Molecular Dynamics Simulations of Epoxy Resin Systems

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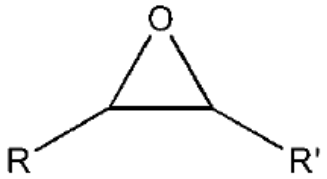
Aug 1, 2019

Epoxy Resins

- Epoxy resins are a class of thermoset polymers.
- The epoxy resins can cross-link with amine hardeners, producing cured resins.
- Applications: adhesives, coatings, encapsulates, casting materials, etc.



Basic chemical structure of epoxy group

M. A. Boyle, et al. (2001).

https://images-fibreglast-com.s3.amazonaws.com/pio-resized/750/System%202000%20Laminating%20Epoxy%20Resin-2.jpg

Advantages of Computational Experiments

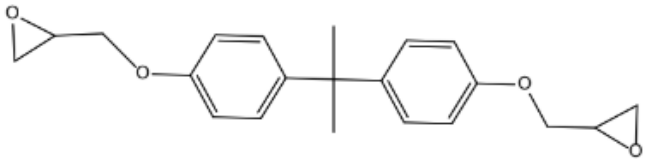
- Lack of materials costs
- Easier to alter experiments
- Growth of supercomputing access / power has helped make experiments have reasonable run time

Cons of Computational Experiments

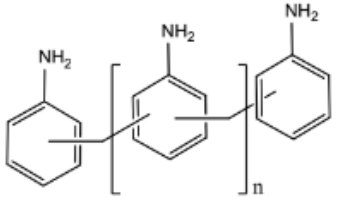
- Reliant on experimental results for validation
- Easy to simulate unphysical situations
- Reaction mechanism is not carried out as it would be in a physical system

PRO-SET® M1002 Resin (Epoxy) and M2046 Hardener (Amine)

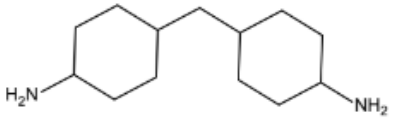
MSDS and Sigma Aldrich



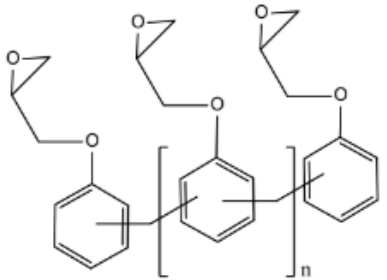
Propane, 2,2-bis[p-(2,3-epoxypropoxy)phenyl [BADGE] (70-100%)



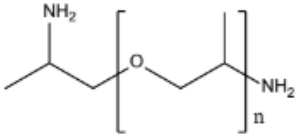
Benzenamine-formaldehyde polymer [Aniline formaldehyde] (15-35%)



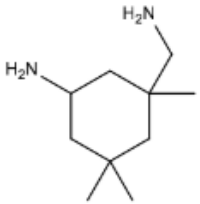
4, 4'-Methylenebiscyclohexanamine [Methylene-BCHA] (10-30%)



Phenol-formaldehyde polymer glycidyl ether [PDGE formaldehyde] (10-20%)

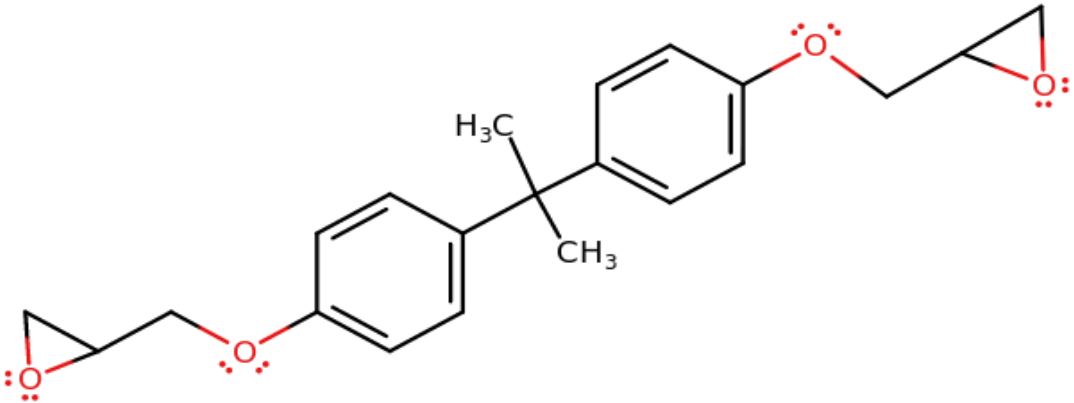


Polyoxyropylenediamine [POPDA] (10-30%)

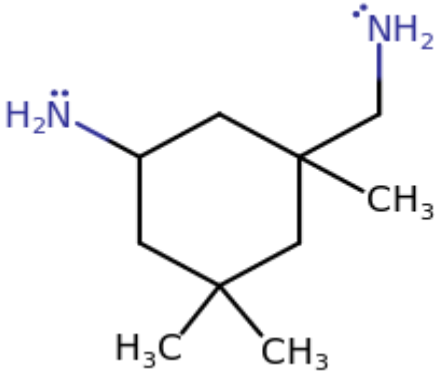


Isophoronediamine [IPDA] (10-30%)

Binary System 1

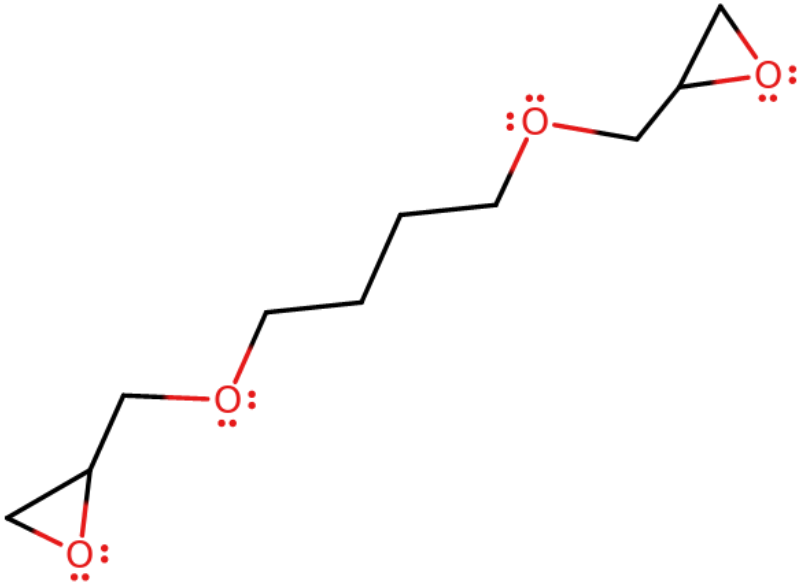


Propane, 2,2-bis[p-(2,3-Epoxypropoxy)phenyl [BADGE]

