Development of a Dissipative Particle Dynamics framework for simulating tetra-PEG gels with degradable crosslinks

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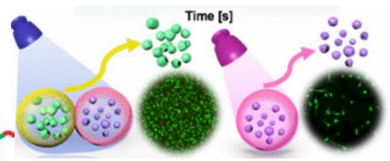
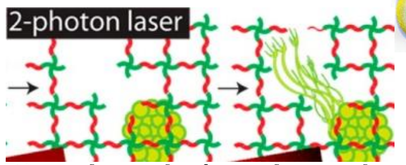
Motivation

Biomedical applications of controllably degradable tetra-PEG gels



Selective cell release

Truong, V. X., et. al. **(2017)**. *ACS Appl. Mat. & Inter.*, *9*(38), 32441



Directed growth of neural networks using degradable gels
McKinnon, D. D. et al. **(2014)** *Biomacro*. 15(7), 2808

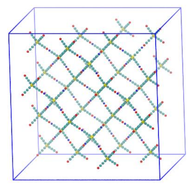
Goal: Develop a coarse-grained numerical framework for simulating degradation in gels

Modeling Gels using DPD

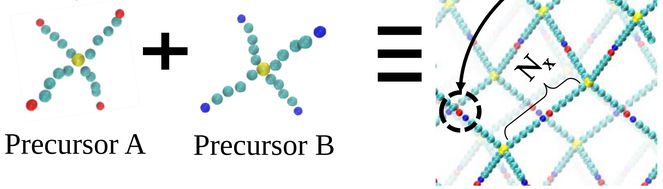
Mesoscale model: DPD

- Multiple atoms → DPD beads
- Soft potential → large time steps
- Conserves momentum

$$\mathbf{F}_{ij}^{C} = a_{ij}\left(1-\frac{r_{ij}}{r_c}\right)\hat{\mathbf{e}}_{ij} \qquad \begin{aligned} a_{ii} &= 78\ k_BT/r_c \\ a_{pw} &= 80\ k_BT/r_c \end{aligned}$$

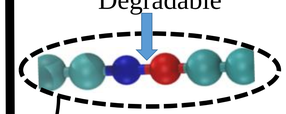


Starting structure for simulations



Bond Breaking with Segment Repulsion

Degradable

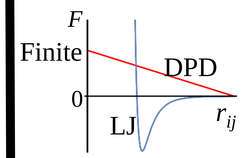


Stochastic model

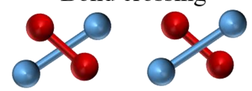
p : bond breaking probability
τ_R: breaking event interval
$k = p/\tau_R$ breaking rate

`fix bond/break`

Suppress bond crossing – apply segment repulsion

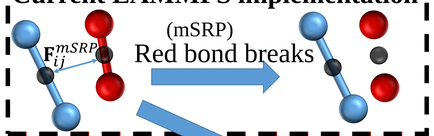


Bond crossing



Modified segmental repulsive potential (mSRP) Sirk, T. W., et. al. **(2012)**. J. Chem. Phys., 136(13)

Current LAMMPS implementation



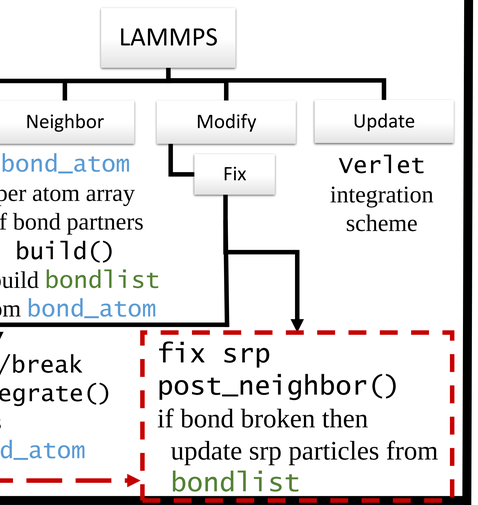
Our extension
When bond is broken, delete corresponding SRP particle

