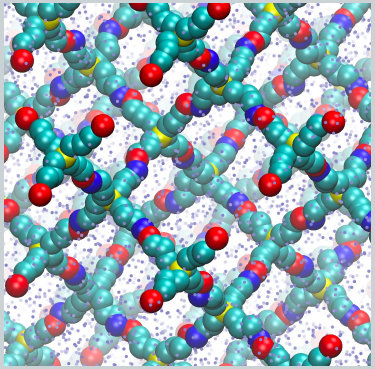
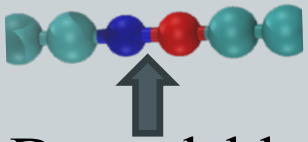
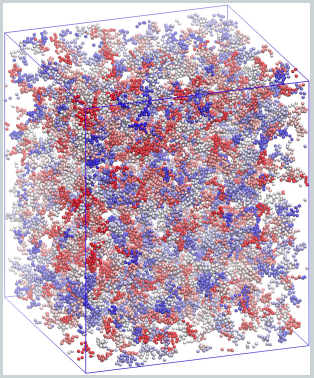






Mesoscale modeling of erosion of polymer networks: characterizing mass loss via extent of reaction

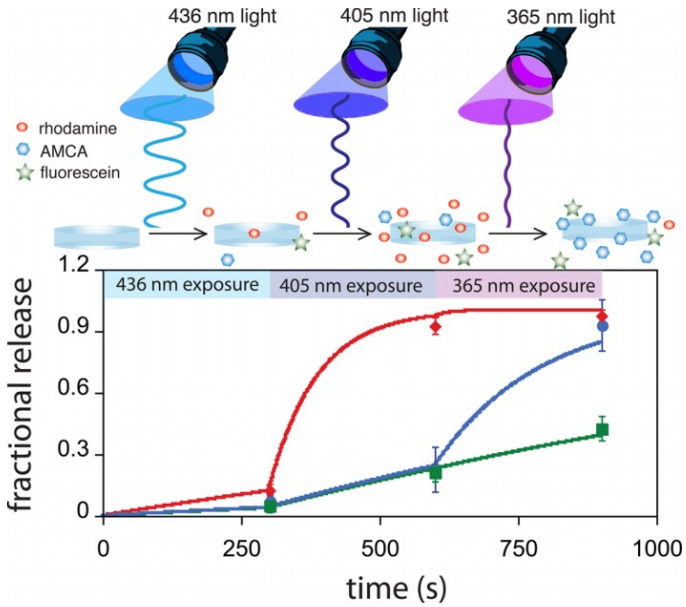
Vaibhav Palkar, Olga Kuksenok
Department of Materials Science and Engineering
Clemson University
LAMMPS Virtual Workshop & Symposium 2021

CLEMSON

Motivation

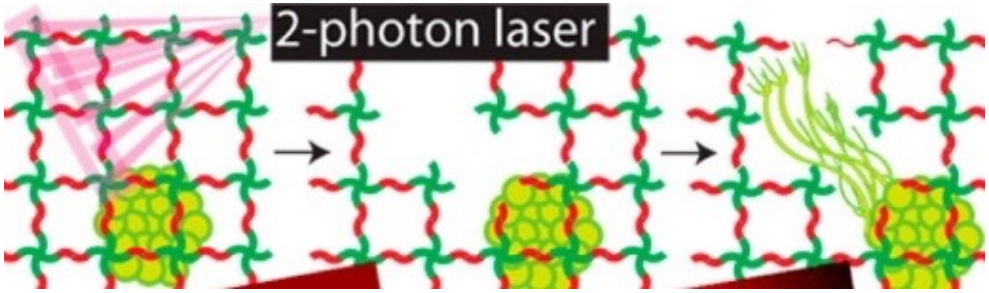
Controlled degradation: designing functional soft materials

Photo-selective drug release



Griffin, D. R., et. al. **(2012)** *ACS macro letters*, 1, 1330

Directed growth of neural network



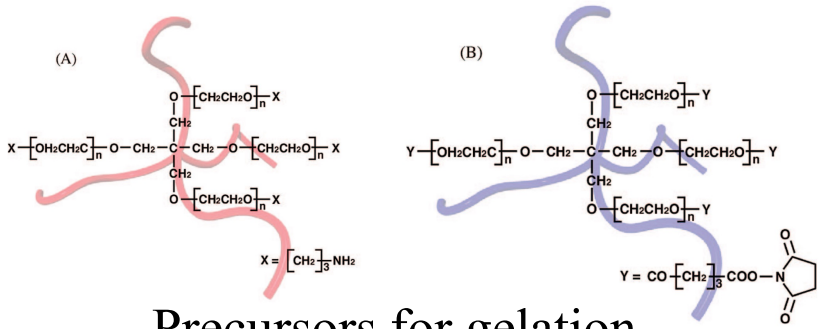
McKinnon, D. D. et al. **(2014)** *Biomacro*. 15, 2808

Goal: Develop mesoscale model for controlled hydrogel degradation

Model hydrogel and simulation approach

Tetra-PEG gels

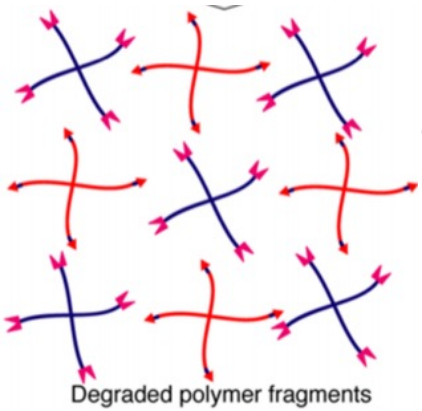
Crosslinked 4-arm polyethylene glycol



Precursors for gelation

Sakai, T., et. al. **(2008)**
Macromolecules, 41, 5379

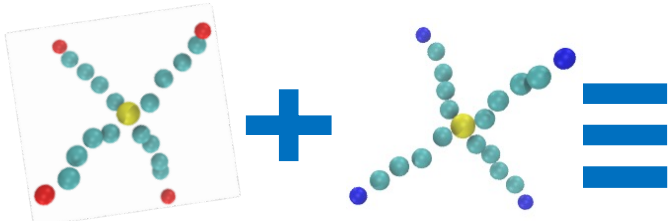
Photodegradation of network



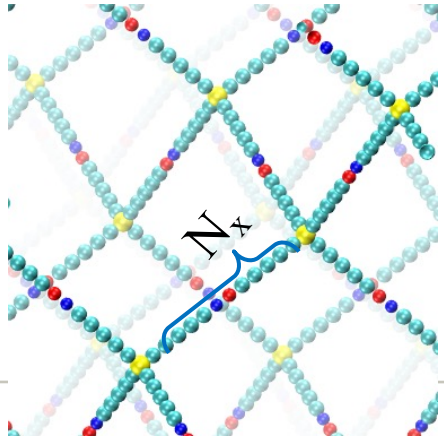
Tetra arm fragments after degradation

Azagarsamy, M. A. et. al. **(2014)**
ACS Macro Letters, 3, 515.

