MD Chemistry

Molecular Dynamics Simulation of Epoxy Resin Systems to Study Physical Properties

2018

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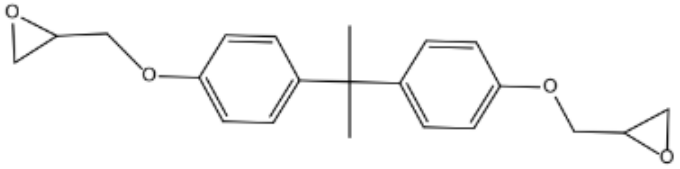
Lonnie Crosby

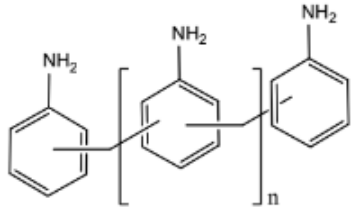
Epoxy-Hardener System

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

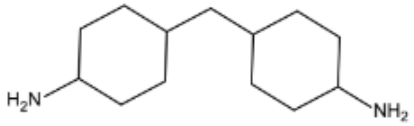
MSDS and Sigma Aldrich



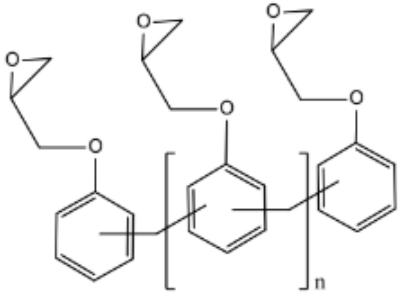
Propane, 2,2-bis[p-(2,3-epoxypropoxy)phenyl [BADGE] (70-100%)



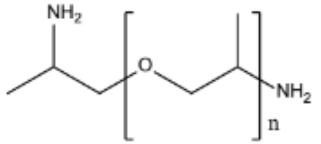
Benzenamine-formaldehyde polymer [Aniline formaldehyde] (15-35%)



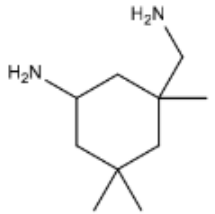
4, 4'-Methylenebiscyclohexanamine [Methylene-BCHA] (10-30%)



