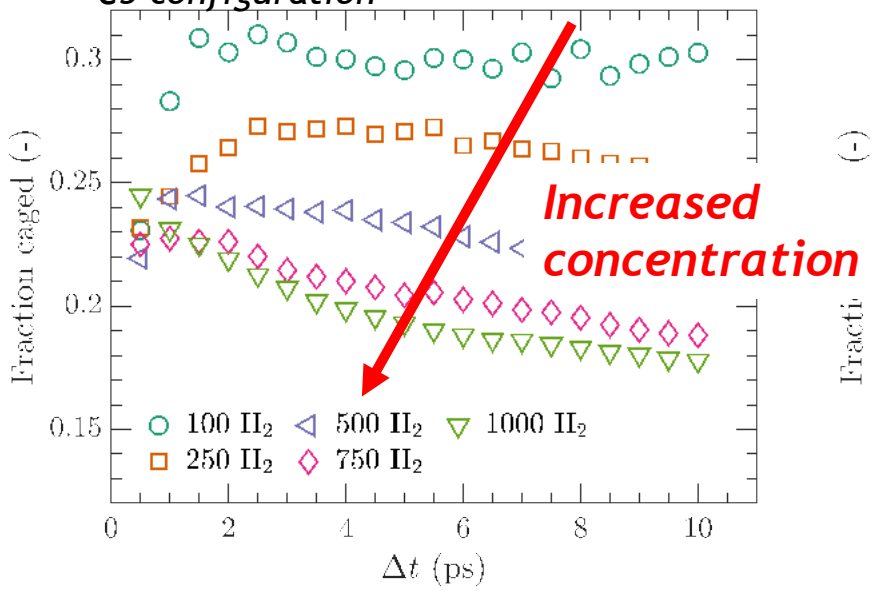
- *C5 configuration*
- *500 molecules*

Temperature



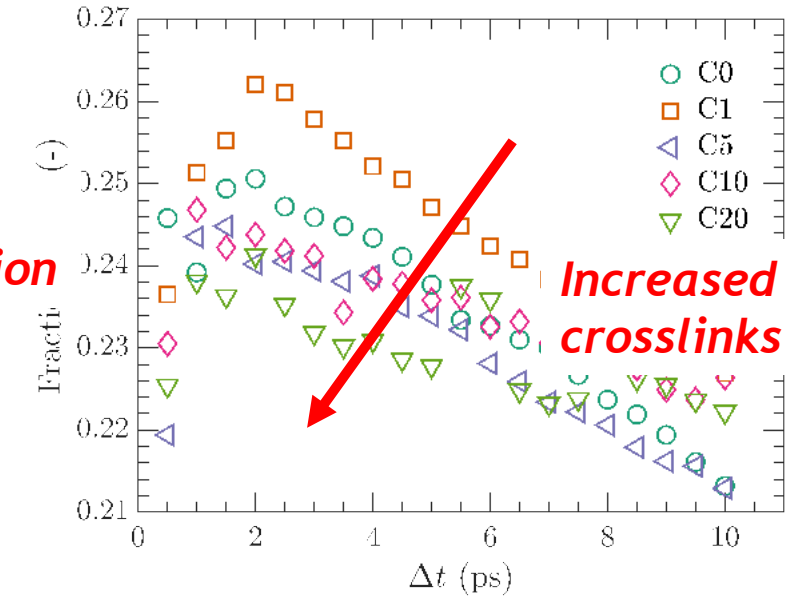
- *300K*
- *C5 configuration*

Concentration



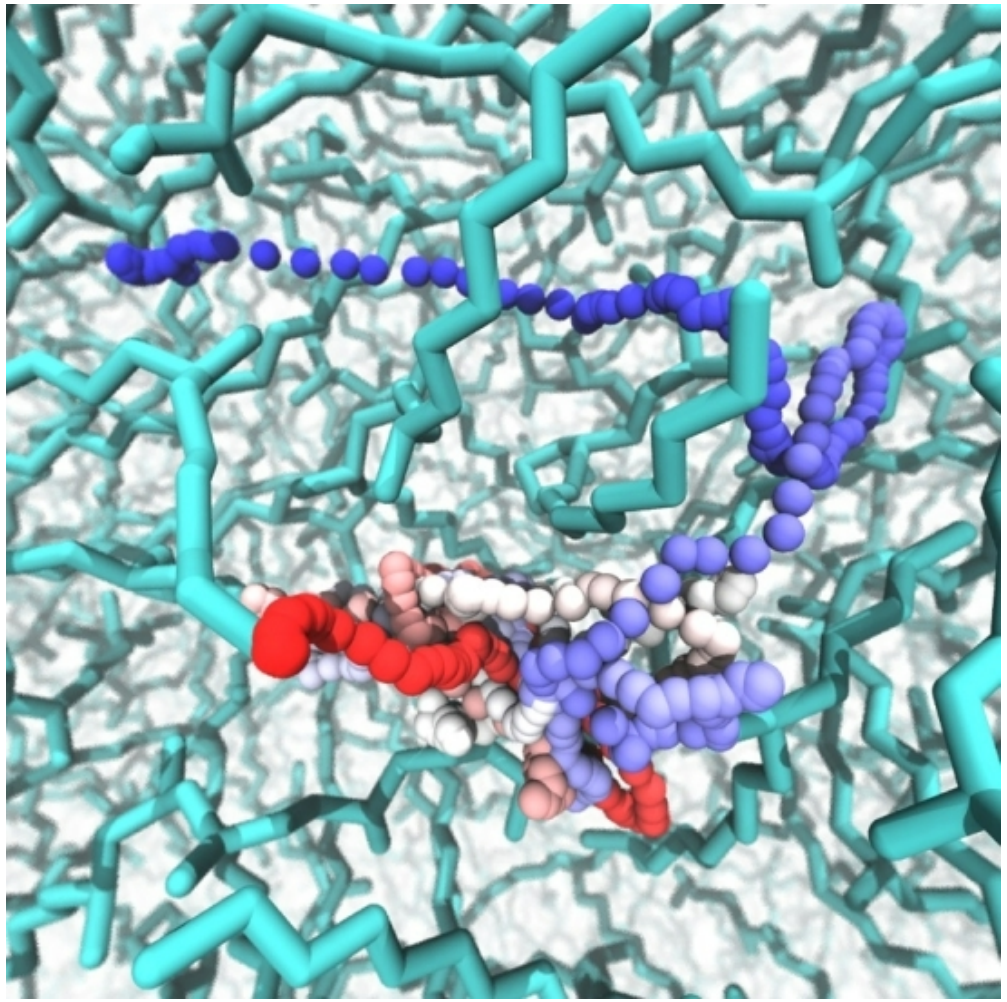
- *300K*
- *500 molecules*

Crosslink



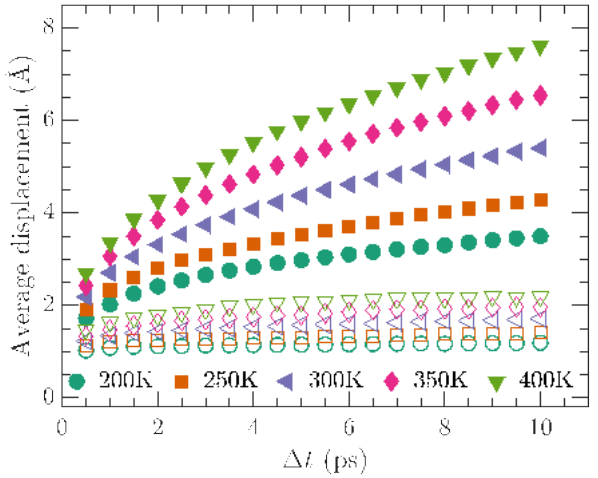
- Calculate population of caged group from fits as $f_c(t) = \sum_{r=0}^{\infty} \frac{\hat{G}_c(r,t)}{\hat{G}_c(r,t) + \hat{G}_m(r,t)}$
- **Observations:**
  - Caged classification is finite in time
  - Increased temperatures results in decrease in caged fraction
  - Increased concentrations decrease caged fraction. Suggestive of finite number of caged sites