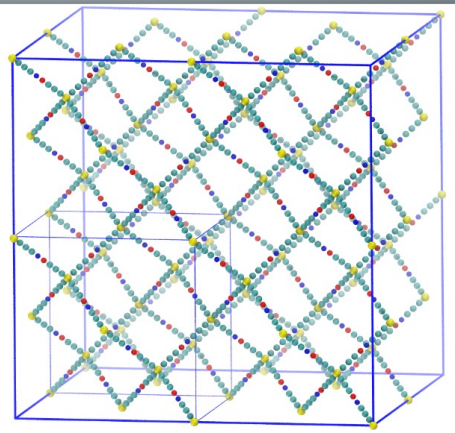
Bead model



Precursor A Precursor B



Dissipative Particle Dynamics



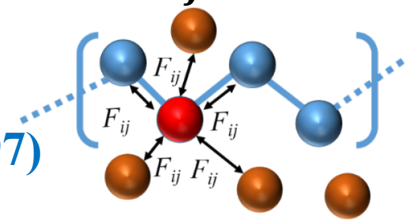
Diamond-like starting structure

Multiple atoms ⇔ DPD beads

$$\frac{d(m_i \boldsymbol{v}_i)}{dt} = \boldsymbol{F_i} = \Sigma_{i \neq j}\left(\boldsymbol{F_{ij}^C} + \boldsymbol{F_{ij}^D} + \boldsymbol{F_{ij}^R} + \boldsymbol{F_{ij}^B} + \boldsymbol{F_{ij}^{mSRP}}\right)$$

DPD: Conservative $\boldsymbol{F_{ij}^C}$, Dissipative $\boldsymbol{F_{ij}^D}$ and Random $\boldsymbol{F_{ij}^R}$

Harmonic bonds $\boldsymbol{F_{ij}^B}$



Groot, R. D., & Warren, P. B. **(1997)** *JCP*, 107, 4423

Groot R.D. et. al **(2001)** *Biophys. J.* 81, 725

Español, P. et al. **(2017)** *JCP.* 146 150901

PEG-Water ($\chi = 0.45$)

Metters, A. et. al., **(2005)** *Biomacro.*, 6, 290

$$a_{ii} = 78 \;\; k_B T/r_c$$
$$a_{pw} = a_{ii} + 3.27\chi$$
$$a_{pw} = 79.5 \;\; k_B T/r_c$$

LAMMPS Simulation Package

https://lammps.org

Plimpton, S. **(1995)**. *Journ. of comp. phys.*, 117, 1

modified Segmental Repulsive Potential $\boldsymbol{F_{ij}^{mSRP}}$

Sirk, T. W., et. al. **(2012)**. *JCP,* 136

Dealing with topology violations

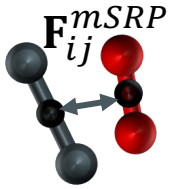
Additional forces between bonds

$$\boldsymbol{F}_{ij}^{mSRP} = \begin{cases} b_{ij}\left(1 - \frac{d_{ij}}{r_c^{SRP}}\right)\boldsymbol{e}_{ij} & d_{ij} \le r_c^{SRP} \\ 0 & d_{ij} > r_c^{SRP} \end{cases}$$

$$b_{ij} = 80 k_B T \, r_c^{-1}; r_c^{SRP} = 0.8 r_c$$

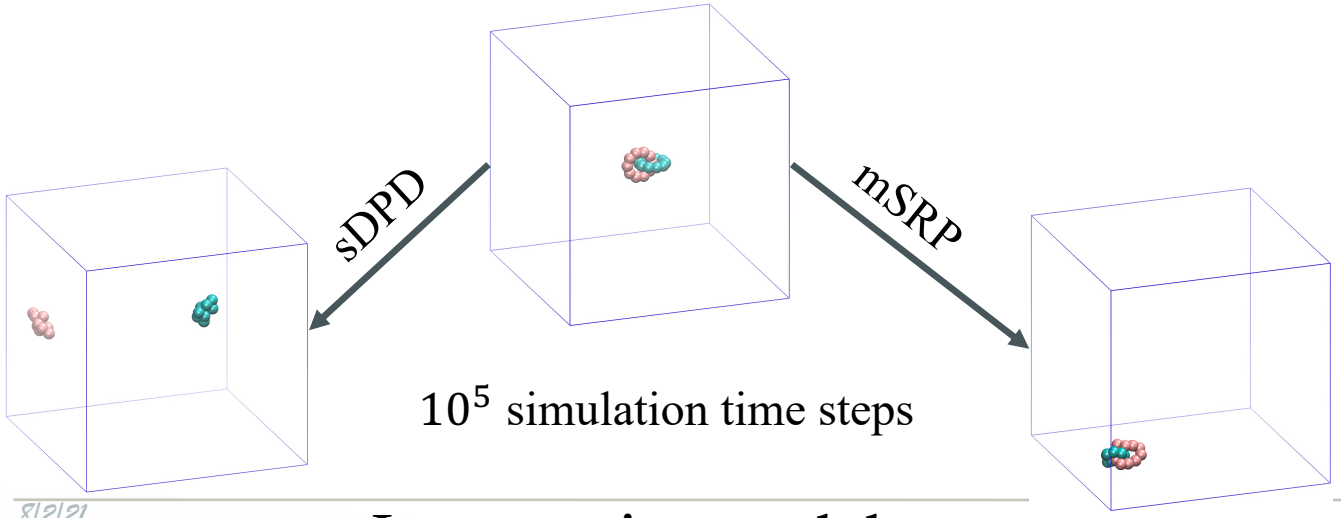
Sirk, T. W., et. al. **(2012)**. *JCP*, 136, 134903.

LAMMPS mSRP implementation



pair srp & fix srp

Entangled polymer loops in a good solvent



Loops remain entangled

Dealing with topology violations

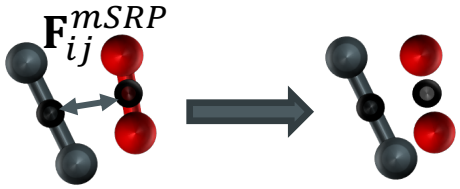
Additional forces between bonds

$$\boldsymbol{F}_{ij}^{mSRP} = \begin{cases} b_{ij}\left(1 - \dfrac{d_{ij}}{r_c^{SRP}}\right)\boldsymbol{e}_{ij} & d_{ij} \le r_c^{SRP} \\ 0 & d_{ij} > r_c^{SRP} \end{cases}$$

$$b_{ij} = 80 k_B T \, r_c^{-1}; r_c^{SRP} = 0.8 r_c$$

Sirk, T. W., et. al. **(2012)**. *JCP*, 136, 134903.