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

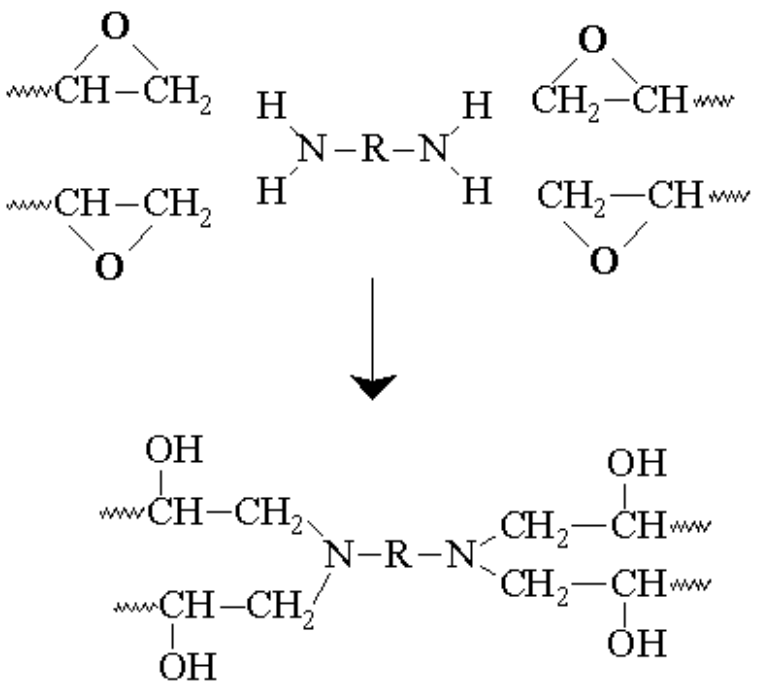


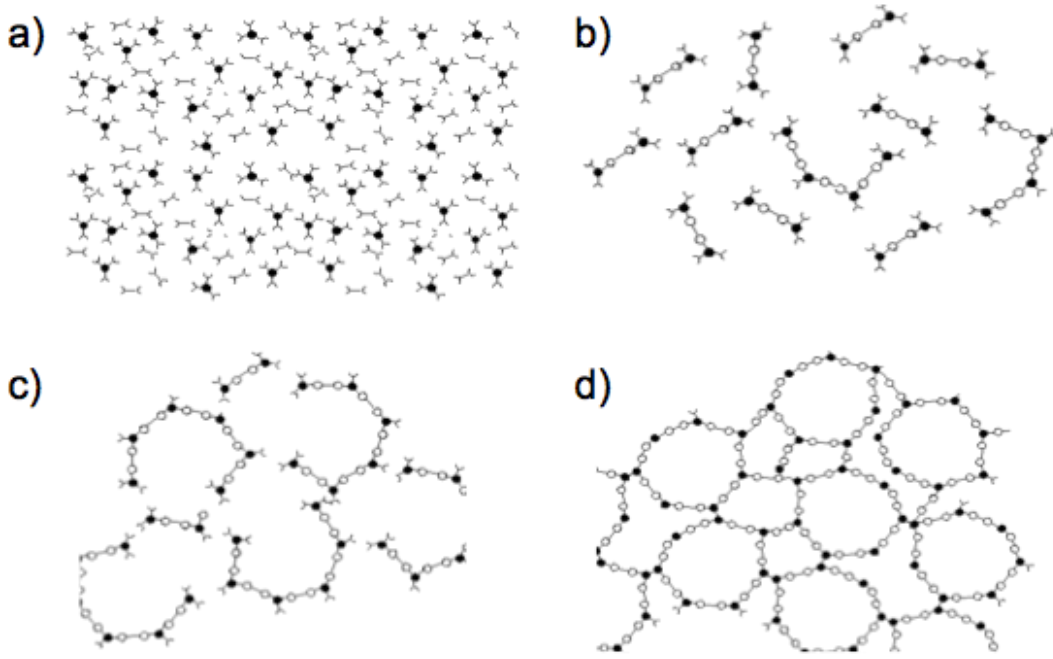
Polyoxyropylenediamine [POPDA] (10-30%)



Isophoronediamine [IPDA] (10-30%)

Curing reaction



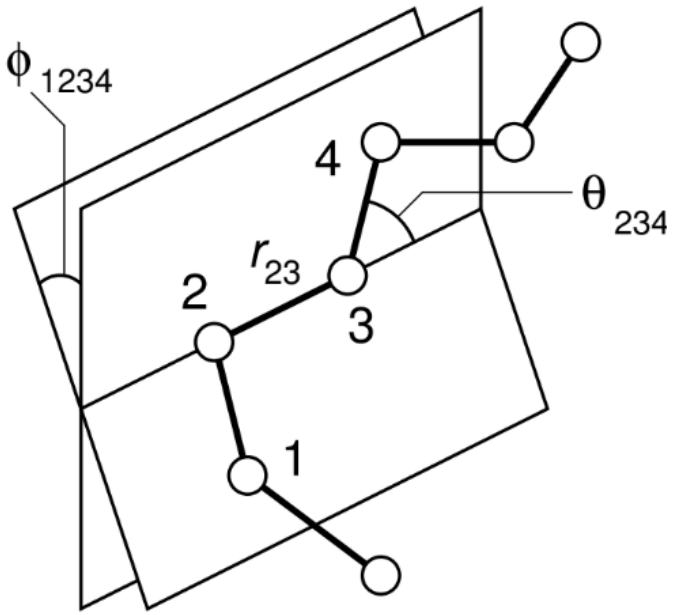


Molecular Dynamics Simulation

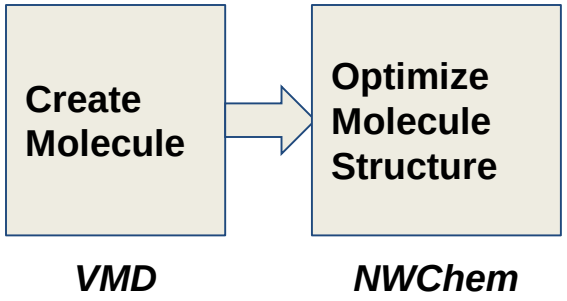
1. Divide time into discrete time steps
2. At each time step:
- Compute the force acting on each atoms, using molecular mechanics force field.
- update position and velocity according to Newton's law of motion

CHARMM Force Field

$$
\begin{aligned}
U_{\text{CHARMM}} = & \sum_{\text{bonds}} K_b(b - b_0)^2 \\
& + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 \\
& + \sum_{\text{dihedrals}} K_\phi(1 + \cos(n\phi - \delta)) \\
& + \sum_{\text{improper}} K_\varphi(\varphi - \varphi_0)^2 \\
& + \sum_{\text{Urey-Bradley}} K_{UB}(r_{1,3} - r_{1,3;0})^2 \\
& + \sum_{\text{CMAP}} u_{\text{CMAP}}(\Phi, \Psi) \\
& + \sum_{\text{nonb,pair}} \frac{q_i q_j}{4\pi D r_{ij}} \\
& + \sum_{\text{nonb,pair}} \varepsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min,ij}}{r_{ij}} \right)^{6} \right]
\end{aligned}
$$