  - Increased crosslinks decrease caged fraction. Indicative that higher-mobility gas accompanies crosslinks

Cage-to-cage hopping from simulation trajectories



EPDM
Hydrogen early in time
Hydrogen later in time

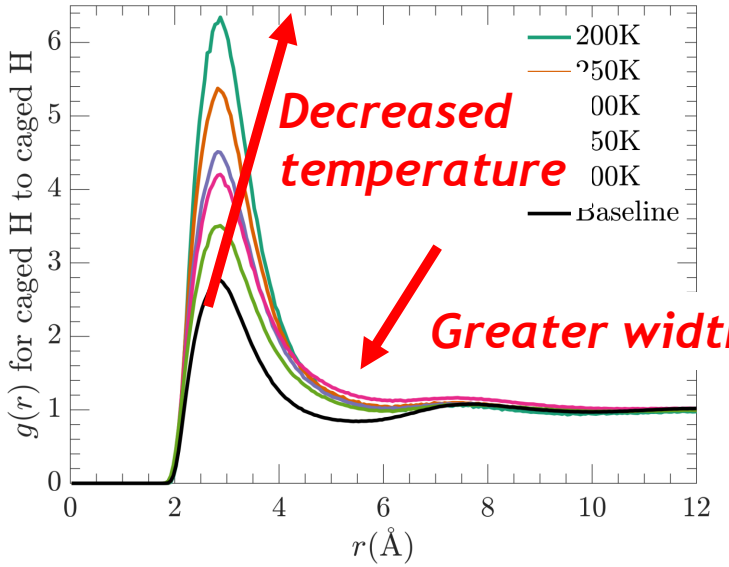
- A caged molecule does not necessarily remain caged
- Trajectories identify that hydrogen often remains localized (caged), and then switches to mobile. "Cage-to-cage hopping"
- Steady-state simulations on average show behavior presented in earlier slides
- Example of where bulk ensemble average behavior does not tell the entire story
- Define a caged classification
  - 2Å in 0.5 ps