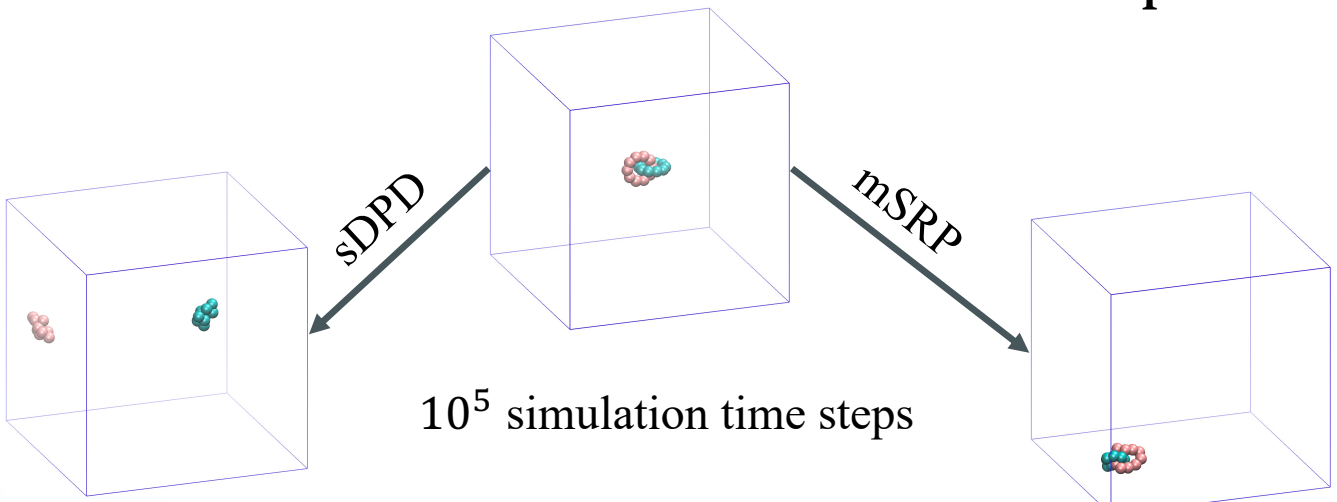
LAMMPS mSRP implementation



pair srp & fix srp

Challenge: remove pseudo beads upon bond breaking

Entangled polymer loops in a good solvent



Loops remain entangled

Network degradation framework

Probability $0 < P < 1$

Reaction time step $\tau_R = 0.2\tau$

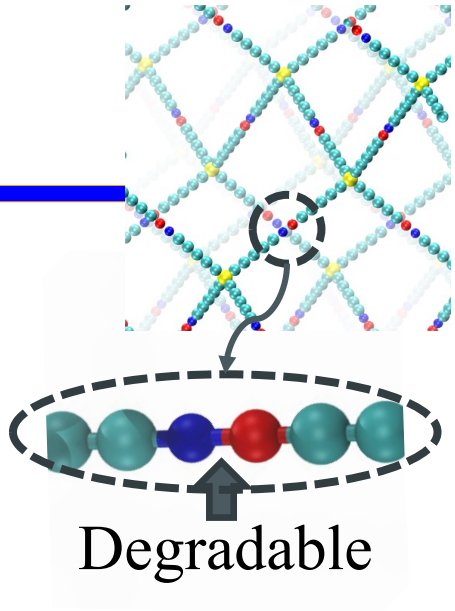
Random ($0 < r_i(t) < 1$) for each degradable bond i

$$p = \frac{N(t)}{N_0} = exp(-kt)$$

Milchev, A., et. al. **(2000)**. *JCP*., 112, 1606

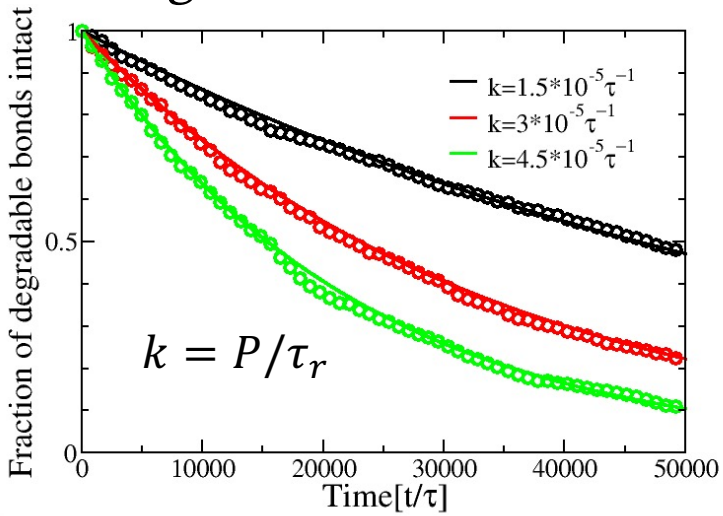
Akkermans, R. L., et. al. **(1998)**. *JCP*. , 109, 2929.

fix bond/break in lammps

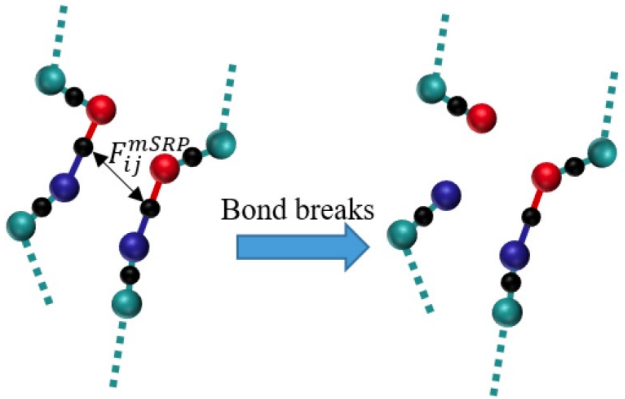


p → fraction of bonds intact

k → degradation rate constant



Communication between fix bond/break & fix srp



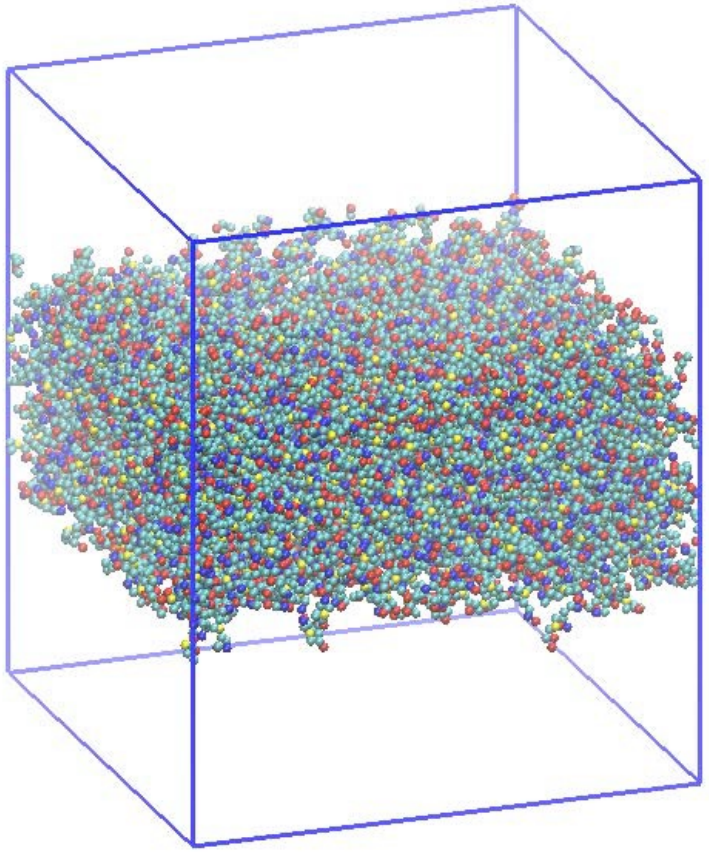
Palkar, V. et al **(2020)**. MRS Advances, 5, 927

First order degradation reaction with mSRP

Qualitative analysis of degradation

Degradation in hydrogel films

- Largest connected cluster highlighted



Initially:

- Film swells
- Surface erosion

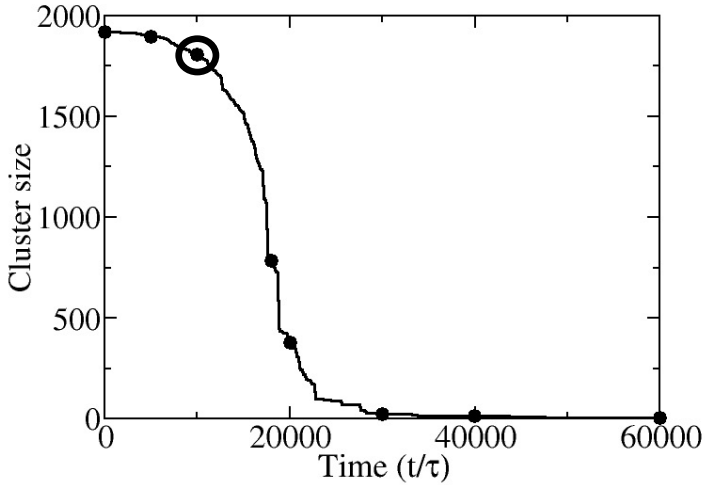
Later time:

- Bulk erosion
- Reverse gelation

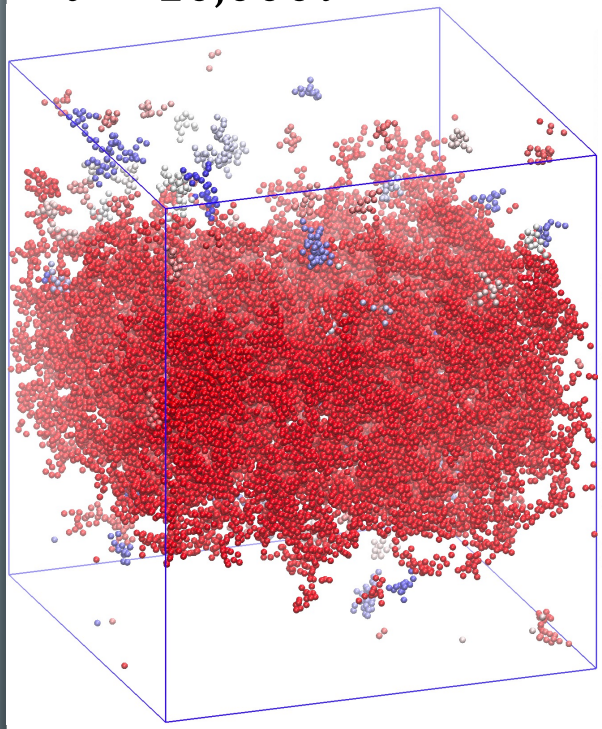
Cluster size distribution

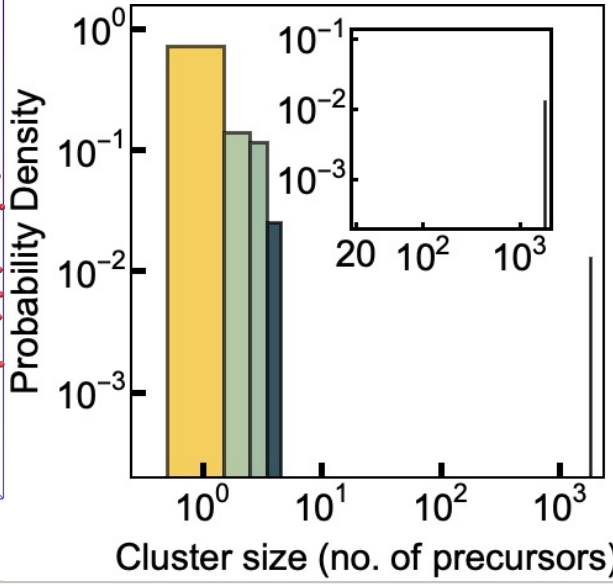
Evolution of cluster sizes

# of precursors in cluster



$t = 10{,}000\tau$





Box size = $42\mathrm{r_c x} 42r_c \mathrm{x} 50r_c$

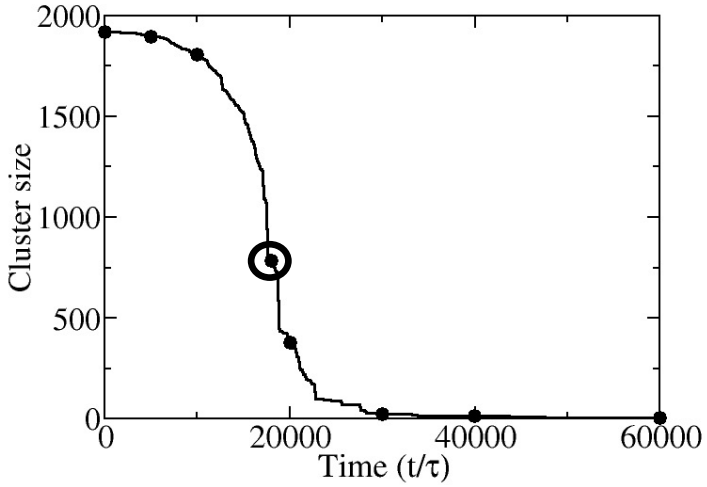
precursors = 1920

$k = 4.5 * 10^{-5}\tau^{-1}$

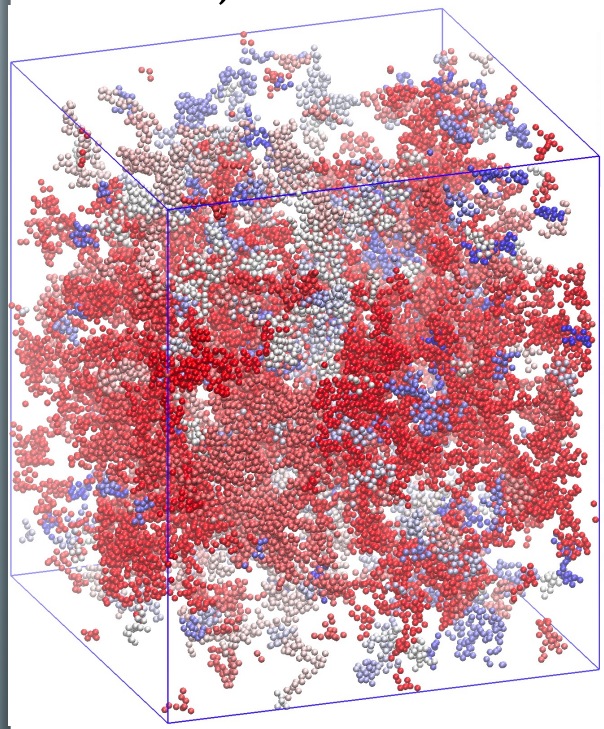
Cluster size distribution

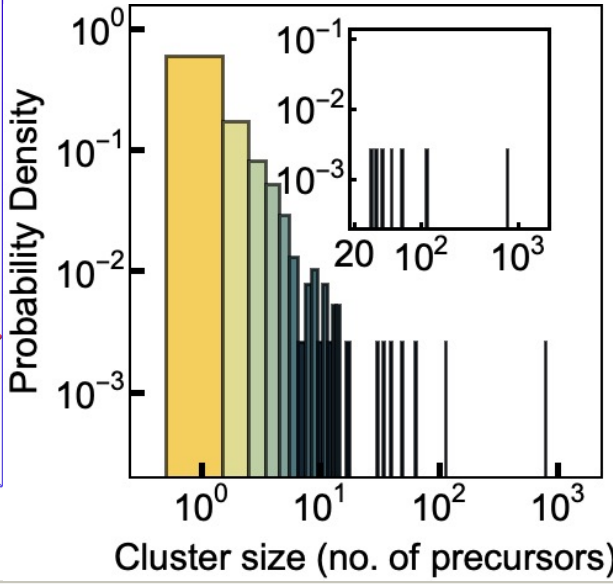
Evolution of cluster sizes

# of precursors in cluster



$t = 18{,}000\tau$





Box size = $42r_c$x$42r_c$x$50r_c$

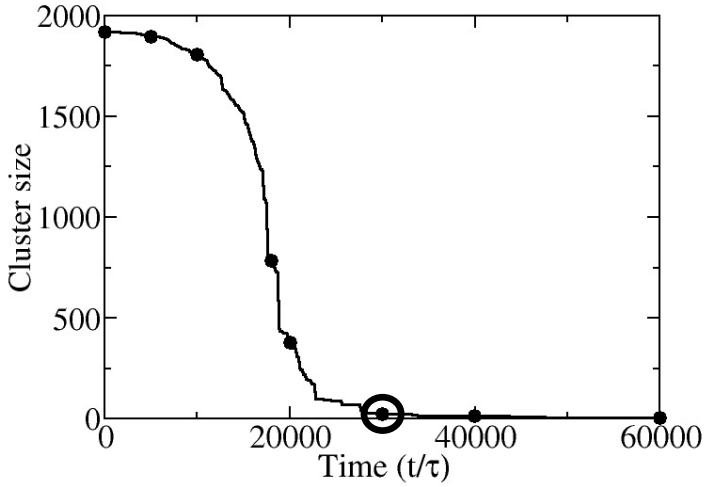
precursors = 1920

$k = 4.5 * 10^{-5}\tau^{-1}$

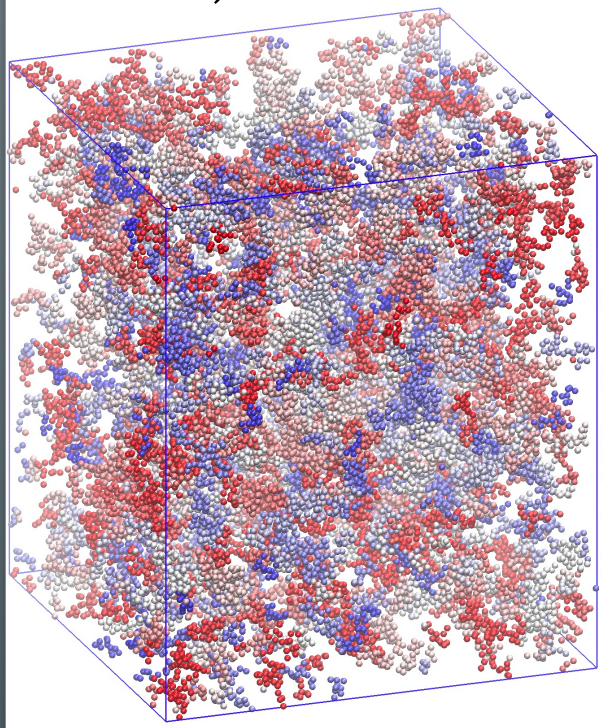
Cluster size distribution

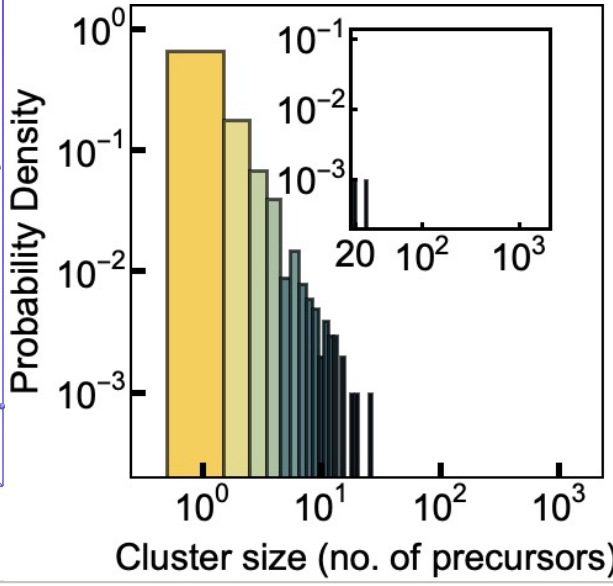
