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Molecular Dynamics Simulation of Fracture Initiation at a Corner

Mark Stevens

Sandia National Laboratories

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Mark Stevens
msteve@sandia.gov

Epoxies are important class of structural adhesives.

Basically, they are a highly crosslinked polymer network.

What is the mechanical behavior of a highly crosslinked network,

and how does it depend on various *molecular* attributes of the network and system?

Past, did modeling & simulation of epoxies as highly crosslinked polymer network.

Mark Stevens
msteve@sandia.gov

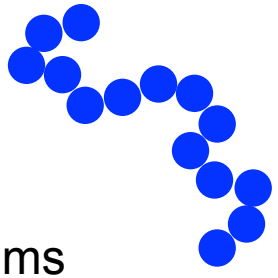
What's New?

- New model that matches T403 crosslinker's geometry
  - Most important, packing at solid substrate does not have layers of crosslinker and resin
- Open surface geometry has corners, which possess stress singularity in continuum limit
- Much larger systems

Mark Stevens
msteve@sandia.gov

Modeling Epoxies

- Polymer models
  - coarse-grained models to treat long time scales
    - bead spring model
    - random walk paradigm
    - focus is on trends (not single quantities) & molecular mechanisms
  - atomistic models
    - available time scales typically too short
      - » time step = 1 fs ⟹ total time ~ 10-100 ns
    - more appropriate for the liquid mixture interaction with surface
    - force-fields available are probably poor



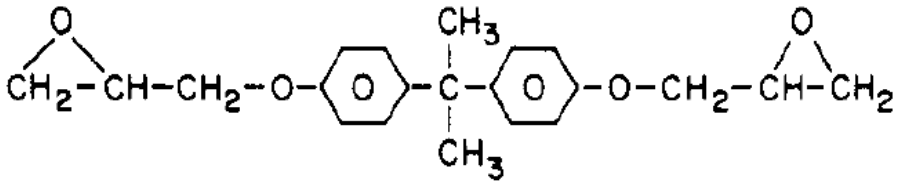
- Epoxies
  - complex chemical structure ⇒ atomistic simulations unreasonable
  - glass ⇒ weak strain rate dependence
  - **view as highly crosslinked polymer network**

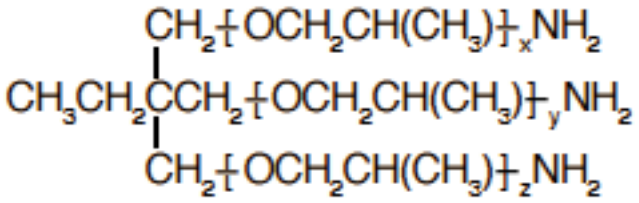
Mark Stevens
msteve@sandia.gov

Original Epoxy Model

- Original model: minimal
  - simple, highly crosslinked network (i.e. very short strands between crosslinks)
  - network has 2 beads between each crosslinker
  - crosslinker is a single particle of functionality *f*
    - new version matches geometry better
      - » important for packing at surface
  - resin model is a dimer

example molecules



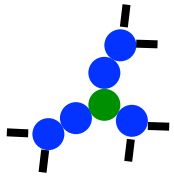


$x + y + z = \sim 5.3$

models

minimal (original)

'T403'

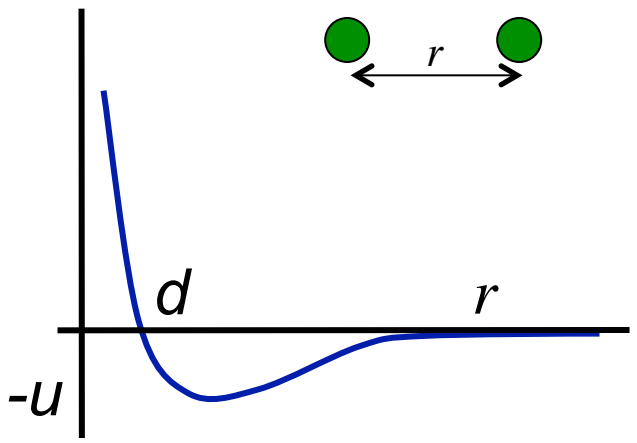


Mark Stevens
msteve@sandia.gov

Potentials

Lennard-Jones (LJ) potential (van der Waals)

$$4u\left[\left(\frac{d}{r_{ij}}\right)^{12}-\left(\frac{d}{r_{ij}}\right)^{6}\right]$$

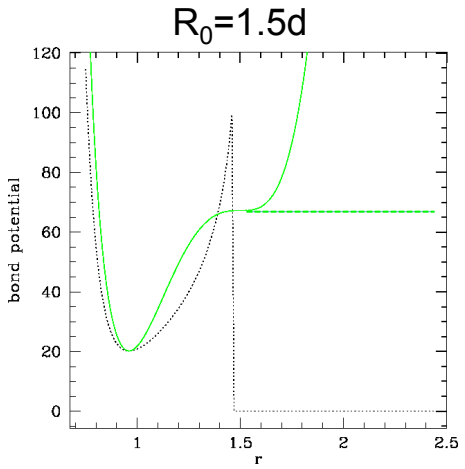


- Energy unit: u
- Length unit: d
- Here all types equivalent

Bond potential

- FENE (non breakable) = $-kR_0 \log(1-(r/R_0)^2)$
- breakable (smooth quartic)