Caged hydrogen tends to localize

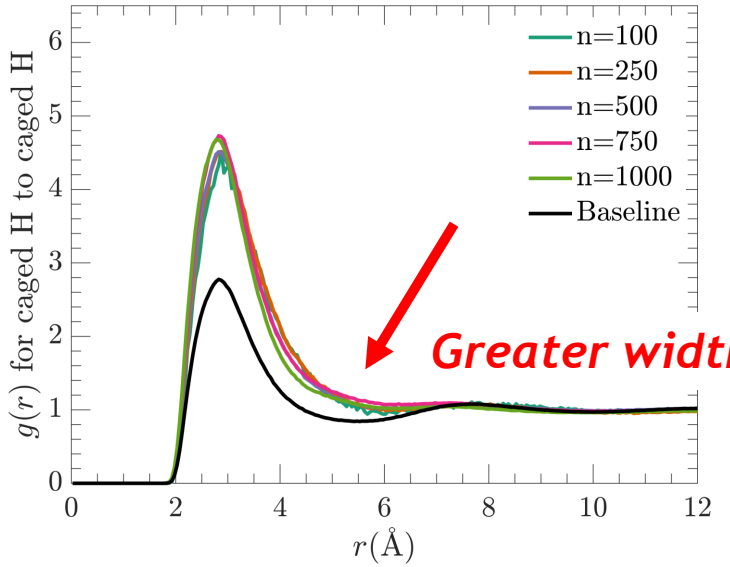
- *C5 configuration*
- *500 molecules*

Temperature



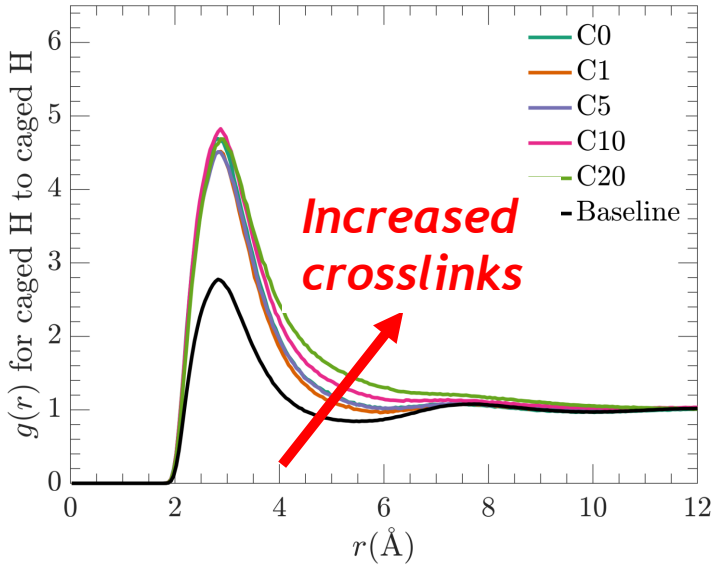
- *300K*
- *C5 configuration*

Concentration



- *300K*
- *500 molecules*

Crosslink

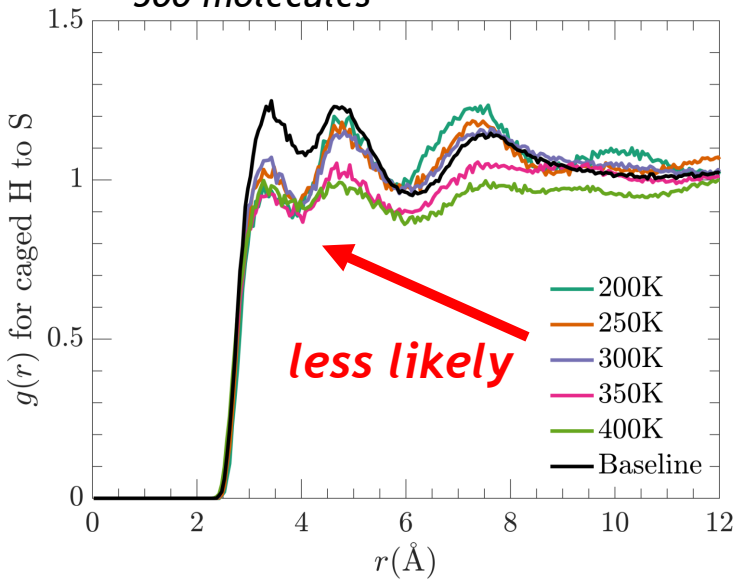


- Where is caged hydrogen located?
  Use a partial radial distribution function (RDF) to identify proximity likelihood
- Compare to “baseline” values of RDFs between **all** hydrogen
- **Observations:**
  - Increased temperatures results in localization of caged hydrogen. Width of caged sites increases
  - Increased concentrations have consistent RDFs with greater width
  - Increased crosslinks increase caged site size