Evolution of cluster sizes

# of precursors in cluster



$t = 30{,}000\tau$





Box size = $42r_c$x$42r_c$x$50r_c$

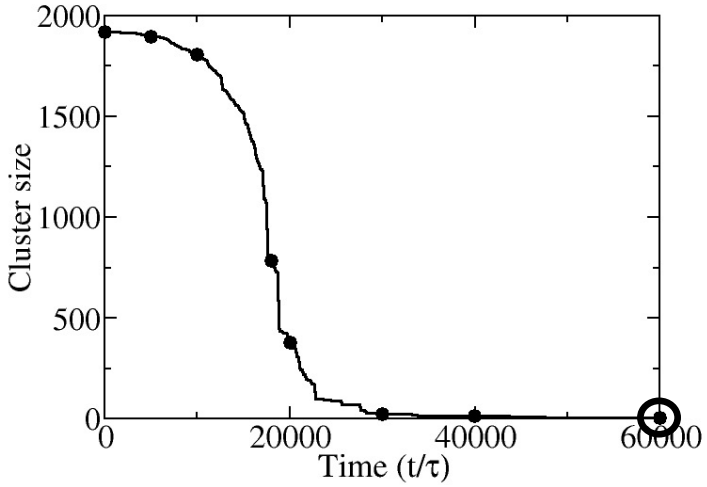
precursors = 1920

$k = 4.5 * 10^{-5}\tau^{-1}$

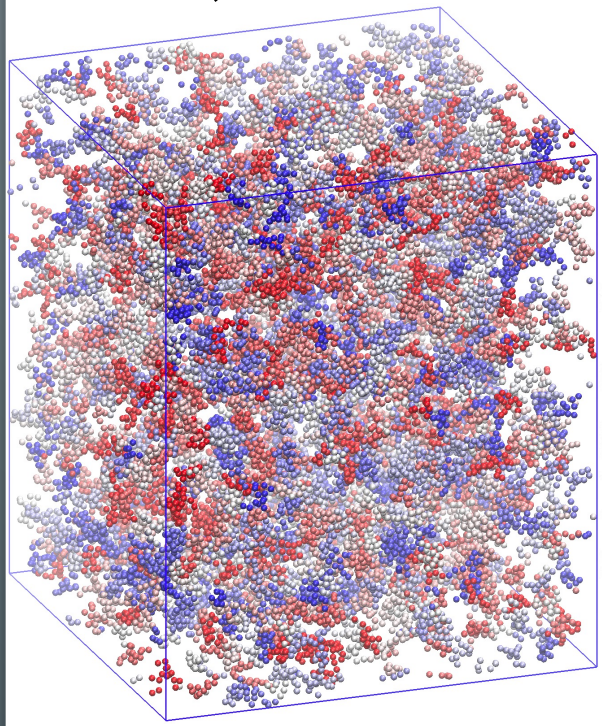
Cluster size distribution

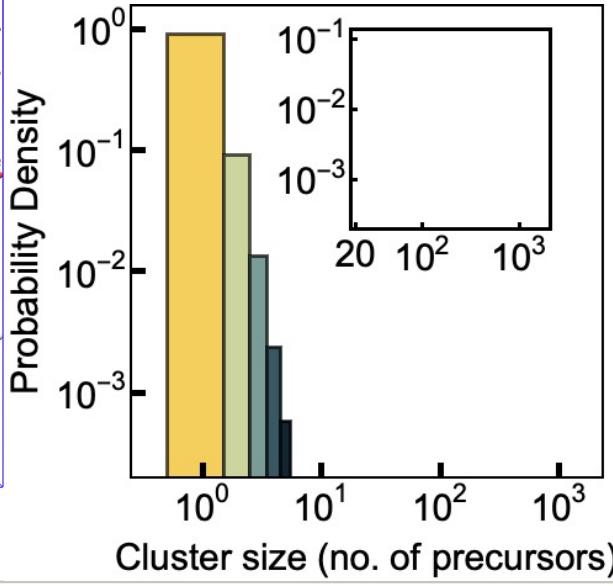
Evolution of cluster sizes

# of precursors in cluster



$t = 60{,}000\tau$





Box size = $42r_c$x$42r_c$x$50r_c$

precursors = 1920

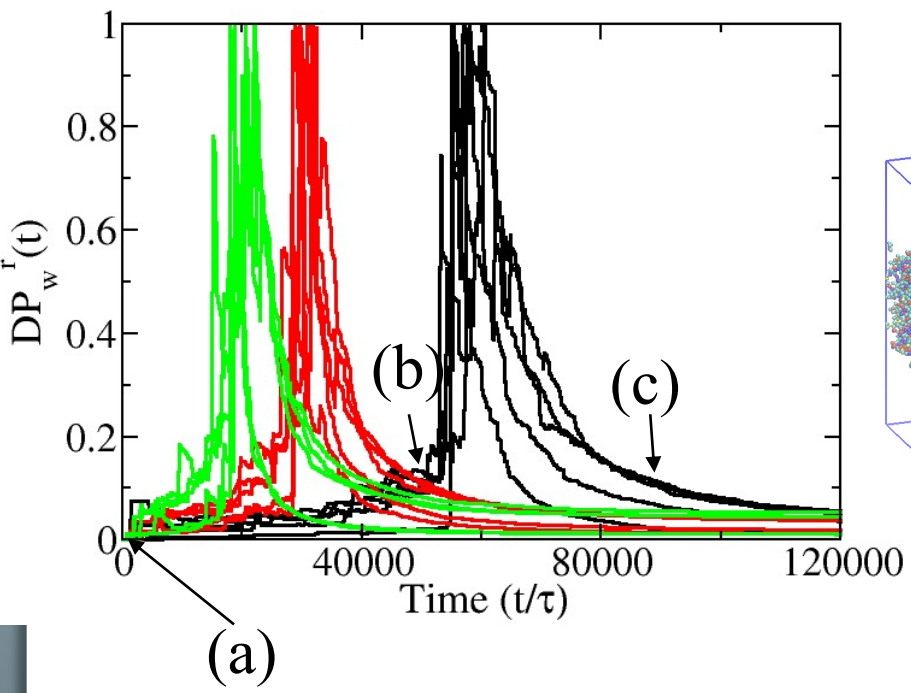
$k = 4.5 * 10^{-5}\tau^{-1}$

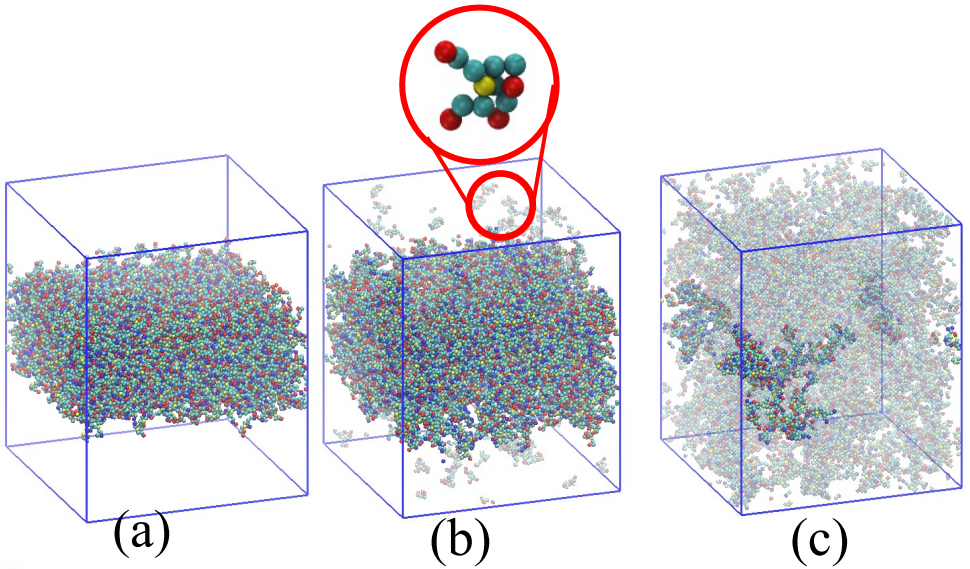
Characterizing degradation

Reduced DP_w: DP_w except largest cluster

$$DP_w^r(t) = \frac{\Sigma' \, n_i(t) \, i^2}{\Sigma' \, n_i(t) \, i}$$

$n_i(t) \rightarrow$ number of clusters with i beads at time t