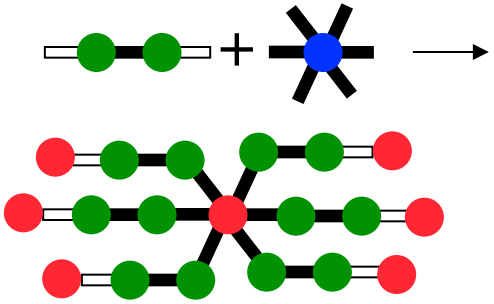
No angle potential: full flexible chains



Mark Stevens
msteve@sandia.gov

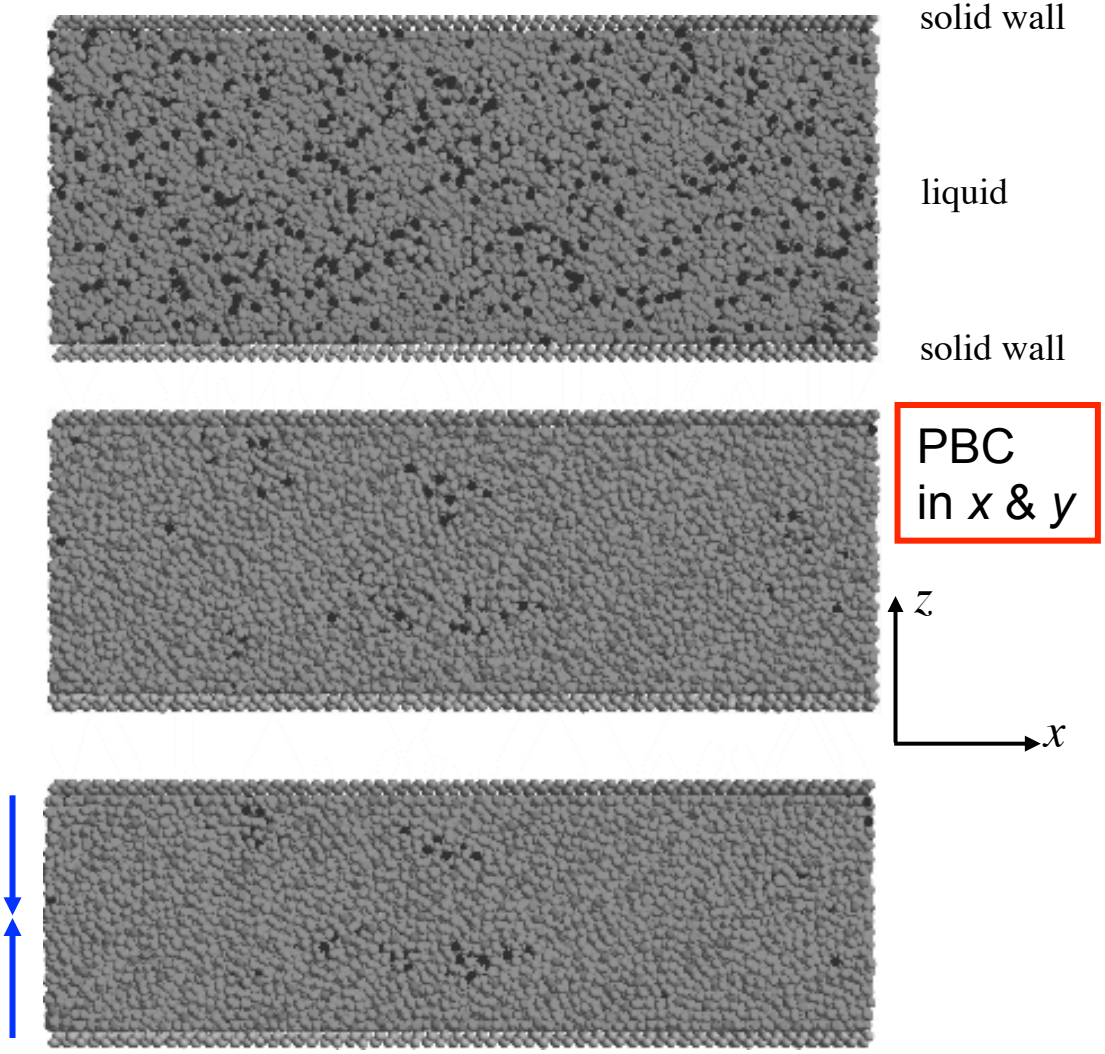
Formation of Model Epoxy Adhesive

Equilibrate liquid mixture at **T** > T_g and zero **load** (allow volume to adjust).



1) Bond to walls
2) crosslink under load
   > 95% cured

Lower to T < T_g.
Shrinks.