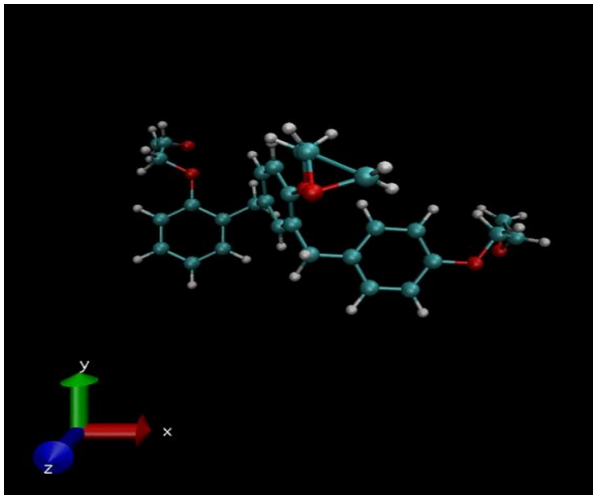


Procedure

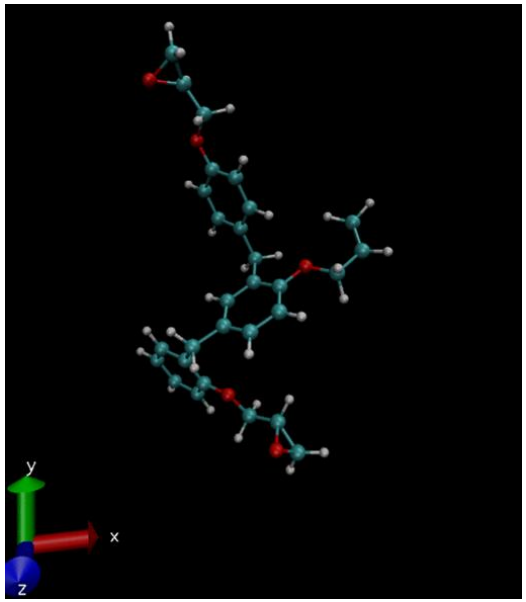


Optimizing Geometry

- Build molecule from fragments
- NWChem optimizes the molecular geometry (angles, bond lengths, etc.)
- Löwdin population analysis determines partial charge on each atom

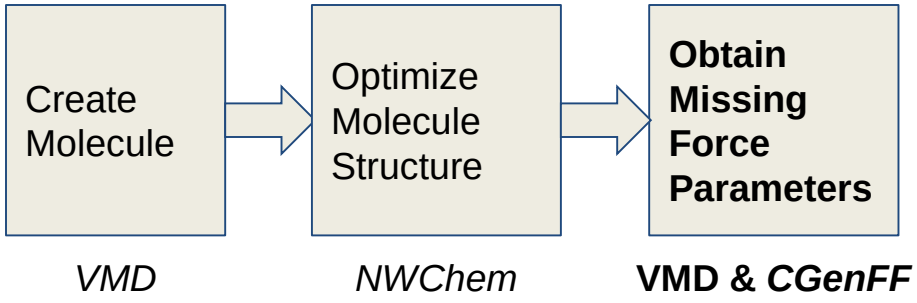


Unoptimized PDGE Formaldehyde



Optimized PDGE Formaldehyde

Procedure

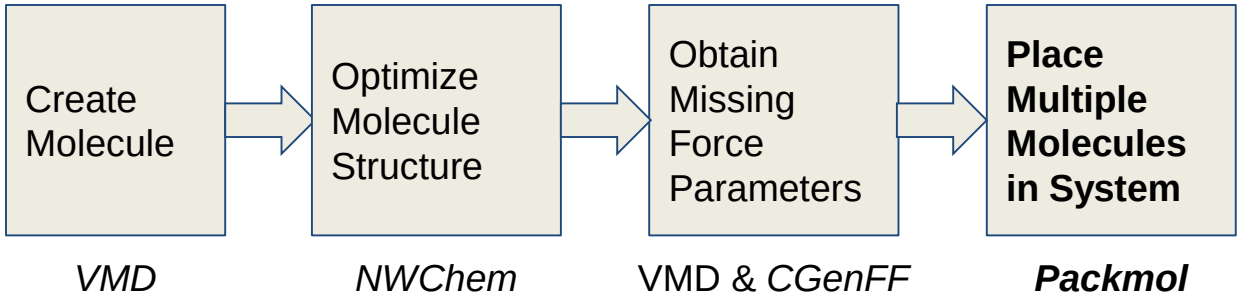

Create Molecule
Optimize Molecule Structure
Obtain Missing Force Parameters
VMD
NWChem
VMD & CGenFF