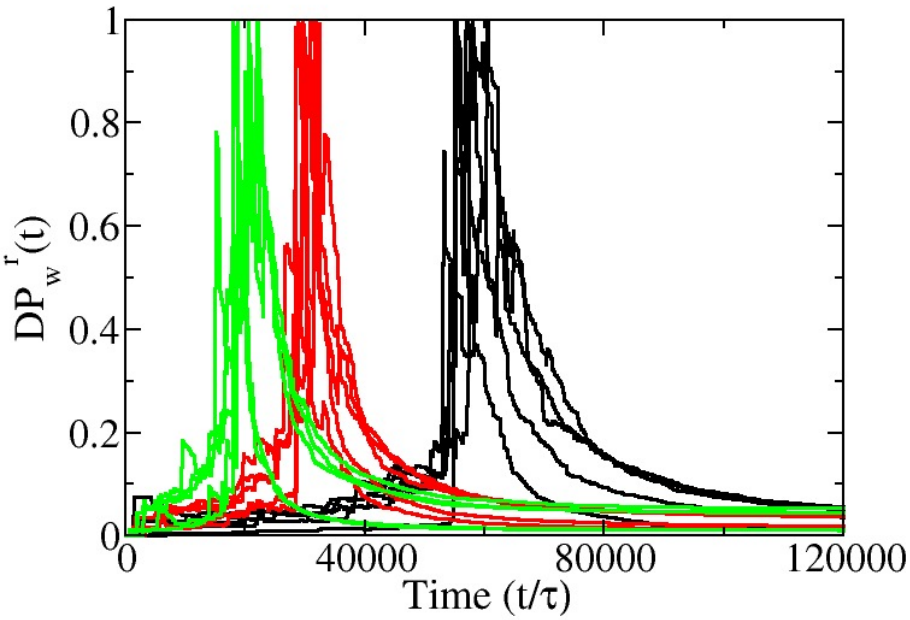




Characterizing degradation

Reduced DP_w: DP_w except largest cluster

$$DP_w^r(t) = \frac{\Sigma' \, n_i(t) \, i^2}{\Sigma' \, n_i(t) \, i}$$



Peak defines reverse gel point

Wang, R. et. al. **(2017)** ACS Macro Letters, 6, 1414

Lin, T. S., et. al. **(2018)** Macromolecules, 51, 1224

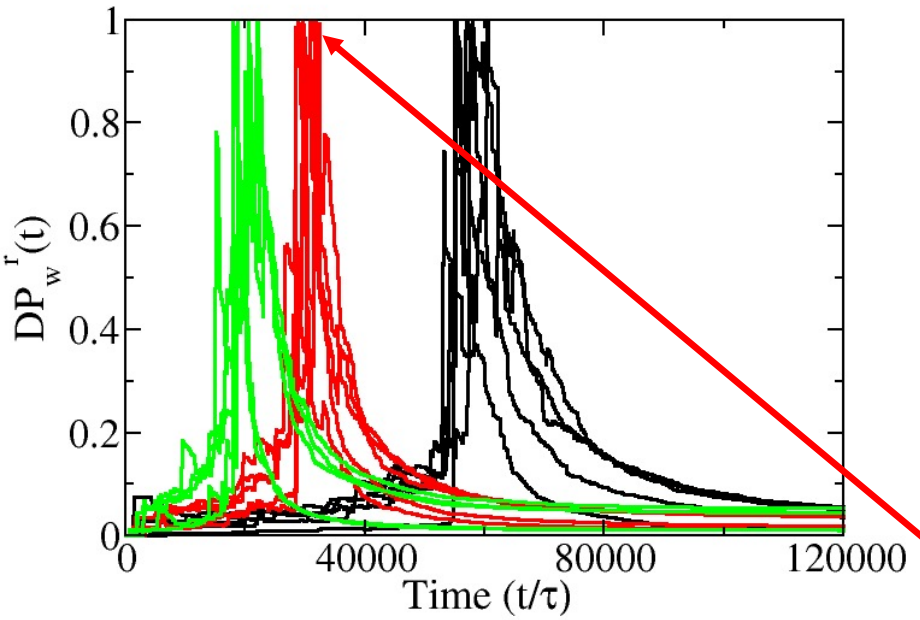
Conversion: fraction of bonds intact

$$p = e^{-kt}$$

Characterizing degradation

Reduced DP_w: DP_w except largest cluster

$$DP_w^r(t) = \frac{\Sigma' \, n_i(t) \, i^2}{\Sigma' \, n_i(t) \, i}$$



Peak defines reverse gel point

Wang, R. et. al. **(2017)** ACS Macro Letters, 6, 1414

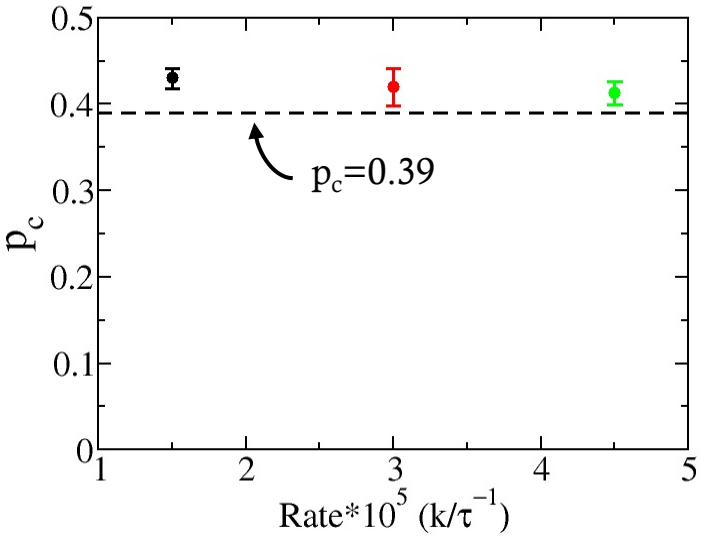
Lin, T. S., et. al. **(2018)** Macromolecules, 51, 1224