Location of the caged group

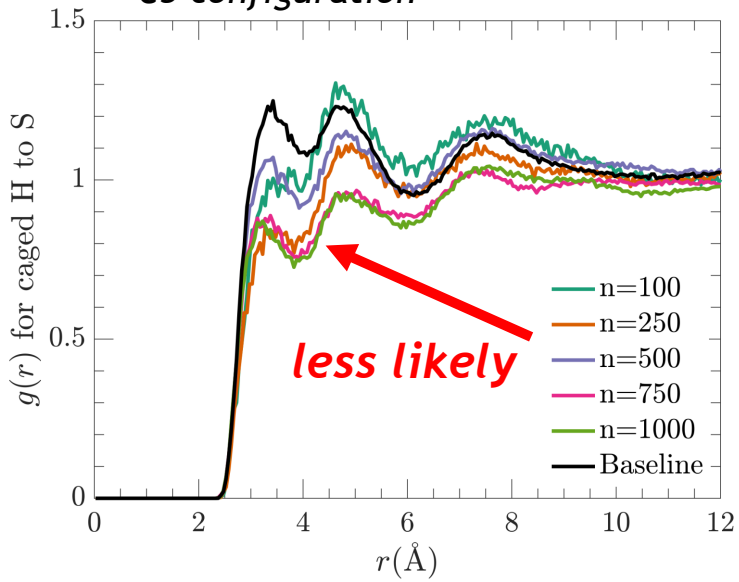
- *C5 configuration*
- *500 molecules*

Temperature



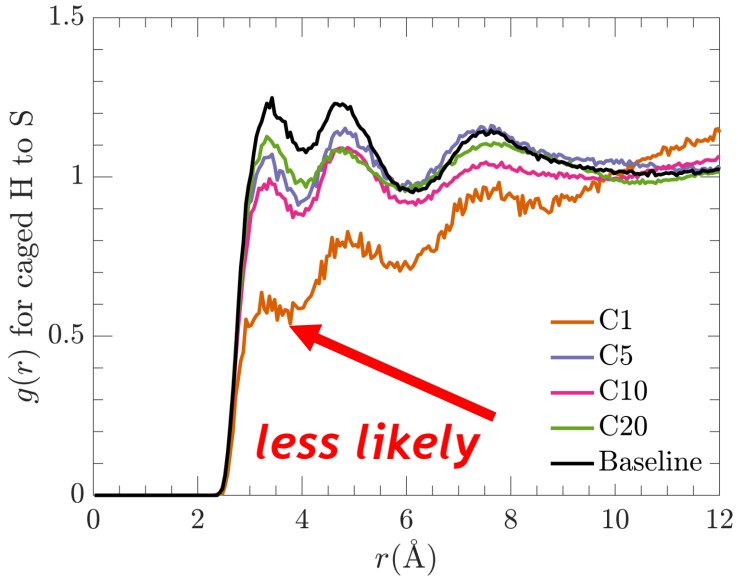
- *300K*
- *C5 configuration*

Concentration



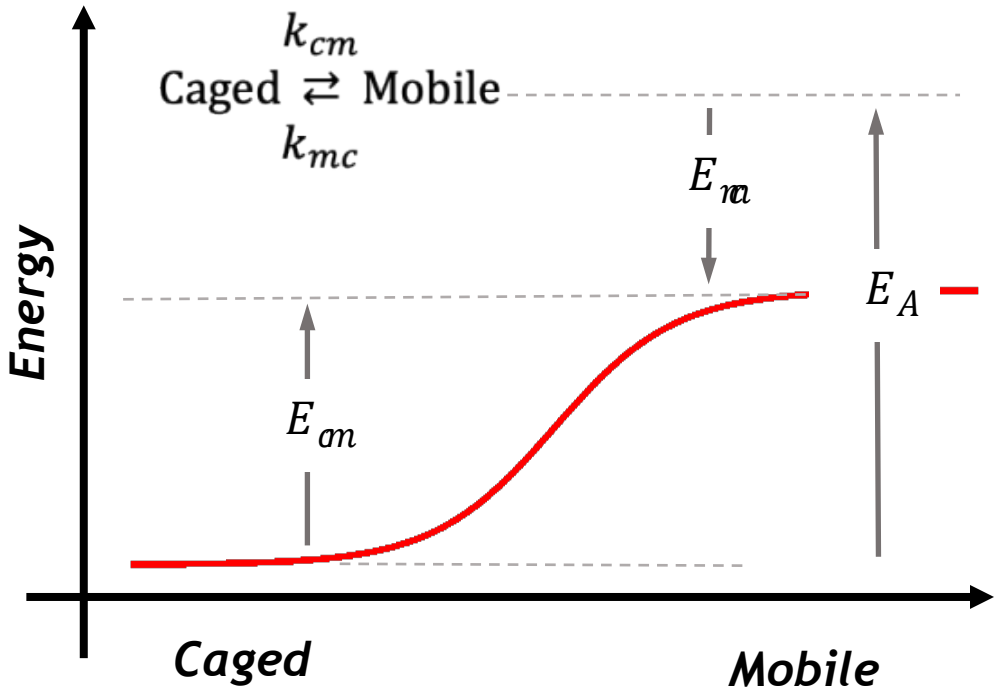