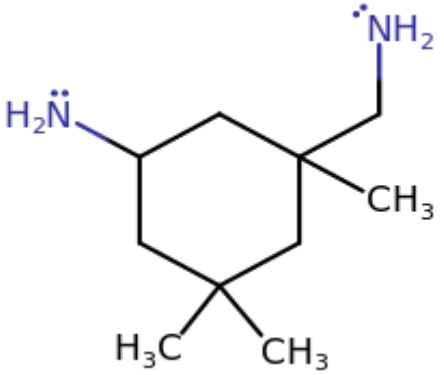


Isophoronediamine [IPDA]

Binary System 2

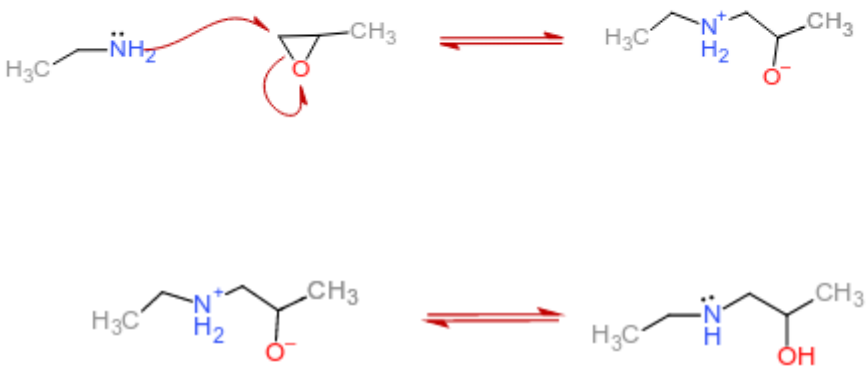


Diglycidyl ether of 1,4-butanediol (DGEBD)



Isophoronediamine
[IPDA]

Crosslinking Reaction



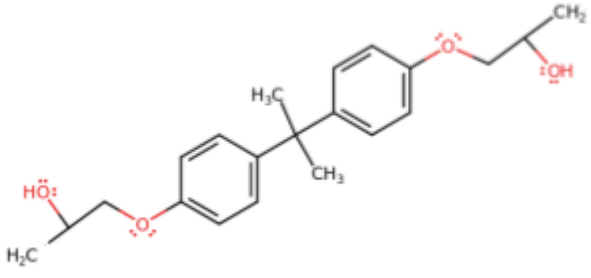
$$crosslinking\ percentage = 1 - \frac{noncrosslinked\ carbon\ radicals}{total\ potential\ crosslinks}$$

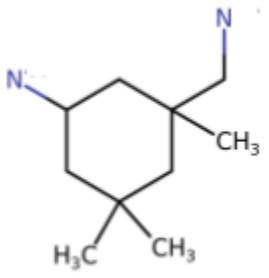
Activated molecules

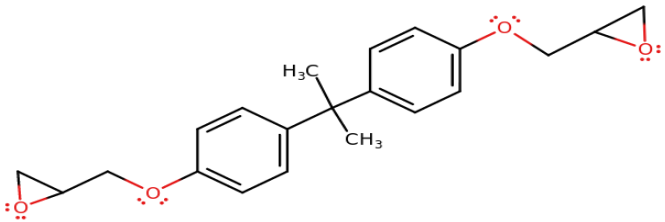
Activated

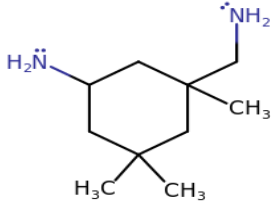
V.S.

Non-activated









Propane, 2,2-bis[p-(2,3-Epoxypropoxy)phenyl [BADGE]

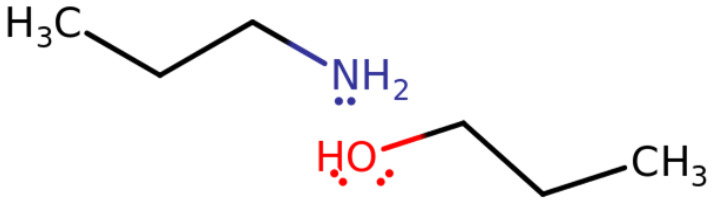
Isophoronediamine [IPDA]

Under the Hood of the Simulation

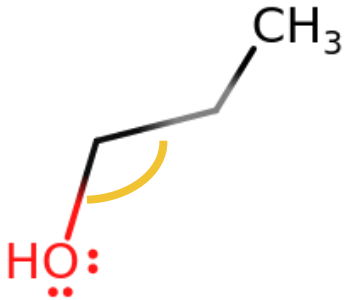
$$U_{\mathrm{CHARMM}} = \sum_{\mathrm{bonds}} K_b(b - b_0)^2 + \sum_{\mathrm{angles}} K_\theta(\theta - \theta_0)^2 + \sum_{\mathrm{dihedrals}} K_\phi(1 + \cos(n\phi - \delta)) + \sum_{\mathrm{nonb,pair}} \frac{q_i q_j}{4\pi D r_{ij}} + \sum_{\mathrm{nonb,pair}} \varepsilon_{ij} \left[\left(\frac{R_{\mathrm{min},ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\mathrm{min},ij}}{r_{ij}} \right)^{6} \right]$$

Vanommeslaeghe, K., et al. (2010).

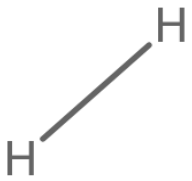
The CHARMM force field used in our simulations



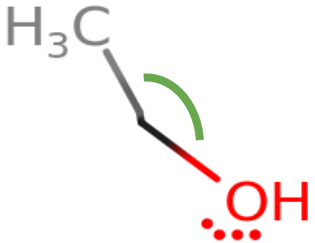
Nitrogen and Oxygen act as a Non-Bonded Pair