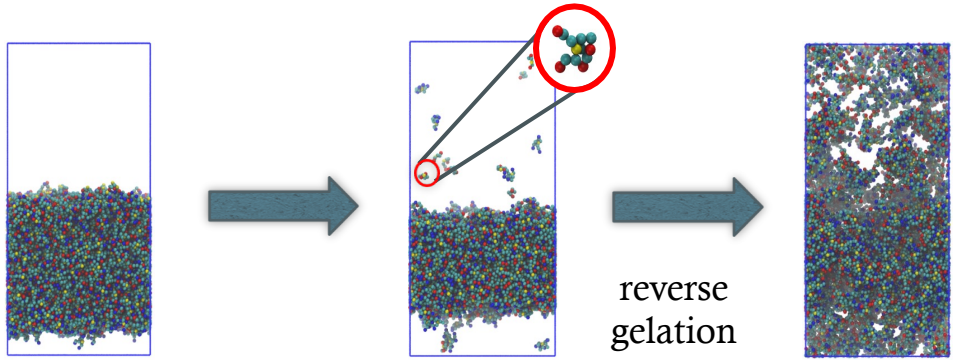
Conversion: fraction of bonds intact

$$p = e^{-kt}$$

$$p_c = \exp(-kt_c)$$

Calculate reverse gel point





Expected reverse gel point:

Gelation of stoichiometric mixture at overlap concentration

Sakai, T., et. al. **(2016)** Polym. J, 48, 629

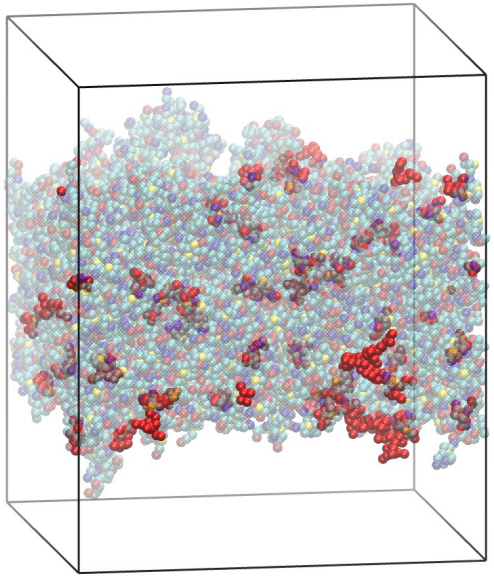
Bond percolation on diamond lattice p_c=0.39 Stauffer, D. et. al. **(1994)**.

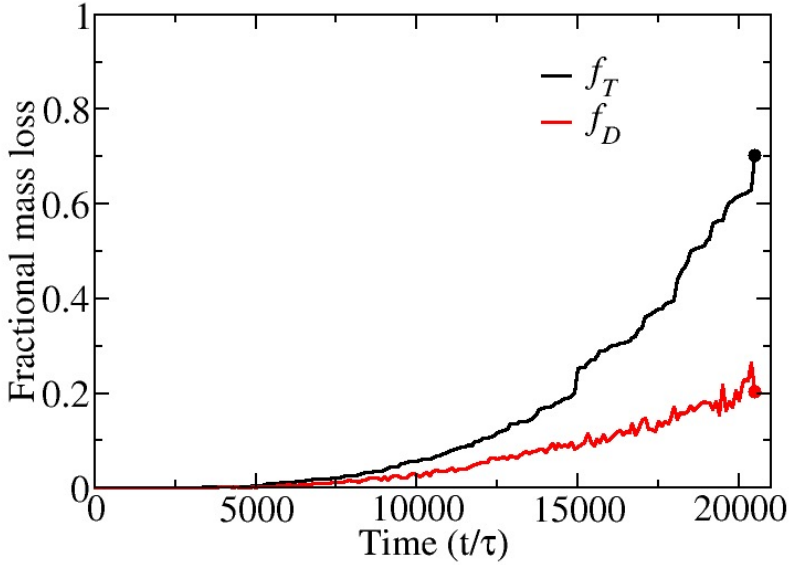
Expected network size effect: $p_c^N = p_c^\infty + N_p^{-\sigma}$

N_p →Number of precursors Wang, R., et. al. **(2017)** ACS Macro Letts, 6, 1414

Spatial distribution of precursors

- Distance based cluster calculation
- Small broken off precursors are trapped within the largest cluster





- Not all precursors that break are lost!