`pair srp` – compute forces – `fix srp` create initial srp particles

Method – Updated Implementation

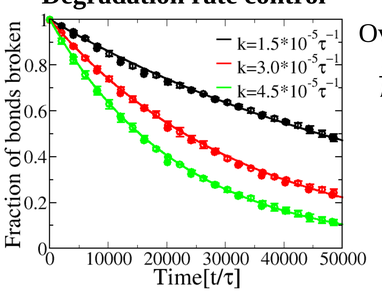
```
Loop over N timesteps
 fix->initial_integrate();
 fix->post_integrate();

 nflag=neighbor->decide();
 if nflag:
  fix->pre_neighbor();
  neighbor->build();
  fix->post_neighbor();
 end if

 fix->pre_force();
 force->compute();
 fix->post_force();

 fix->final_integrate();
```

`Verlet` pseudocode



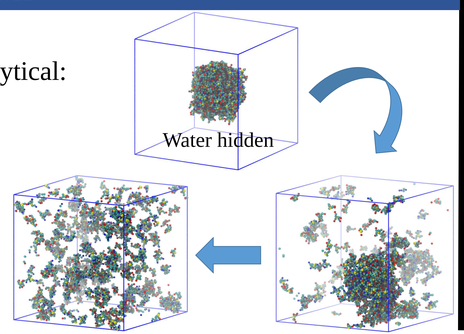
Validation

Degradation rate control



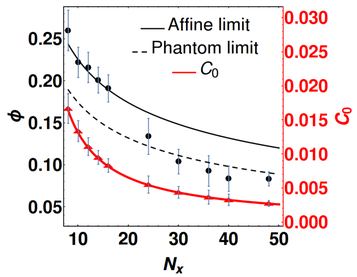
Overlap with analytical:

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



Results

Swelling without degradation



Lines: Fit with Flory-Rehner theory

Dimensionless crosslink density

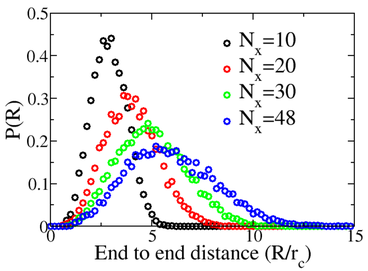
$$\phi + \chi\phi^2 + \ln(1-\phi) - C_0\left(\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right) = 0$$

Fitting parameters: χ=0.45, ϕ_0=0.4

Transition from affine to phantom network models agrees with experiments

Akagi, Y. et. al **(2013)** *Macromolecules*, 46(3), 1035

Chain length distribution in swollen gels



$$a_{pw} = 83\ k_BT/r_c$$

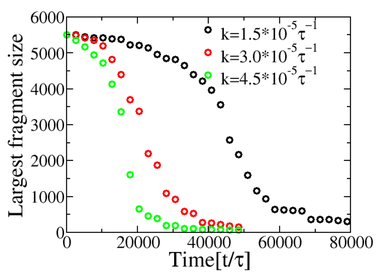
$$r = \frac{< R^4 >}{< R^2 >^2} = \frac{\int_0^\infty R^4 P(R)dR}{\left(\int_0^\infty R^2 P(R)dR\right)^2} = \frac{5}{3} = 1.67$$

r : Gaussian character

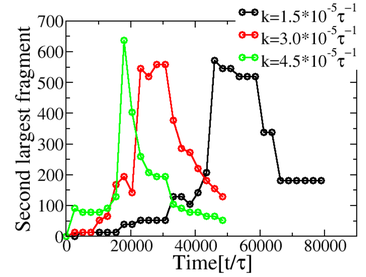
Kremer, K., & Grest, G. S. **(1990)**. J. Chem. Phys., 92(8), 5057

N_x	r
10	1.30
20	1.37
30	1.40
48	1.48

Fragment size evolution analysis: fragment size – # of beads



Largest fragment size decreases over time



"Reverse gelation" peak

Conclusions and Future work

- ✓ Initial framework for simulating degradable gels
- ✓ Control over degradation rate
- "Reverse gelation" vs. surface erosion
- Introduce reversible bonds

Acknowledgements

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