Angle



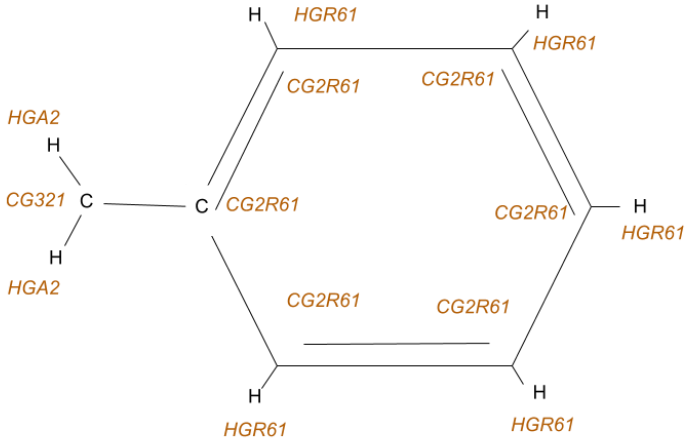
Bond



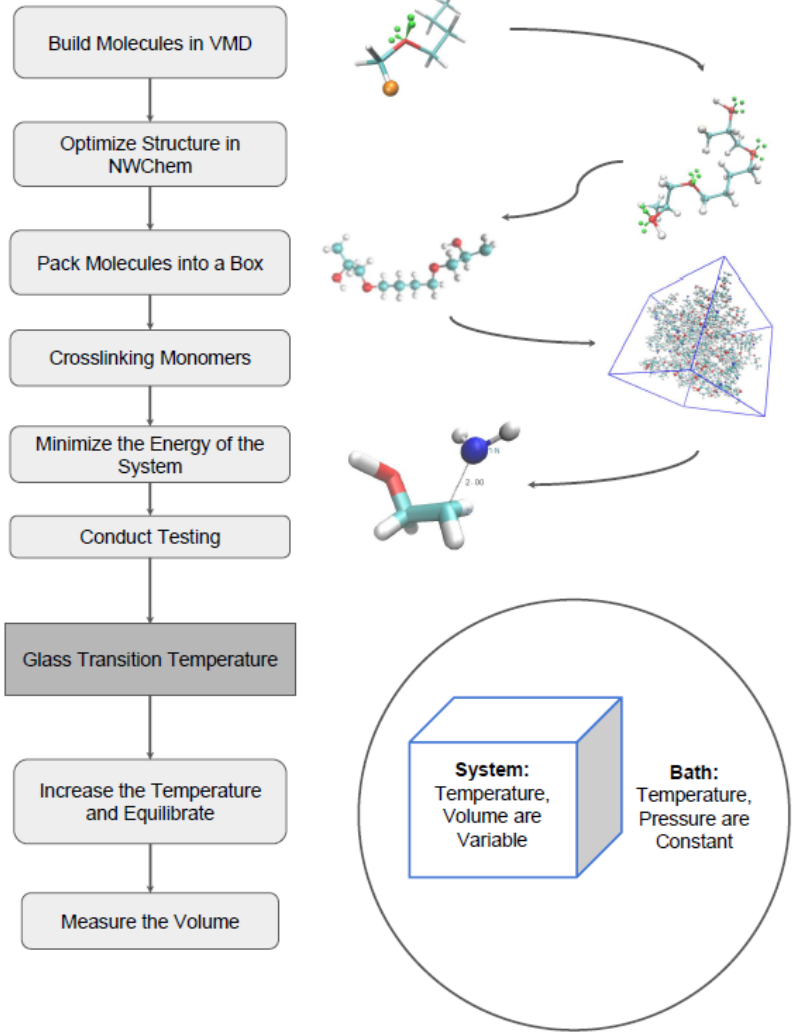
Dihedral / Torsion

Encode Atoms (Parameterization)

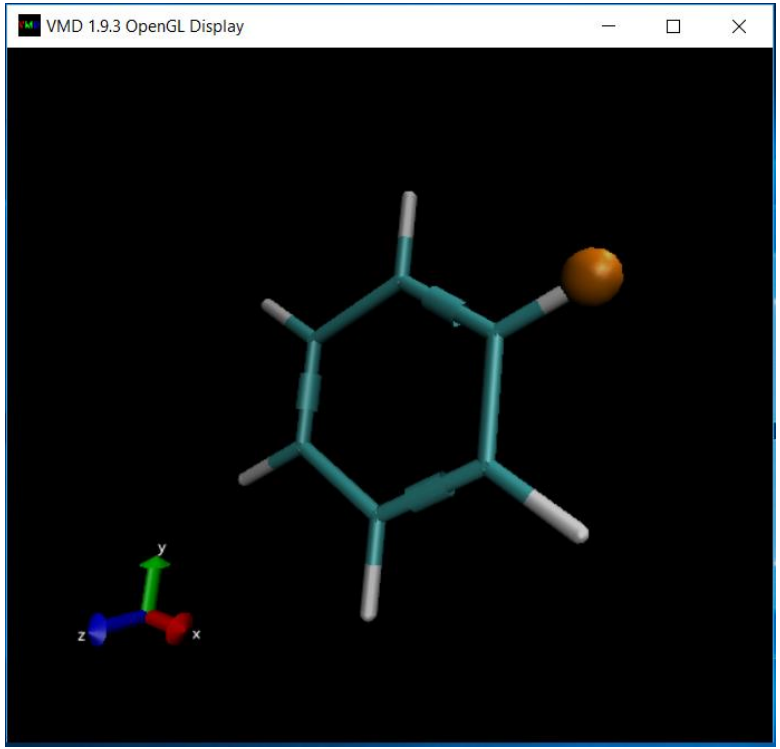
- First letter is atomic element
  - CG321 -> Carbon
- Letters and numbers after refer to specific types of each atom.
  - CG321 -> G321 type of Carbon
- Other encoding includes partial charge
  - CG321Z0.06 -> Charge of 0.06
  - CG321Z-0.06-> Charge of -0.06

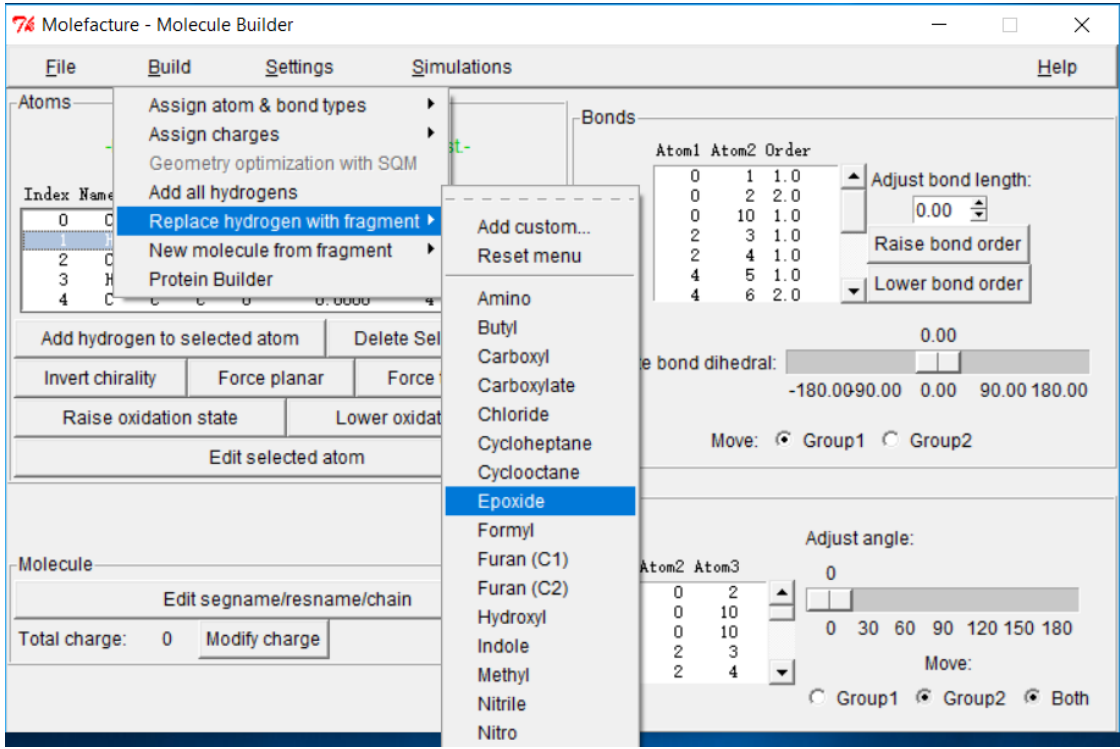


Workflow


Build Molecules in VMD
Optimize Structure in NWChem
Pack Molecules into a Box
Crosslinking Monomers
Minimize the Energy of the System
Conduct Testing
Glass Transition Temperature
Increase the Temperature and Equilibrate
Measure the Volume
System: Temperature, Volume are Variable
Bath: Temperature, Pressure are Constant