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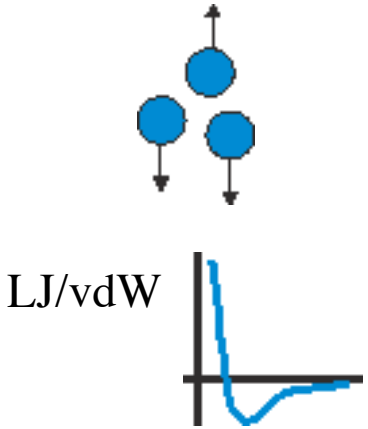
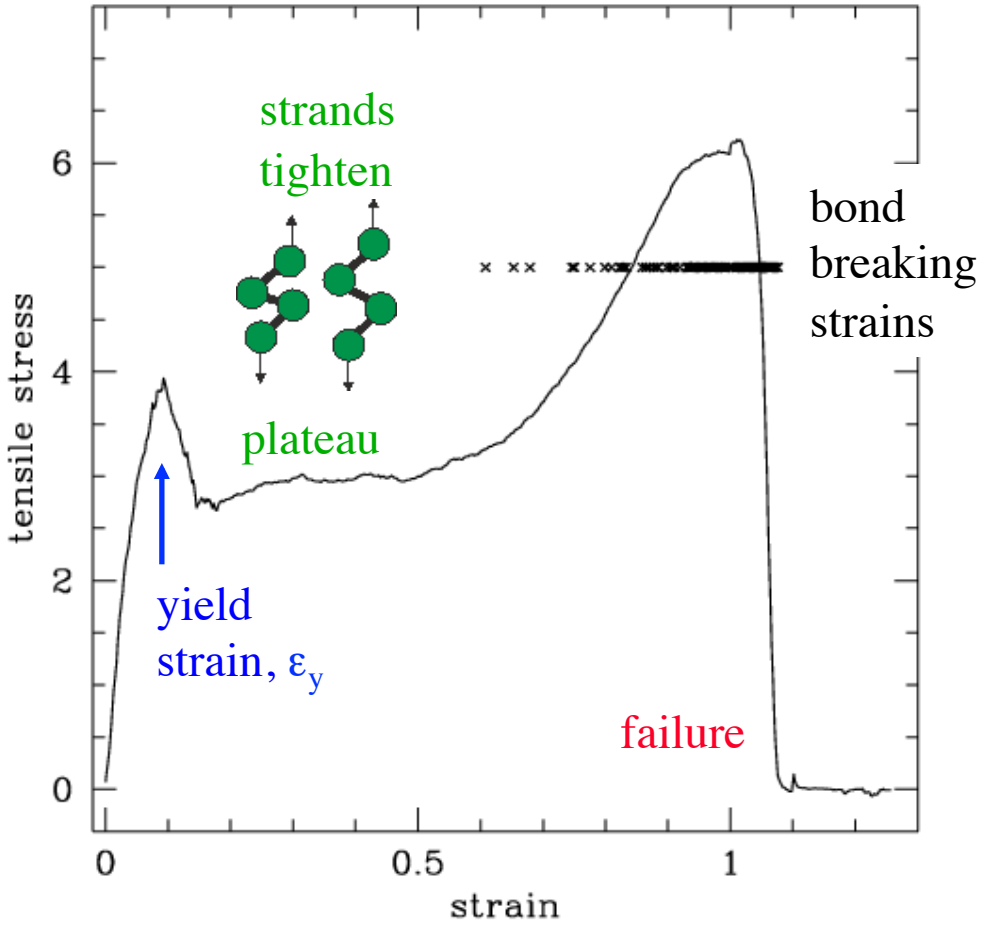
Mark Stevens
msteve@sandia.gov

Tensile stress-strain curve: Molecular Mechanisms



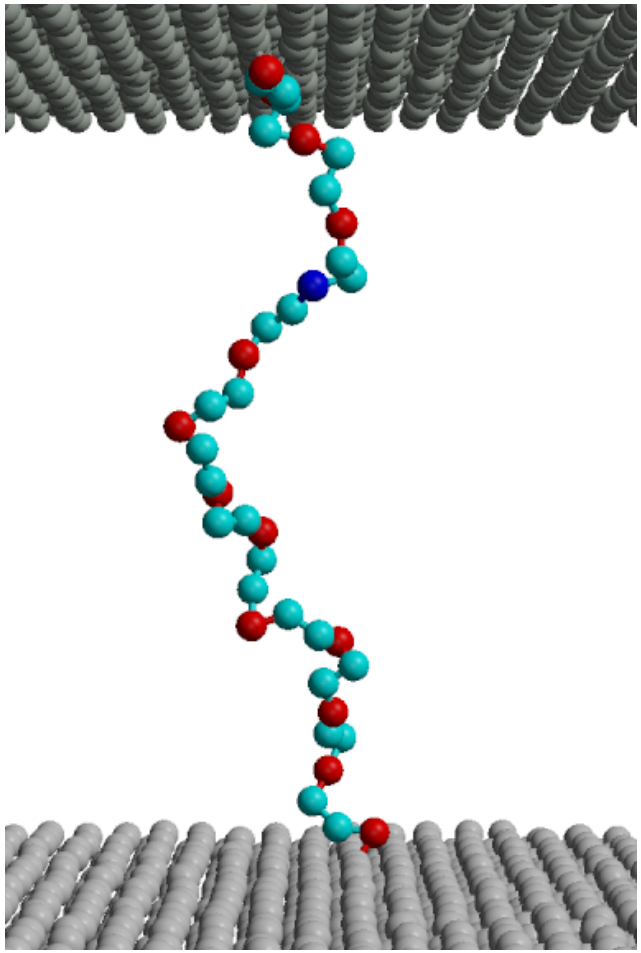


Mark Stevens
msteve@sandia.gov

Failure Strain: Minimal Paths in Network

For each bond to the top surface there is a **minimal path** of length *P* through the network to the bottom surface

- Failure strain is determined by maximum minimal path
  - At the strain equivalent to the maximum *P,* all bonds in the paths connecting the two surfaces must be stressed
- In the presence of defects, failure occurs at smaller strains, because of nonuniform strains.