- *300K*
- *500 molecules*

Crosslink



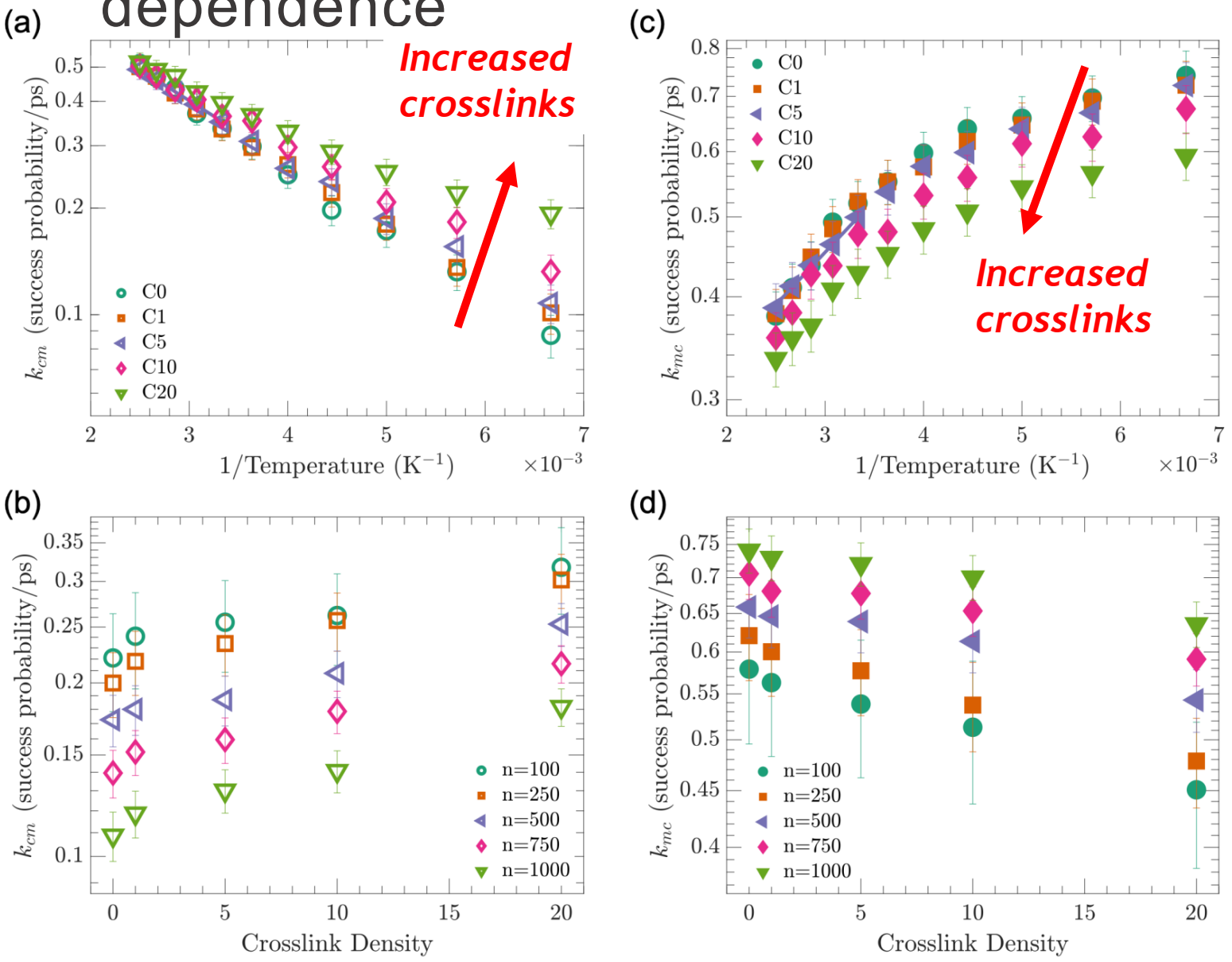
- Where is caged hydrogen located?
- **Observations:**
  - Caged is less likely to be located near sulfur atoms (crosslinks), as compared to baseline values