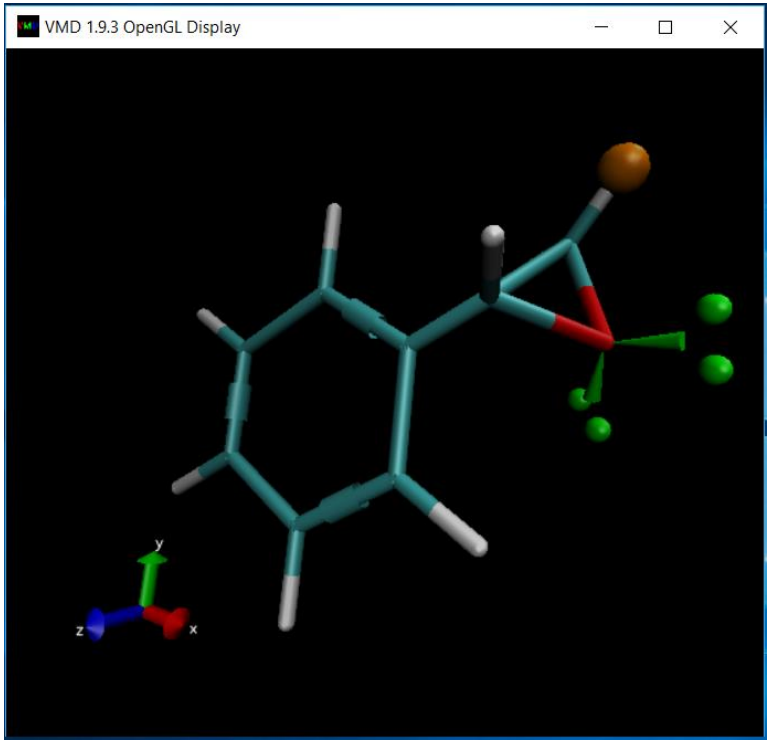
Building Molecules in VMD





Humphrey, W., et al. (1996).

Building Molecules in VMD



By repeatedly replacing the atoms with functional groups, we can build complicated molecular structure.

Humphrey, W., et al. (1996).

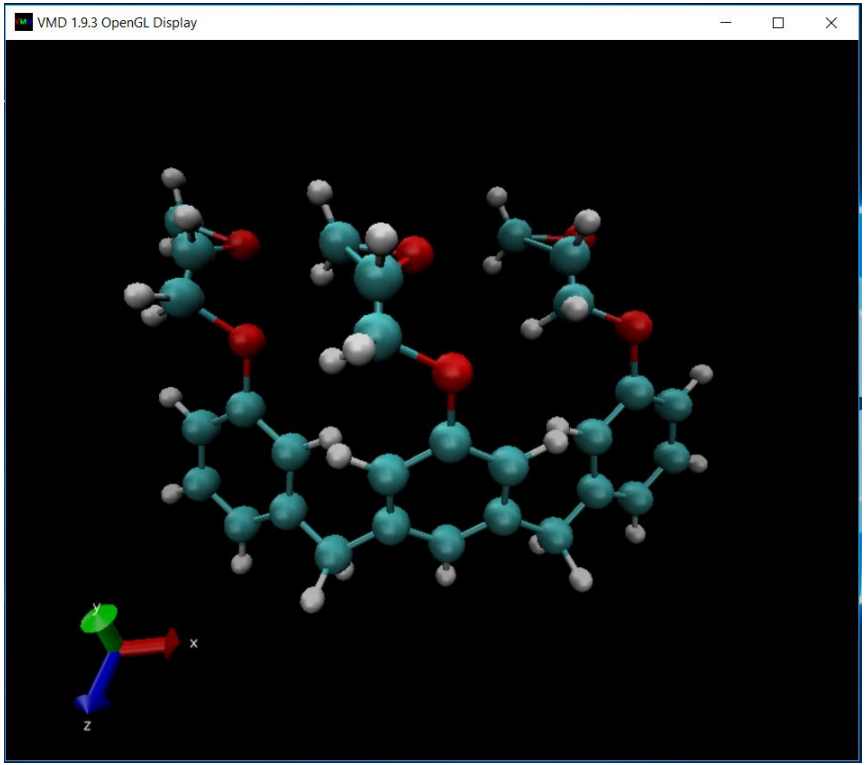
Molecular Structure Optimization

- We adopted the NWChem program to perform structural geometry optimization.
- The optimization is based on density functional theory (DFT), which is a quantum mechanical method widely used in computational chemistry.
- Through the optimization, the molecules will become more stable.

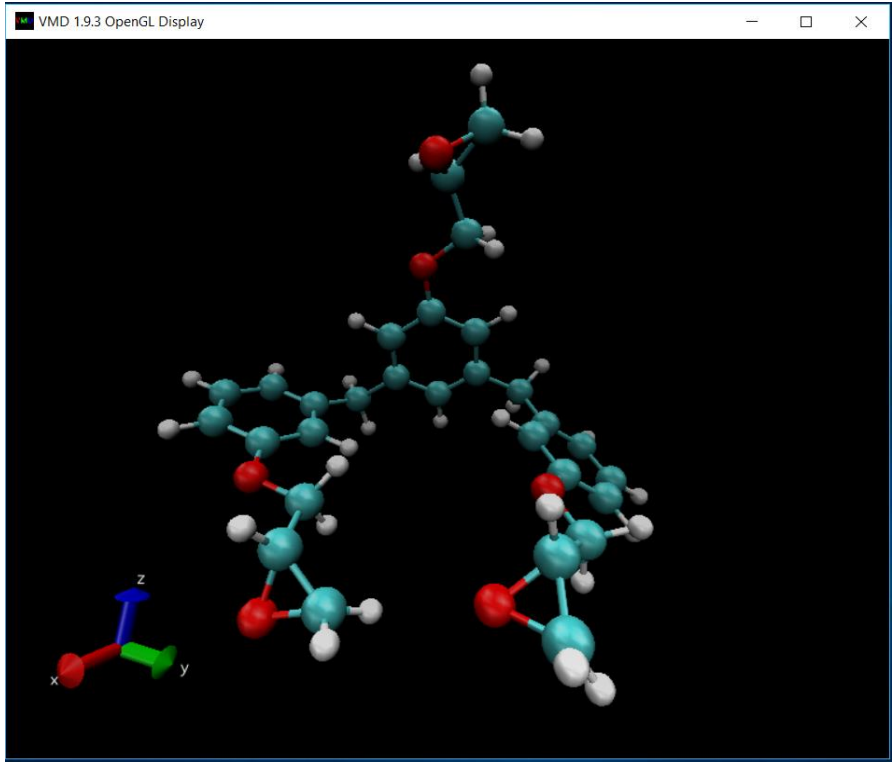
NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