$$f_T = 1 - \frac{N_T(t)}{N_0}$$ N_T size of largest topological cluster at t

$$f_D = 1 - \frac{N_D(t)}{N_0}$$ N_D size of largest distance-based cluster at t

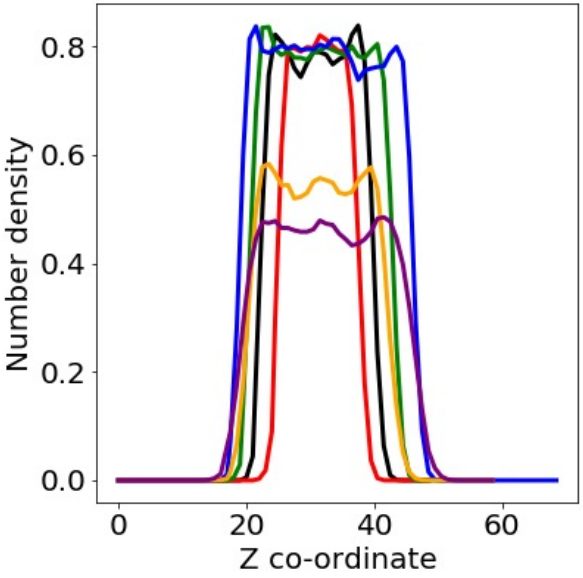
N_0 total number of precursors

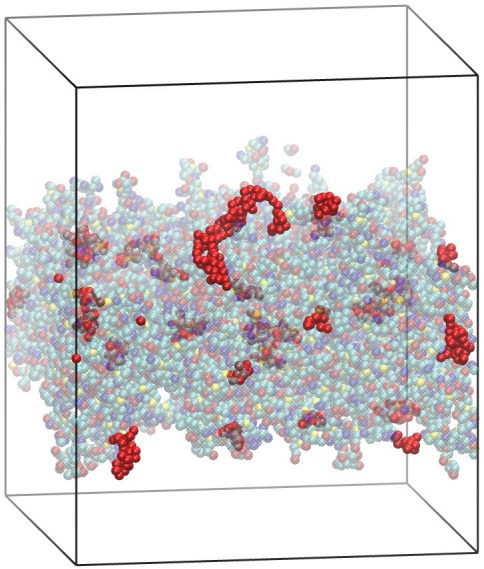
Proximity to reverse gel point

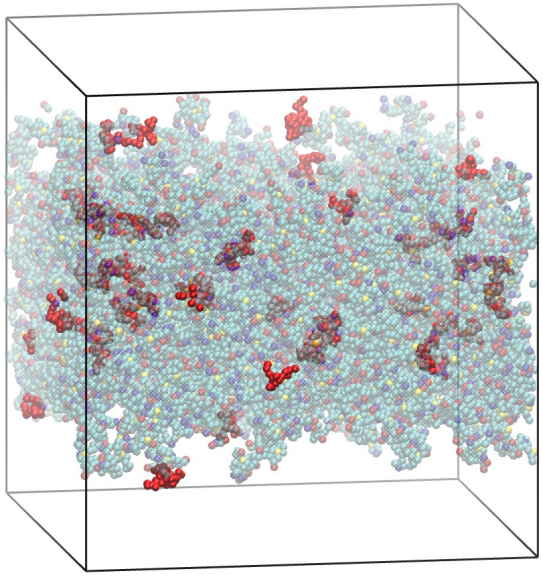
- Extent of degradation reaction
  - $1 - p$: fraction of degradable bonds broken
- Relative extent of reaction
  - Reflects proximity to reverse gel point

$$\epsilon = \frac{p_c - p}{1 - p_c}$$

-1: start of degradation
0: at reverse gel point
>0: after reverse gel point







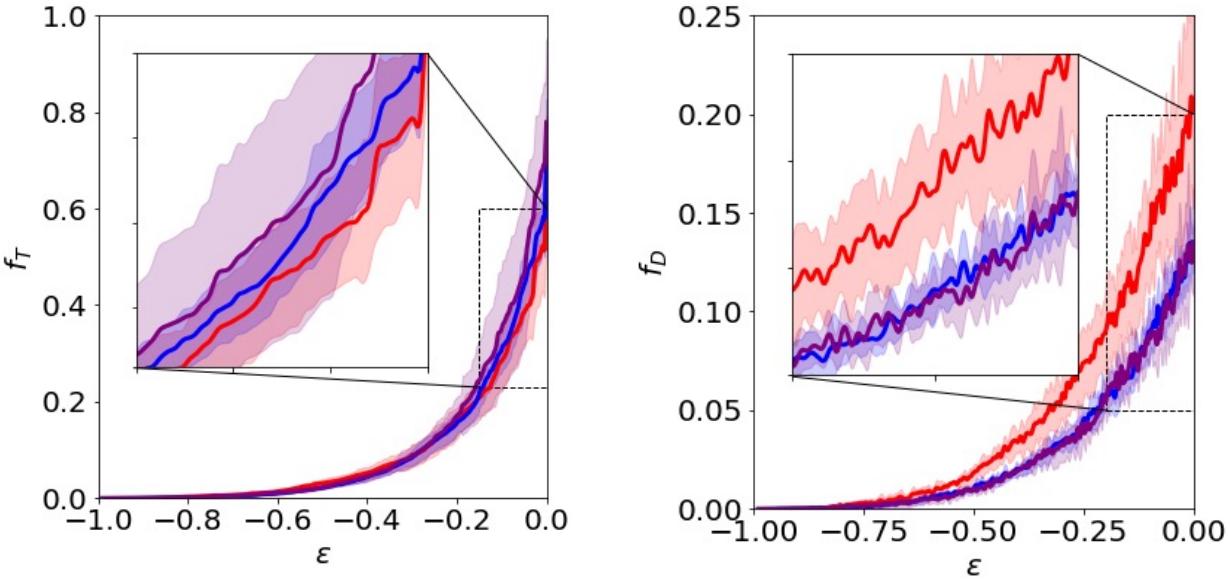
Spatial cluster distribution is needed to characterize erosion

Proximity to reverse gel point

- Extent of degradation reaction
  - $1 - p$: fraction of degradable bonds broken
- Relative extent of reaction
  - Reflects proximity to reverse gel point

$$\epsilon = \frac{p_c - p}{1 - p_c}$$

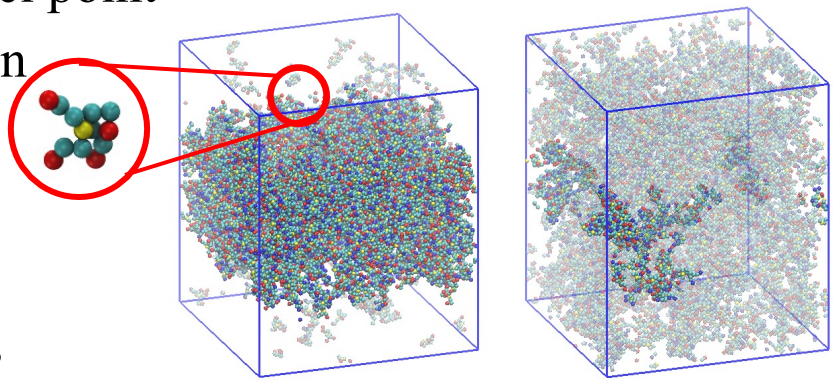
-1: start of degradation
0: at reverse gel point
>0: after reverse gel point

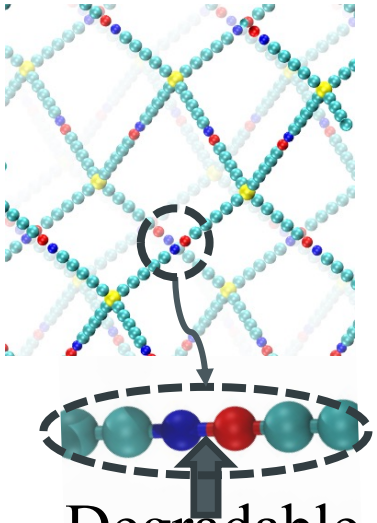


Erosion depends on ϵ and film thickness

Conclusions and acknowledgements

- ✓ Developed DPD framework for controlled degradation
- ✓ Quantified reverse gel point
- ✓ Characterized erosion





- **Acknowledgements**
  - This research was supported financially by the National Science Foundation EPSCoR Program under Award No. OIA-1655740
  - Clemson University is acknowledged for compute time on Palmetto cluster