Quantifying transitions between groups



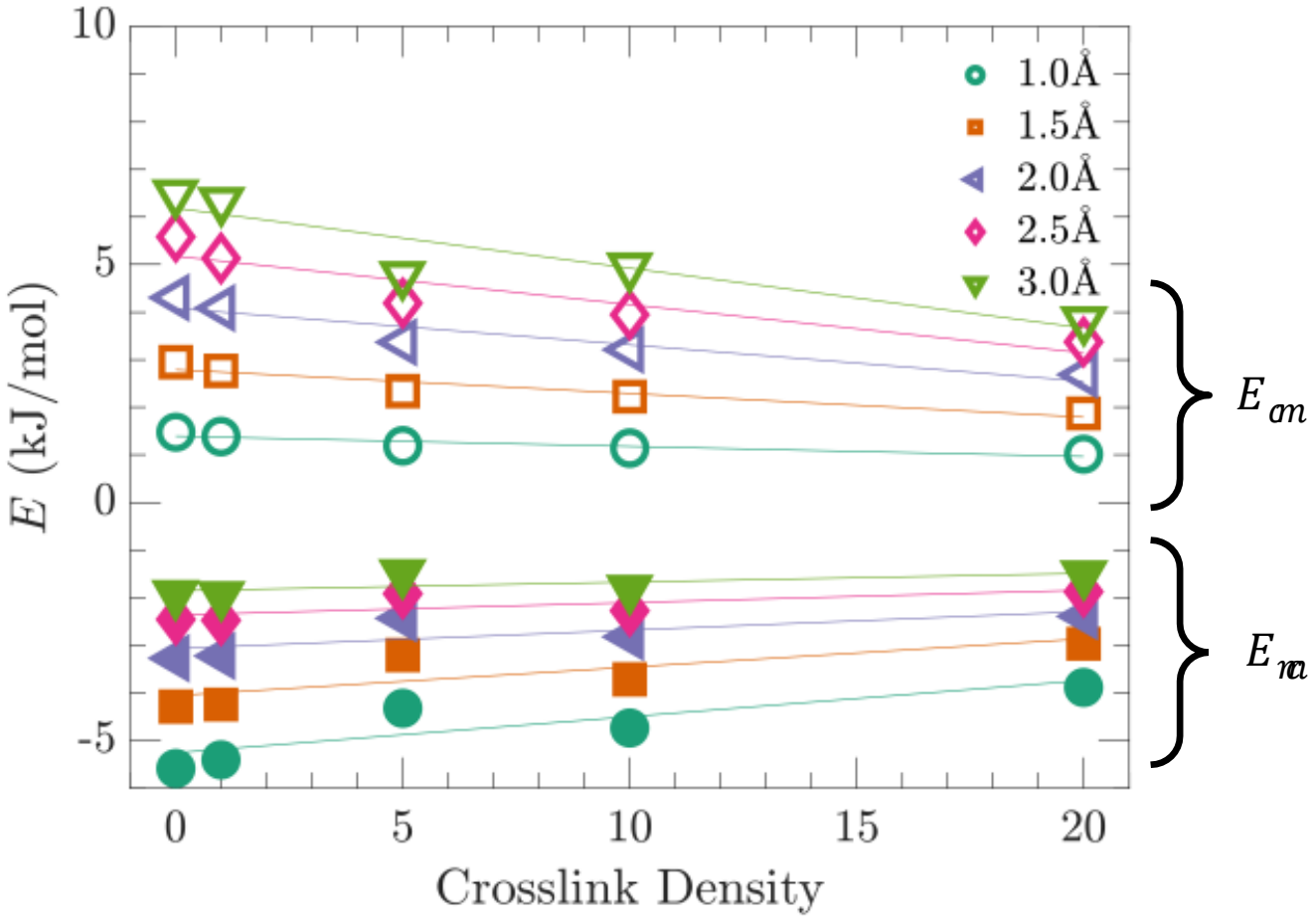
- Use a two-state kinetic model to quantify energetics association with changes in mobility
- Caged atoms are low on the energy scale
- Mobile atoms have any energy greater than the caged-to-mobile barrier height
- Calculate transition frequency, defined as a success probability
- From temperature dependent rates, we can calculate energetic barriers as $k = k_0 \exp(-E/RT)$

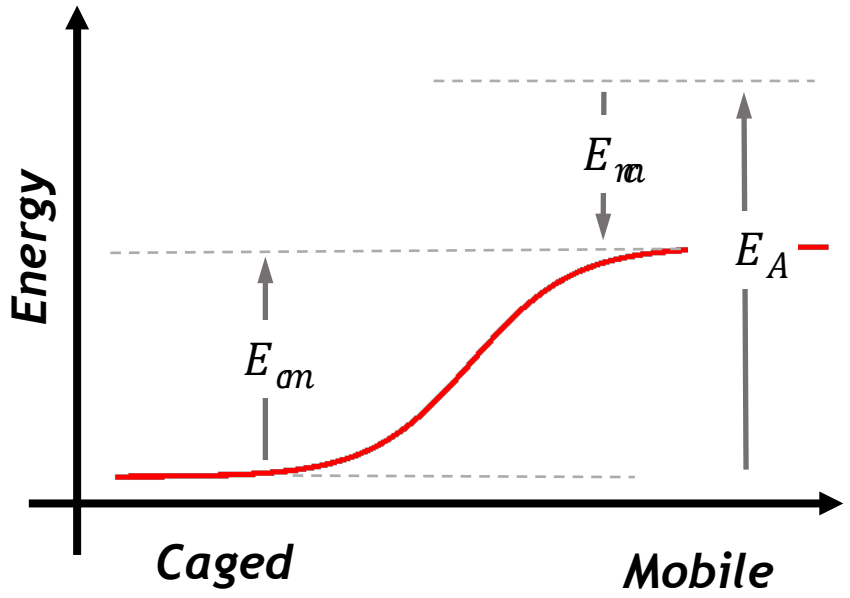
Transition rates show Tg and crosslink dependence