M. Valiev, et al. (2010).

Molecular Structure Optimization

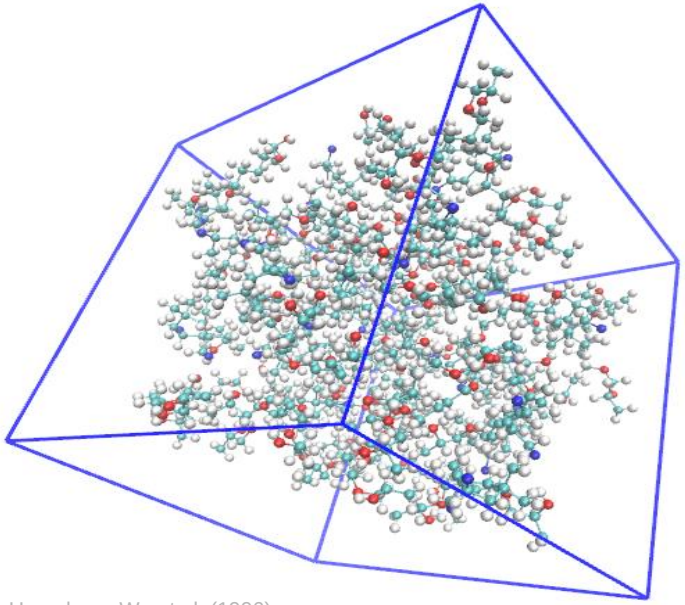


Unoptimized PDGE



Optimized PDGE

Pack molecules into a box



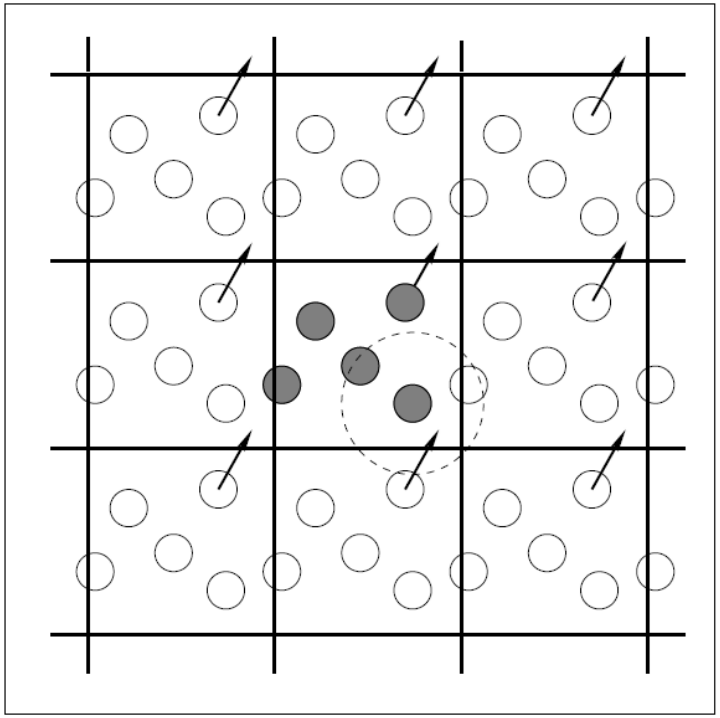
Humphrey, W., et al. (1996).

We built a simulation box with Packmol program.

Crosslinking reaction will be conducted within the box.

Periodic boundary condition will be applied in the simulation.

Periodic Boundary Condition



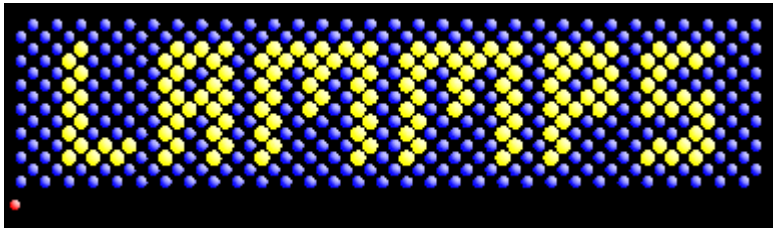
Allen, M. P. (2004).

Up to now, it's still not realistic for the computer to simulate a system containing atoms on the order of Avogadro's number (6.02×10^{23}).

With periodic boundary condition, we can "enlarge" the small simulation box.

LAMMPS

- Large-Scale Atomic/Molecular Massively Parallel Simulator
- Customizable to a wide variety of experiments and fields of study