Mark Stevens
msteve@sandia.gov

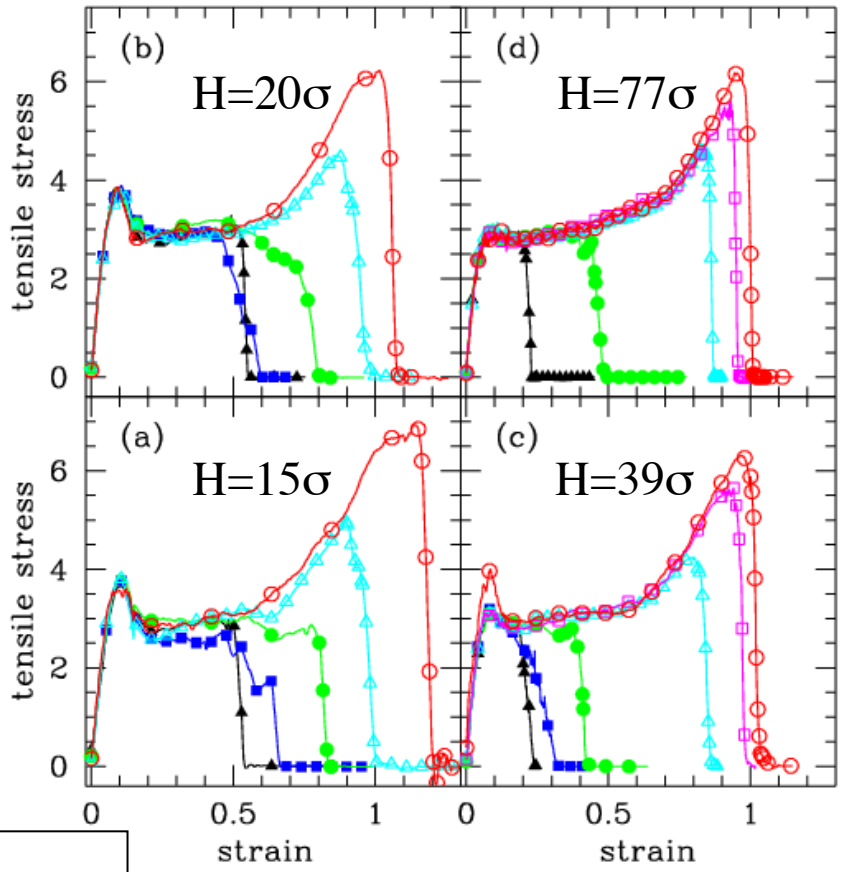
(Old) Tensile strain data

Lot of data for original model

- System size dependence
- Interfacial bond density dependence

surface bond coverage

- 0%
- 10%
- 25%
- 50%
- 75%
- 100%



- Failure strain varies with height.
- Failure stress does not vary with height.
- 100% coverage has master stress-strain curve.
- Partial coverages follow master curve til failure.

Macromolecules **2001,** *34*, 2710-2718

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Mark Stevens
msteve@sandia.gov

Bulk Data

Same procedure, but no surfaces and full PBC.

Calculate elastic moduli by deforming simulation cell.

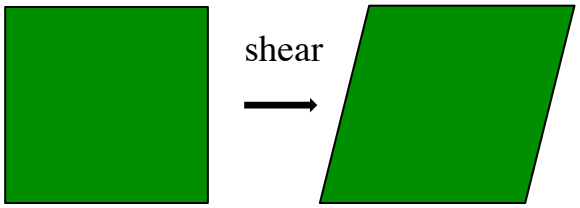
original model:

$E = 33.0\ u_0/d^3$

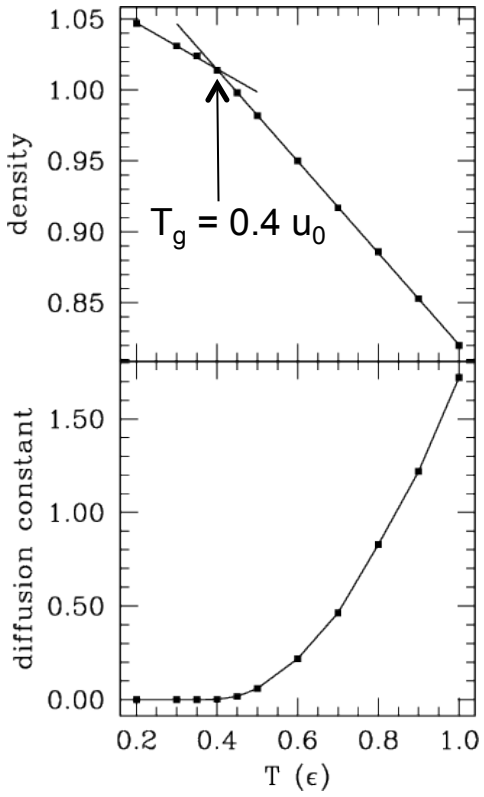
$G = 65.0\ u_0/d^3$

$K = 11.7\ u_0/d^3$

$\nu = 0.41$



Calculating T_g
T403 model



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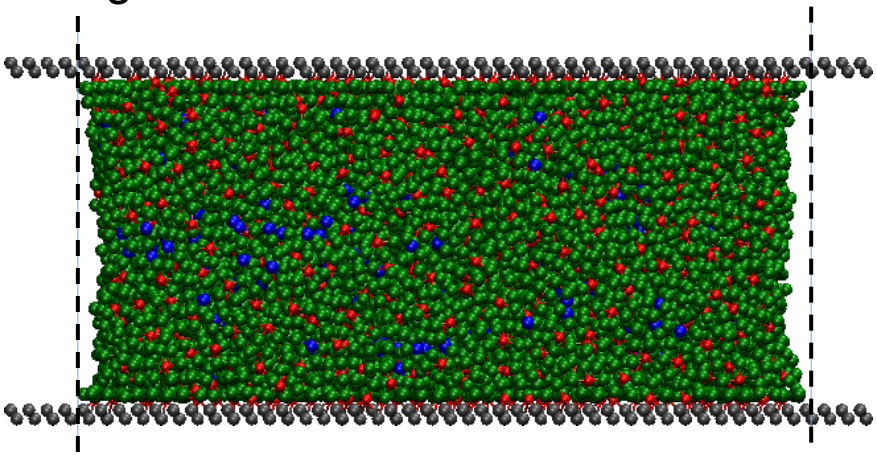
Mark Stevens
msteve@sandia.gov

System with corners

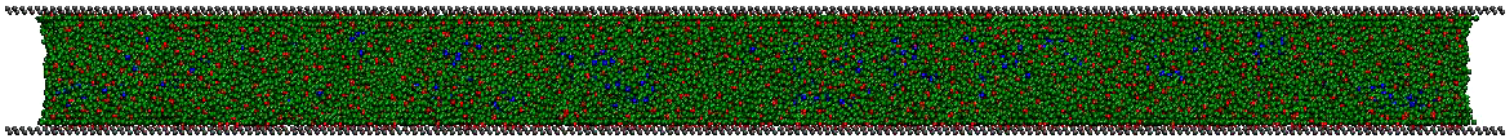
- To create system with corner, the PBC is removed in one direction
- To contain liquid, a temporary wall potential is used to confine the system during initial equilibration and bonding to wall
- Crosslink liquid without wall potential



Tensile pull

constant velocity
(or strain rate)

v



Mark Stevens
msteve@sandia.gov

Systems

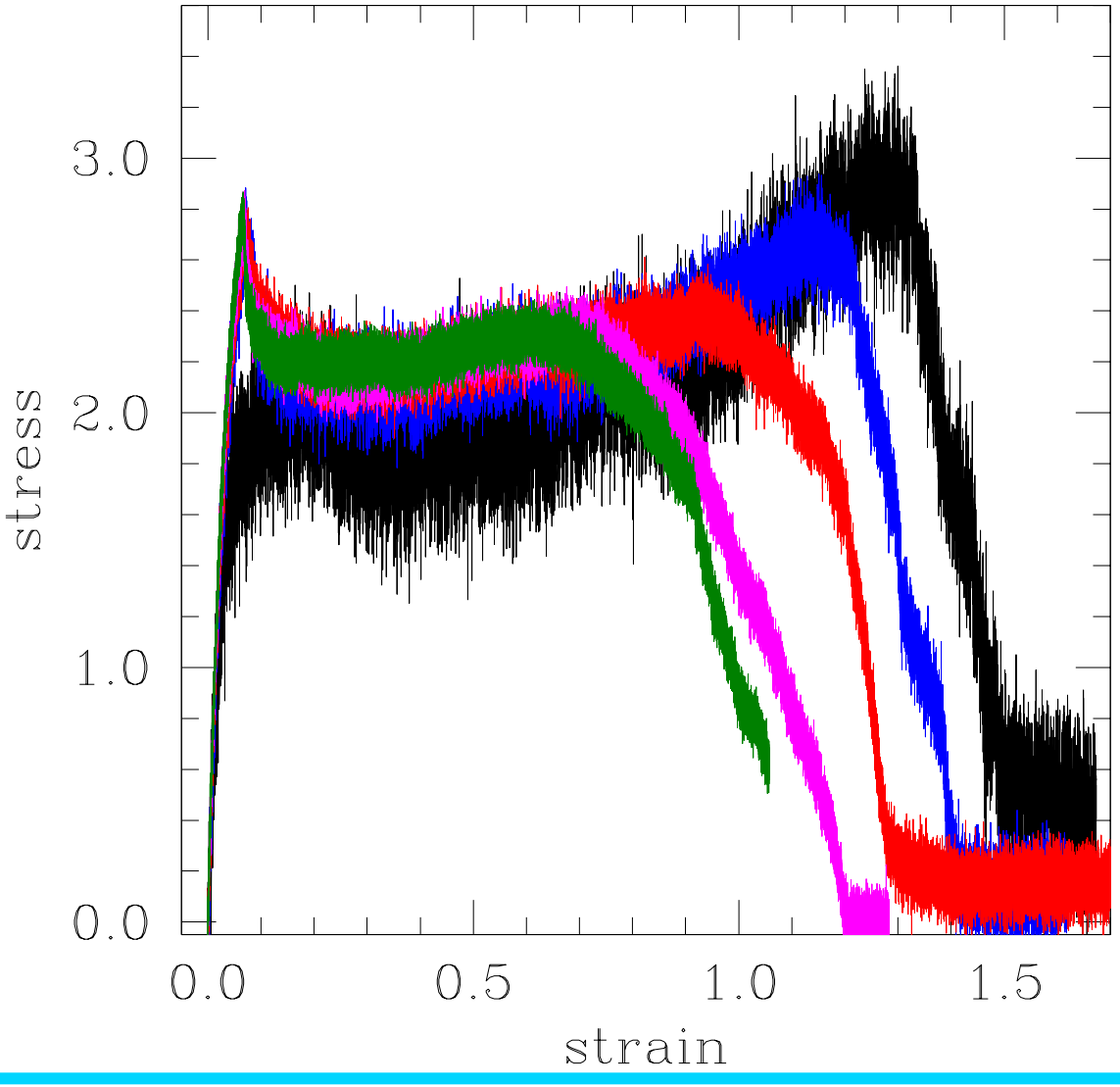
	h	N	w
1	42.4	256 k	208
2	76.1	2.0 M	832
3	149.0	7.7 M	1668
4	222.5	17.1M	2502
5	295.0	30.7M	3338