- General trends:
  - caged-to-mobile increases with temperature
  - mobile-to-caged decreases
- Two regimes exist $T > T_g$ and $T < T_g$
- Low-temperature values overestimate Arrhenius behavior
- Increased crosslinks increases caged-to-mobile and decreases mobile-to-caged
- From temperature dependent rates, we can calculate energetic barriers as $k = k_0 \exp(-E/RT)$

Crosslinks lower energetic barriers





- Increased crosslinks lowers energetic barriers to state transitions
- Increased cutoff raises E_{cm} and lowers E_{mc}

[A] G.J. Van Ameronge, J. Appl. Phys., (1946)

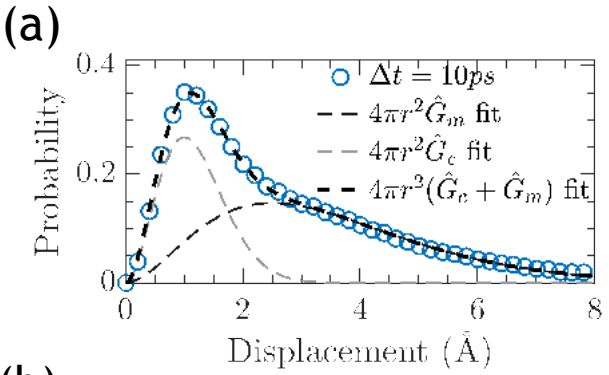
Simulation label	C0	C1	C5	C10	C20	EXP
E_A (kJ/mol)	14.3 ± 0.3	13.5 ± 0.9	13.7 ± 1.1	13.0 ± 0.9	12.9 ± 0.5	~20 [A]
E_{cm} (kJ/mol)	4.14 ± 0.02	3.92 ± 0.02	3.23 ± 0.01	3.08 ± 0.02	2.56 ± 0.02	--
E_{mc} (kJ/mol)	-3.36 ± 0.50	-3.29 ± 0.49	-2.56 ± 0.26	-2.93 ± 0.34	-2.51±0.22	--

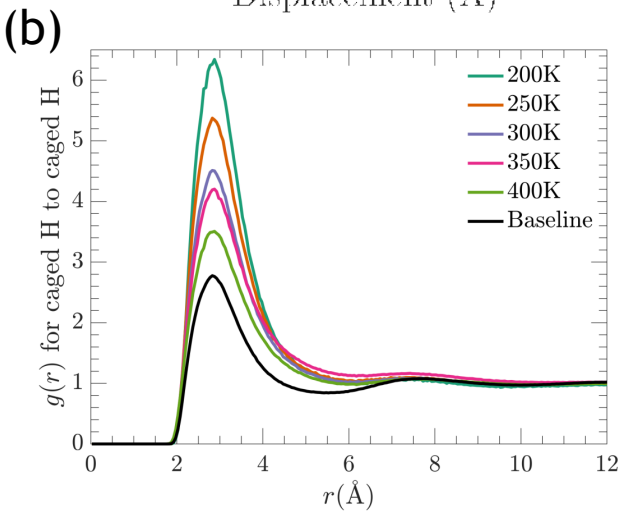
Summary and interpretation

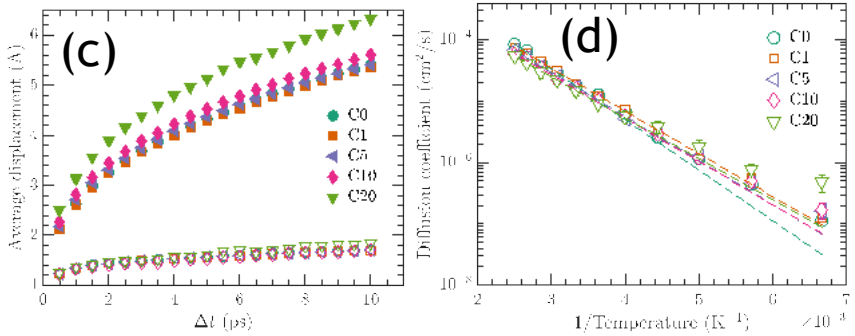
- Two groups of hydrogen with differing mobility are seen in simulation of hydrogen exposed EPDM **(a)**
- Sub-diffusive is a combination of the mobility of the two groups