S. Plimpton. (1995).

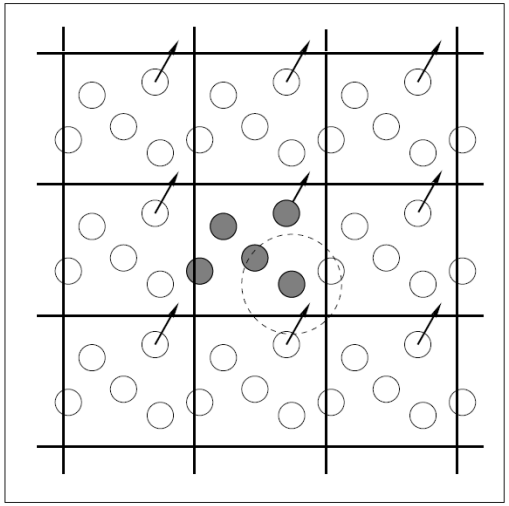
Simulation Procedure

$1fs = 10^{-15}s$; $1ps = 10^{-12}s$

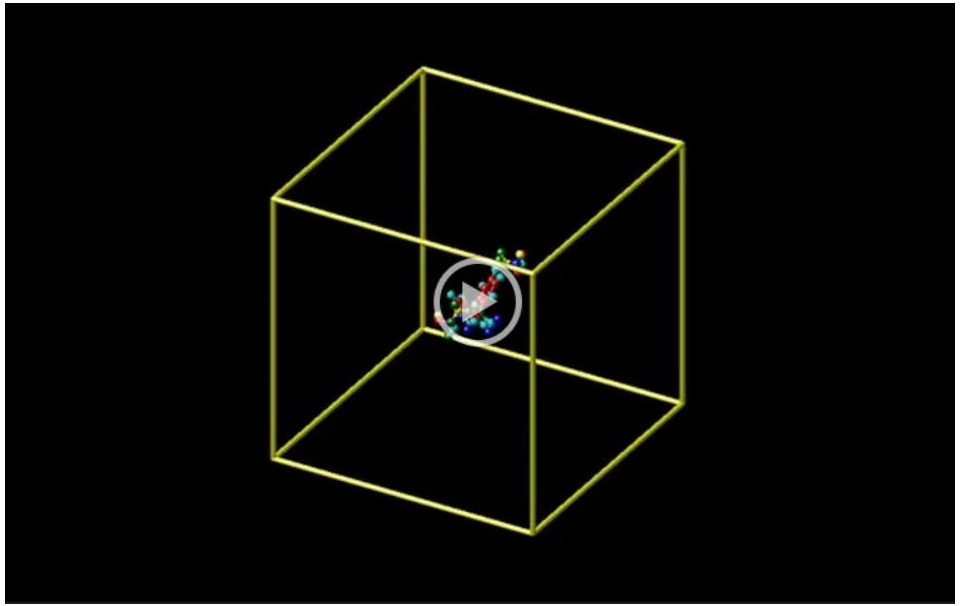
1. Set the length of a timestep to be 0.5fs.
2. Perform energy minimization on the simulation box.
3. Equilibrate the system at 800 Kelvin, 1 atm, for 100 ps in canonical (NVT) ensemble followed by 400ps in isothermal–isobaric (NPT) ensemble.
4. Cool down the system from 800K to 10K with an interval of 10K. At each temperature, run 10 ps of NVT ensemble followed by 40ps of NPT ensemble. The volume is averaged over the last 2.5ps of the NPT simulation.

Issues Faced in LAMMPS

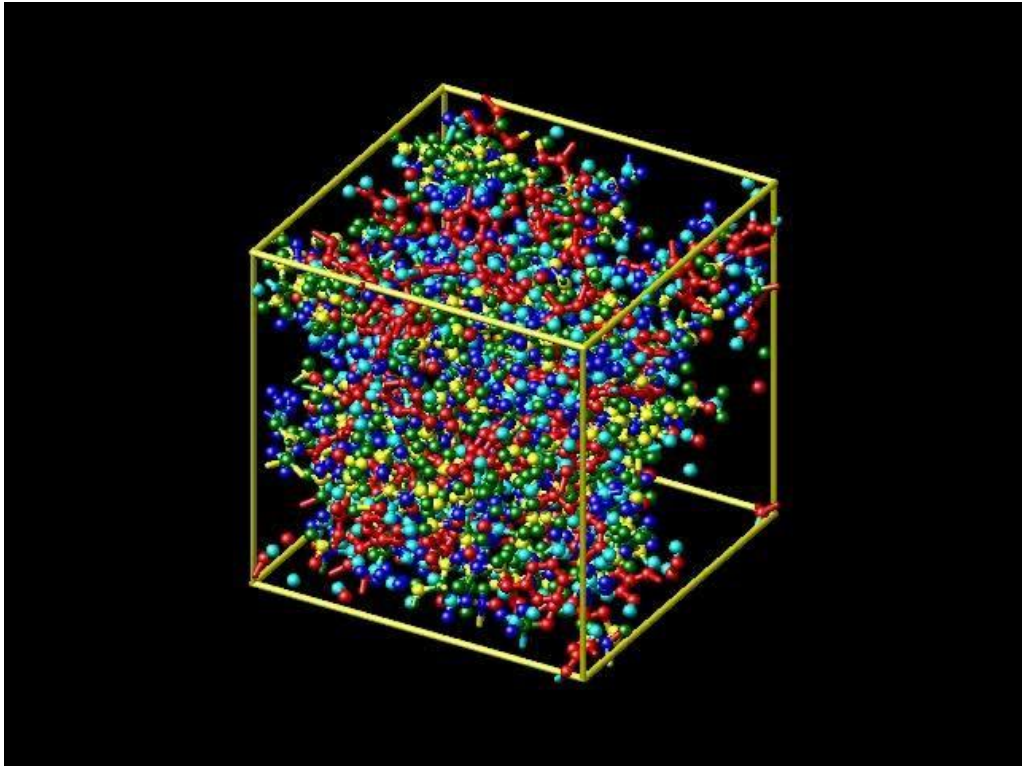
- Mistyping/ Improper reading of input data types
- Atom Bonds not on processor 3



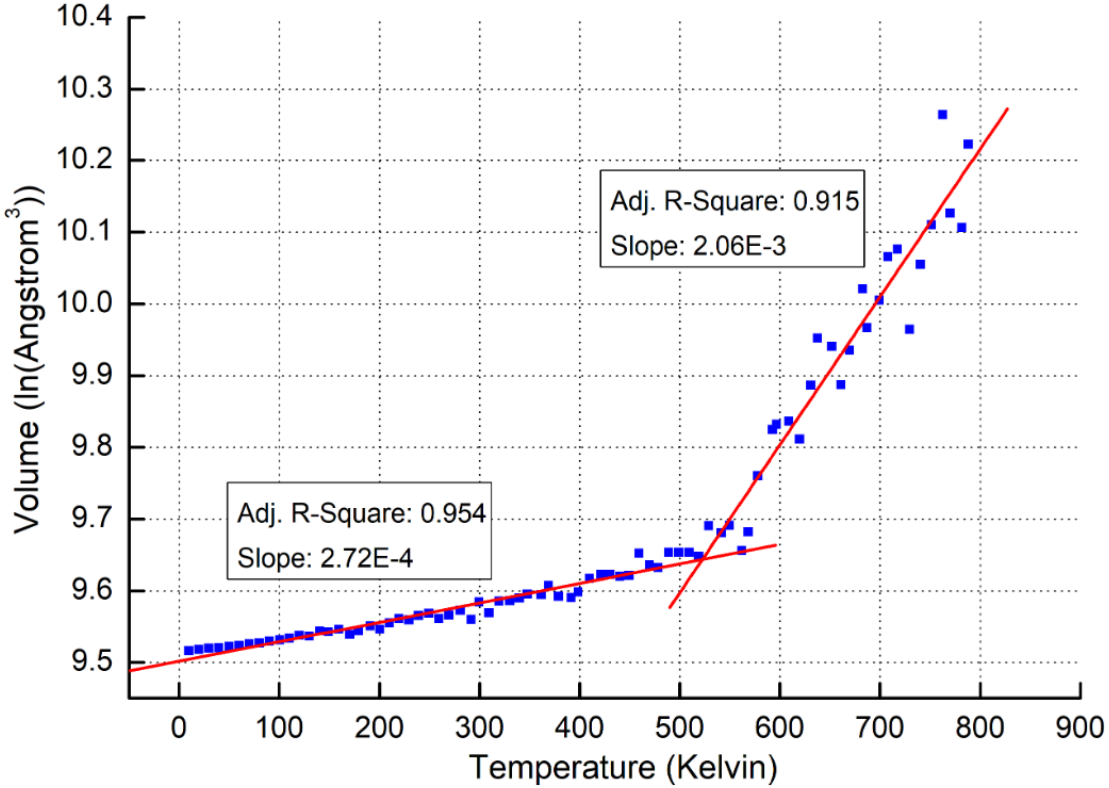
Allen, M. P. (2004).