w/h ~ 10

	h	N	failure strain	crack strain	w
1	42.4	256 k	1.41	1.35	208
2	76.1	2.0 M	1.31	1.08	832
3	149.0	7.7 M	1.23	0.96	1668
4	222.5	17.1M	1.05	0.74	2502
5	295.0	30.7M	0.96	0.58	3338

Mark Stevens
msteve@sandia.gov

Stress vs. Strain



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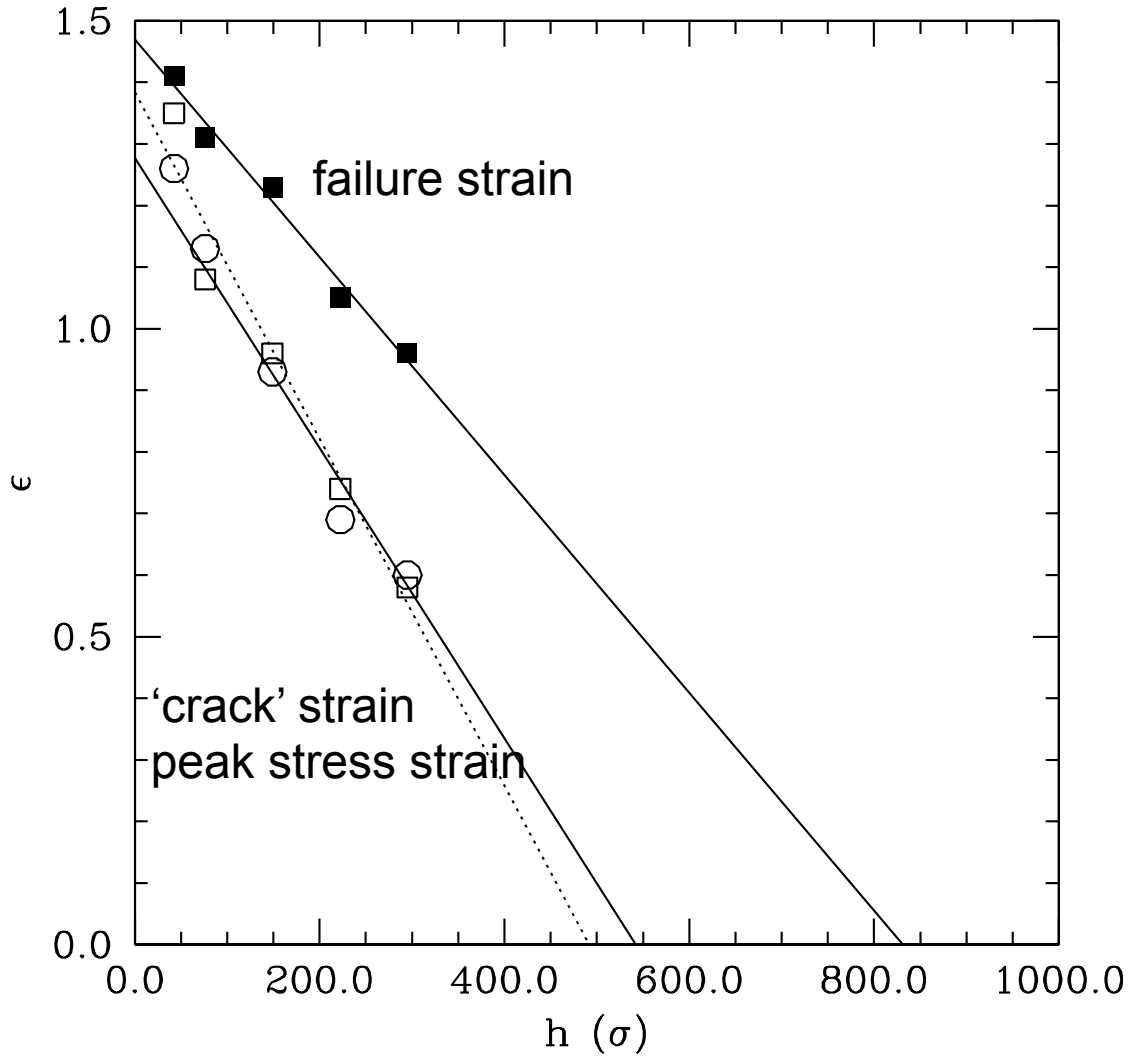
Mark Stevens
msteve@sandia.gov