- Provided cavitation is the onset of gas localization due to diffusion–limited oversaturation, **the caged group is identified as undesirable:**
  - Slower diffusional properties
  - Localization of gas creating larger caged sites **(b)** away from crosslinks

- We identify **an increase in crosslinks to improve**
  - Mobile group diffusion **(c)**
  - Increased low-temperature diffusion coefficients where dynamics is slowed **(d)**
  - Lower energetic barrier to mobile state. Increase frequency of

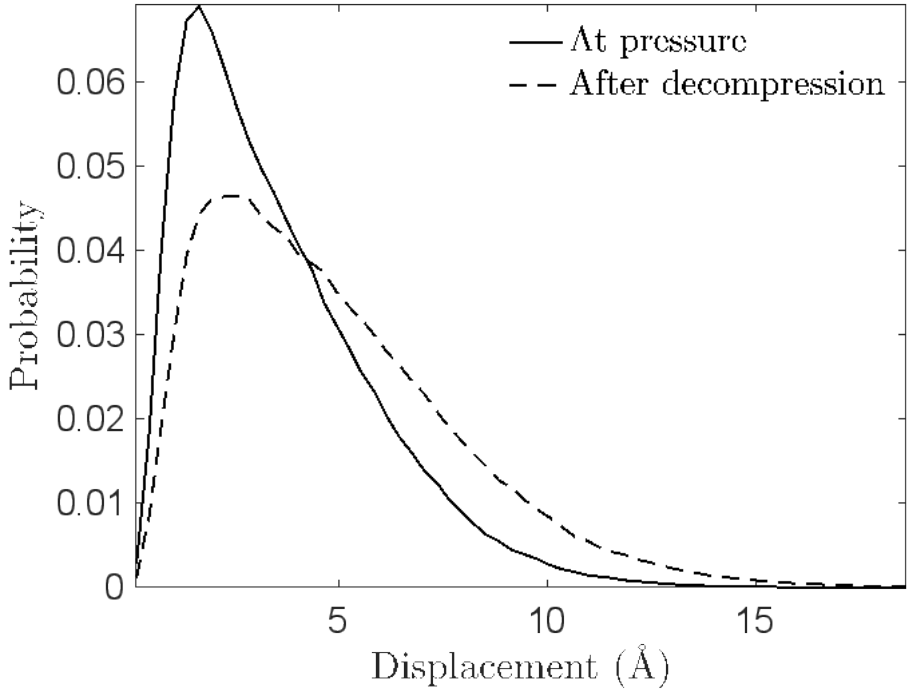




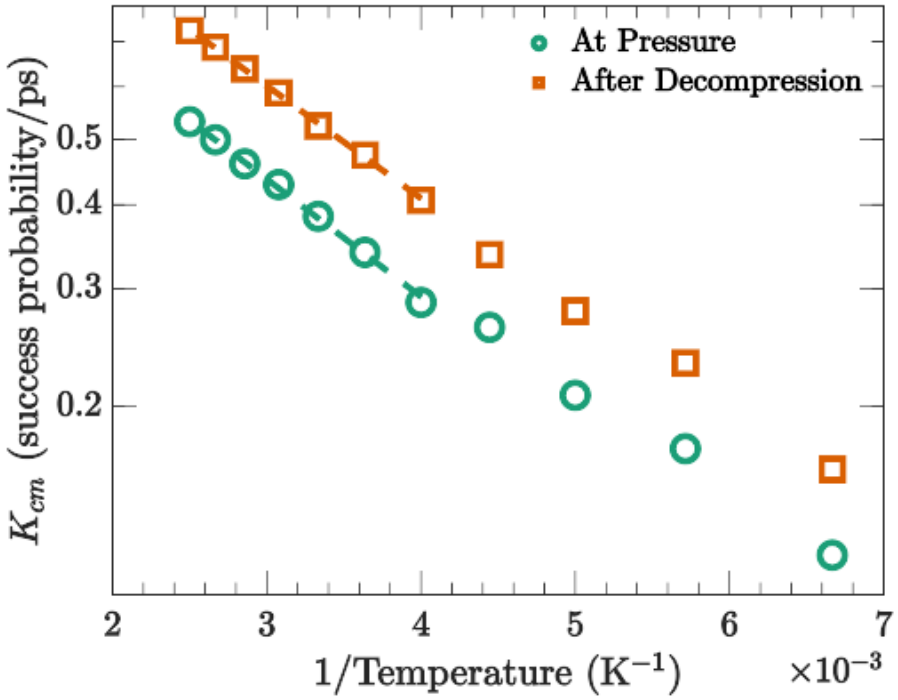


Where are we heading for FY22?

- *C5 configuration*
- *500 molecules*



- *C5 configuration*
- *500 molecules*



- Two-state model analysis following decompression
- Assess movement of free volume (FV) that occurs during the restructuring associated with decompression, as pressurized FV has been located near crosslinks and decompressed FV necessarily resides away from crosslinks.
- Relate transitions in mobility to spatial-temporal variations in free volume.