Generate LAMMPS data file

```
LAMMPS data file. CGCMM style. atom_style
 68 atoms
 70 bonds
 117 angles
 165 dihedrals
 0 impropers

 11 atom types
 12 bond types
 20 angle types
 25 dihedral types
 0 improper types
 -0.500000 0.500000  xlo xhi
 -0.500000 0.500000  ylo yhi
 -0.500000 0.500000  zlo zhi

Masses

 1 12.010700 # CG2R61
 2 12.010700 # CG311
 3 12.010700 # CG321
 4 12.010700 # CG331
 5 1.007940 # HGA1
 6 1.007940 # HGA2
 7 1.007940 # HGA3
 8 1.007940 # HGP1
 9 1.007940 # HGR61
 10 15.999400 # OG301
 11 15.999400 # OG311
```

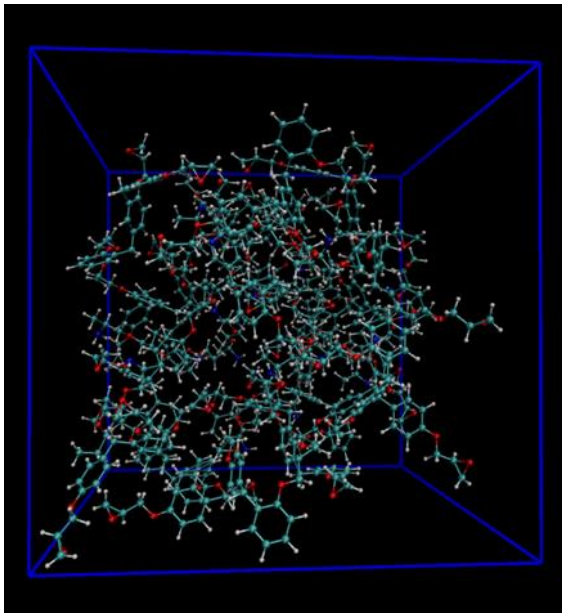
```
Bond Coeffs # harmonic

1       305.00  1.3750  #CG2R61-CG2R61
2       230.00  1.4900  #CG2R61-CG321
3       340.00  1.0800  #CG2R61-HGR61
4       230.00  1.3820  #CG2R61-OG301
5       222.50  1.5380  #CG311-CG321
6       222.50  1.5380  #CG311-CG331
7       309.00  1.1110  #CG311-HGA1
8       428.00  1.4200  #CG311-OG311
9       309.00  1.1110  #CG321-HGA2
10      360.00  1.4150  #CG321-OG301
11      322.00  1.1110  #CG331-HGA3
12      545.00  0.9600  #HGP1-OG311

Angle Coeffs # charmm

1       40.00   120.00  35.00   2.41620 #CG2R61-CG2R61-CG2R61
2       45.80   120.00  0       0       #CG2R61-CG2R61-CG321
3       30.00   120.00  22.00   2.15250 #CG2R61-CG2R61-HGR61
4       110.00  120.00  0       0       #CG2R61-CG2R61-OG301
5       51.80   107.50  0       0       #CG2R61-CG321-CG2R61
6       49.30   107.50  0       0       #CG2R61-CG321-HGA2
7       65.00   108.00  0       0       #CG2R61-OG301-CG321
8       33.43   110.10  22.53   2.17900 #CG311-CG321-HGA2
9       45.00   111.50  0       0       #CG311-CG321-OG301 ***Rep
10      33.43   110.10  22.53   2.17900 #CG311-CG331-HGA3
11      50.00   106.00  0       0       #CG311-OG311-HGP1
12      53.35   114.00  8.00    2.561   #CG321-CG311-CG331
13      34.50   110.10  22.53   2.17900 #CG321-CG311-HGA1
14      75.70   110.00  0       0       #CG321-CG311-OG311
15      34.50   110.10  22.53   2.17900 #CG331-CG311-HGA1
16      75.70   110.10  0       0       #CG331-CG311-OG311
17      45.90   108.89  0       0       #HGA1-CG311-OG311
18      35.50   109.00  5.40    1.802   #HGA2-CG321-HGA2
19      45.90   108.89  0       0       #HGA2-CG321-OG301
20      35.50   108.40  5.40    1.80200 #HGA3-CG331-HGA3
```