Strains vs. Thickness



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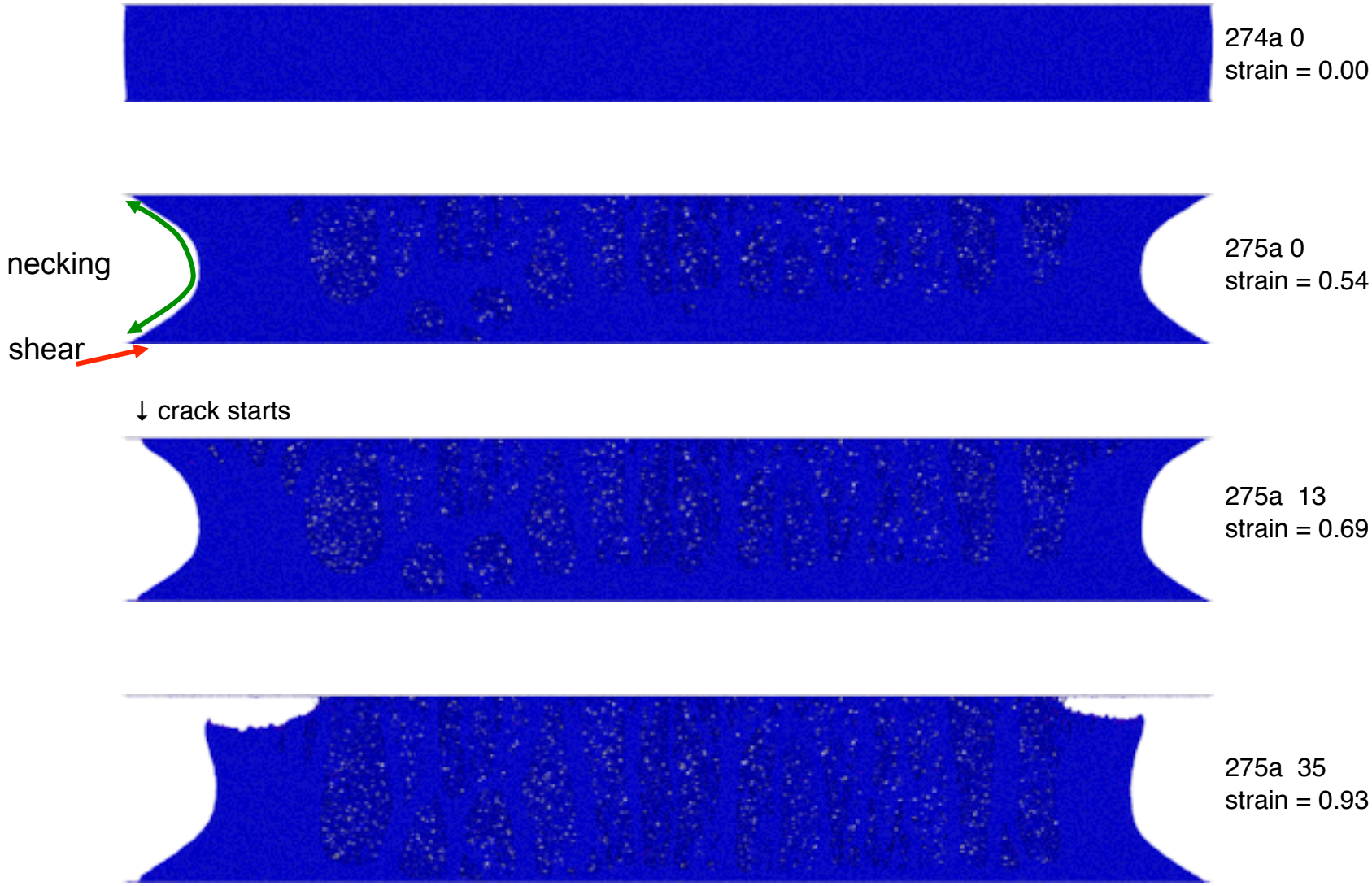
Mark Stevens
msteve@sandia.gov