Cooling Down the System



Results: BADGE-IPDA

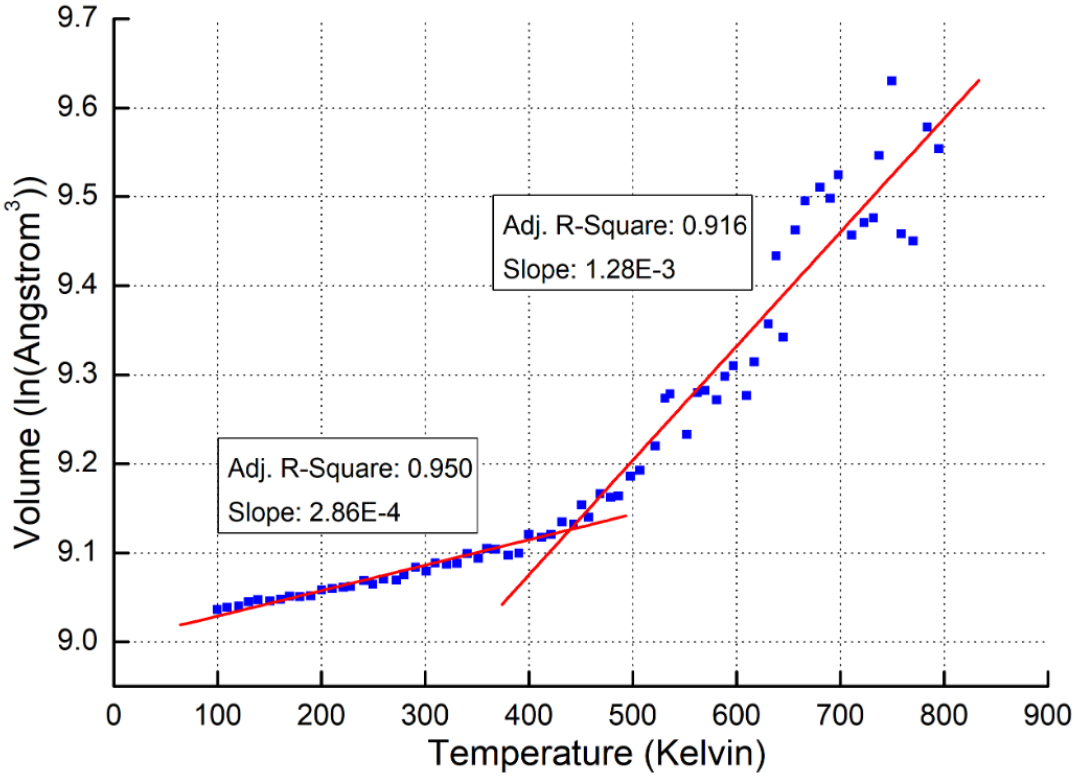


For the 90% crosslinked BADGE-IPDA system, we measured the glass transition temperature to be 524.06K (experimental value: 436K).

The thermal expansion coefficient (α) we measured in glassy state is 2.72e-4 K^{-1}, while in rubbery state is 2.06e-3 K^{-1}.

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P = (\frac{\partial ln(V)}{\partial T})_P$$

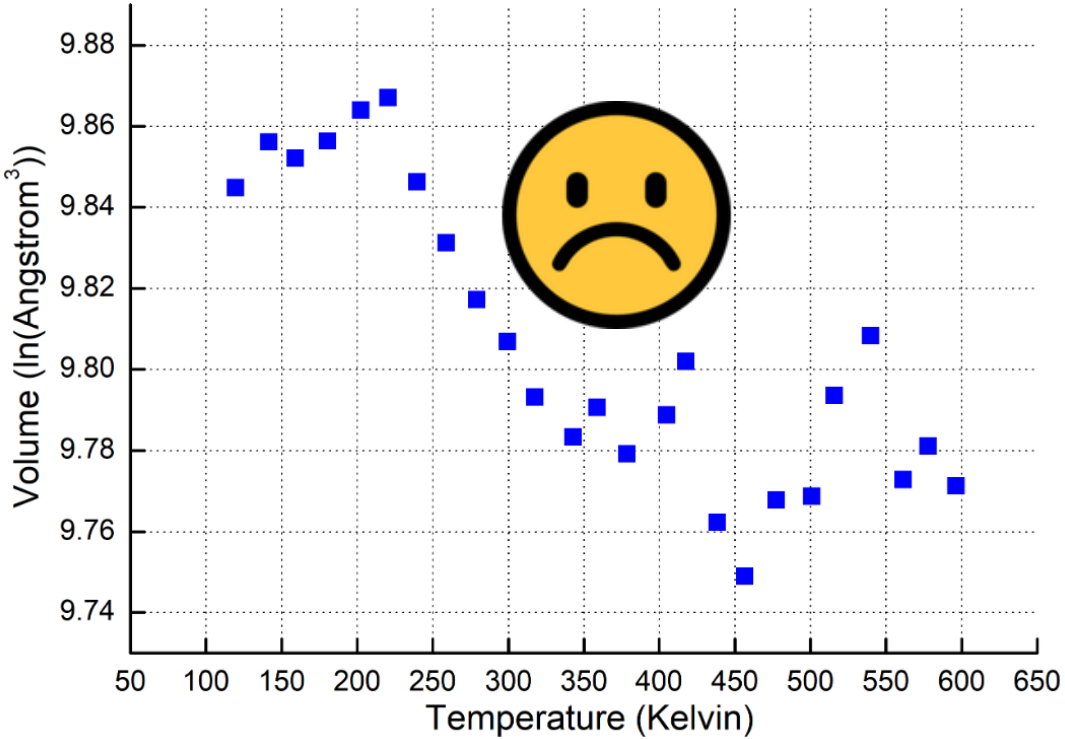
Results: DGEBD-IPDA



As for the 90% crosslinked DGEBD-IPDA system, we measured the glass transition temperature to be 439.86K (experimental value: 326K).

The thermal expansion coefficient we measured in glassy state is 2.86e-4 K^{-1}, while in rubbery state is 1.28e-3 K^{-1}.