Procedure

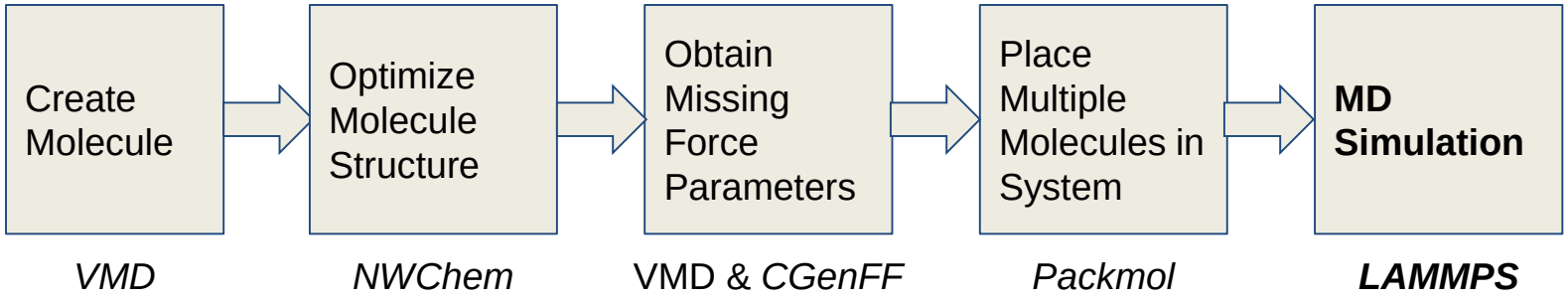

Create Molecule
Optimize Molecule Structure
Obtain Missing Force Parameters
Place Multiple Molecules in System
VMD
NWChem
VMD & CGenFF
Packmol

Initialize System in Packmol

- Allows us to place multiple of our optimized molecules into a closed system
- The system is a periodic box
- Prevents atoms and molecules from escaping without placing additional restraints on the system

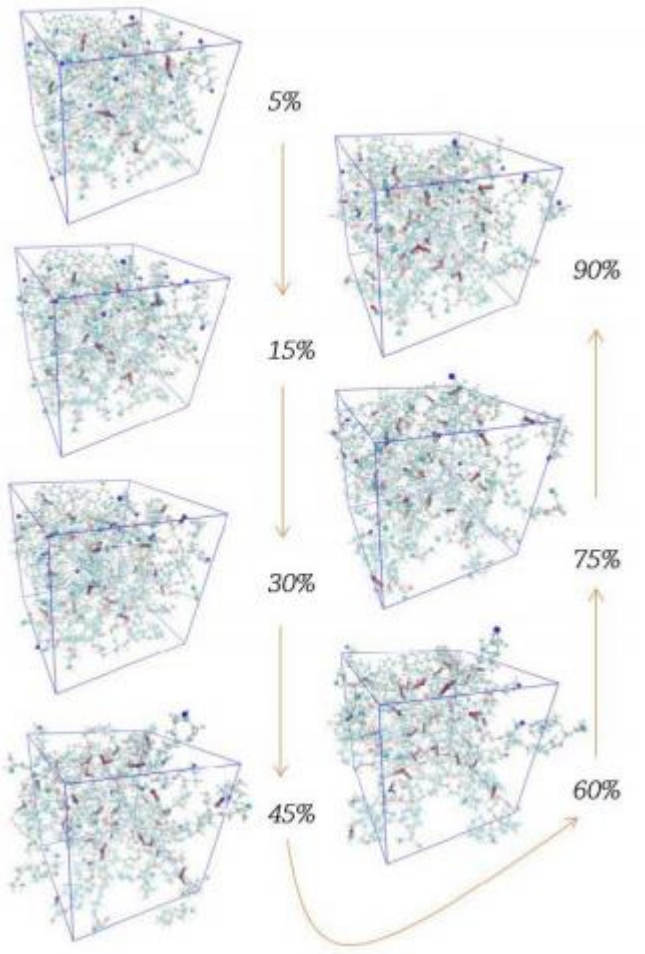


Procedure


Create Molecule
Optimize Molecule Structure
Obtain Missing Force Parameters
Place Multiple Molecules in System
MD Simulation
VMD
NWChem
VMD & CGenFF
Packmol
LAMMPS

Next Steps

- Finalize force parameters
- Minimize energy and run NVT and NPT ensemble equilibration
- Add script to create bonds between epoxy and hardener groups--crosslinked structure



Next Steps continued

- Run thermodynamics experiments on our model system
- Measure physical properties under various conditions
  - Glass Transition Temperature
  - Thermal Expansion Coefficient
  - Isothermal Compressibility

References

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