Results



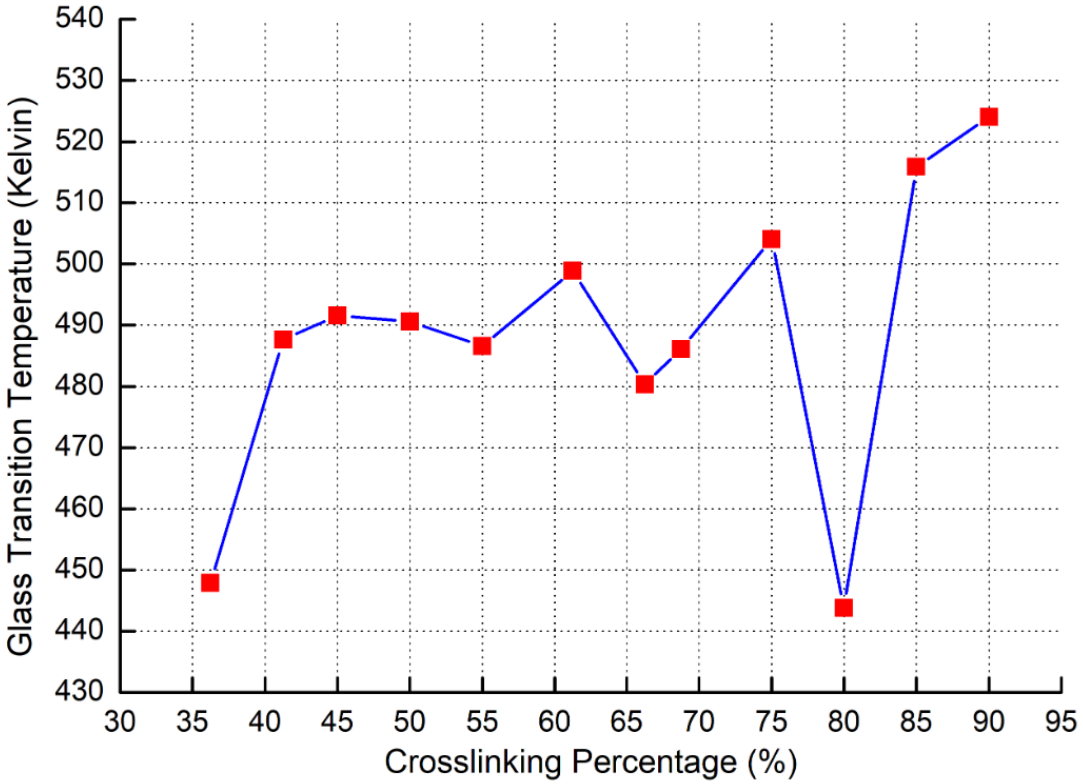
Why cooling down the system?

At low temperature, the kinetic energy of molecules is low.

The system needs more time to reach the equilibrium.

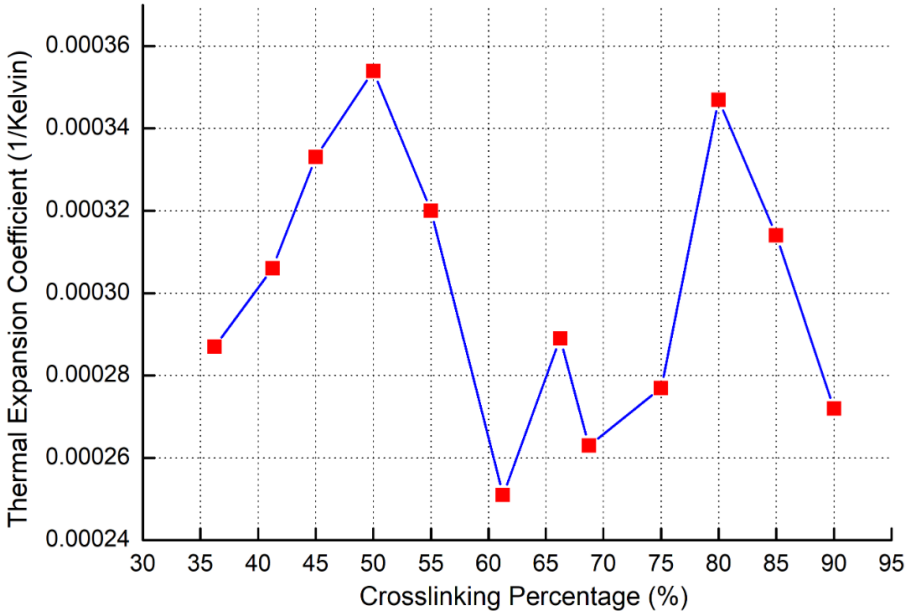
For heating up the system from low temperature, if the simulation time is short, we will obtain incorrect results!

Results: Crosslinking percentage v.s. T_g

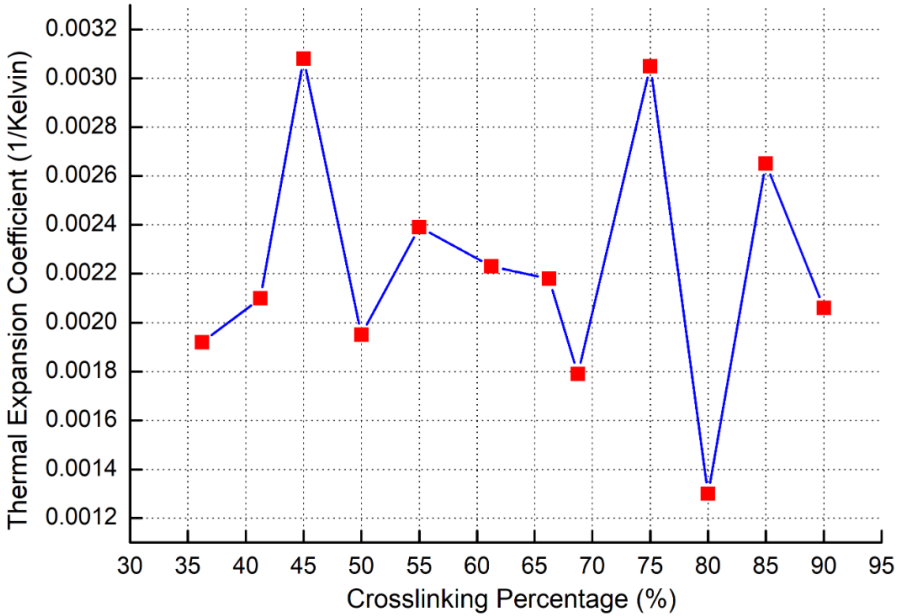


The effect of crosslinking percentage on glass transition temperature of the BADGE-IPDA system.

Results: Crosslinking percentage v.s. α



In glassy state



In rubbery state

Future Work

Use the methods developed over the course of the summer to work on systems that have unknown properties.

Find the reason why the glass transition temperatures are larger than the experimental measurements.

Use larger volumes of the same system to see if results are replicable for computations involving a larger system.

Investigate CGenFF in depth: Automatic Atom Typing Software.

References

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