System 4



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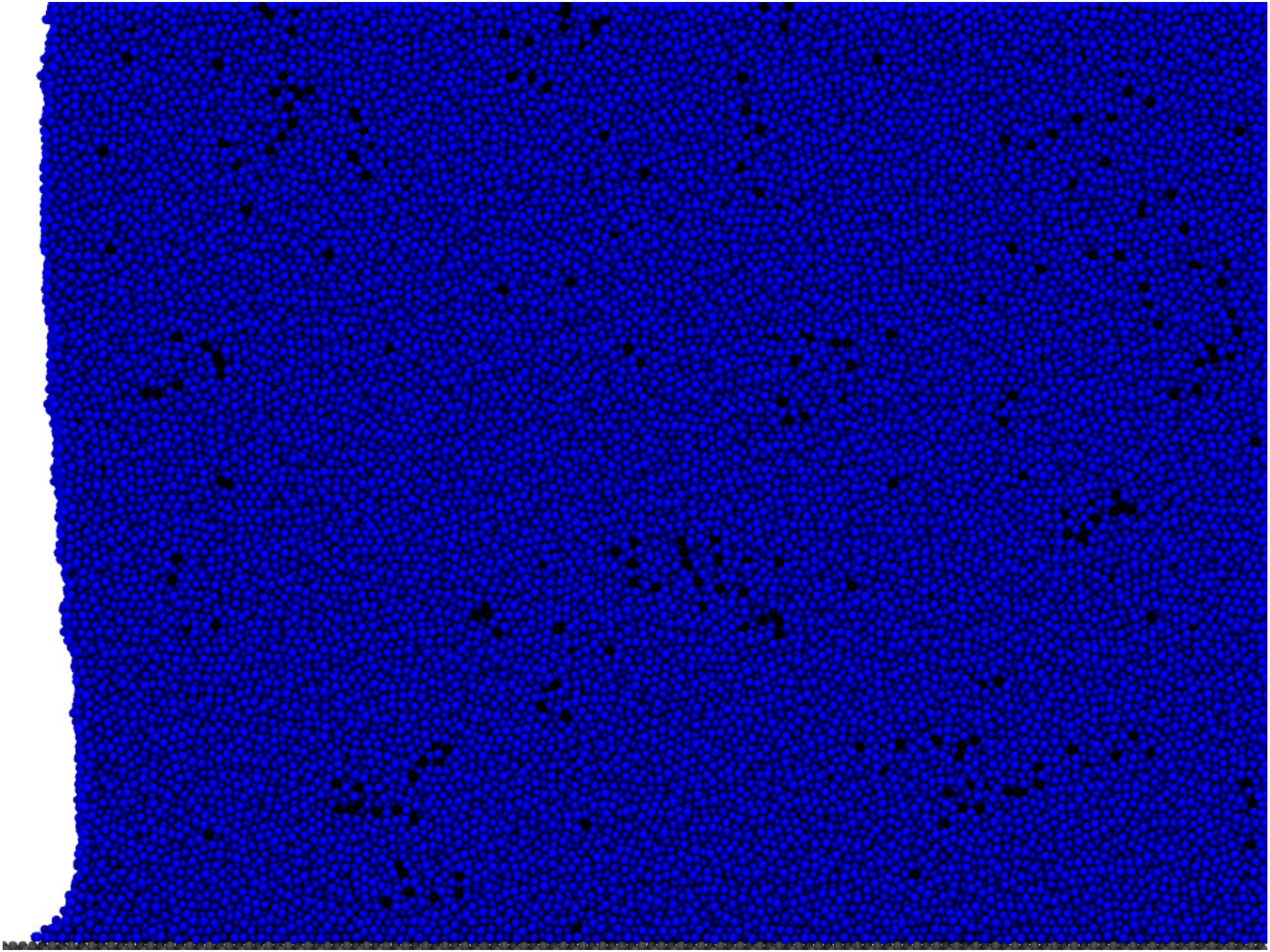
Mark Stevens
msteve@sandia.gov

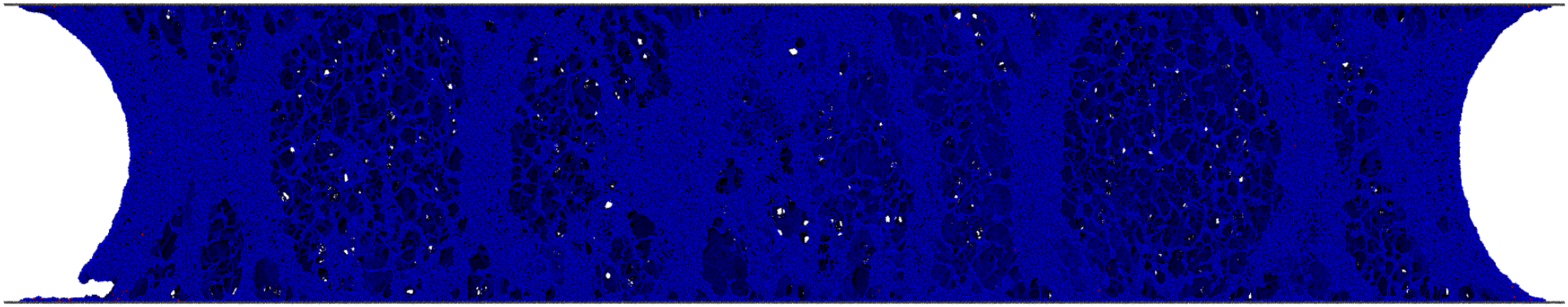
Zoom to crack initiation

275a 16 zoom
strain = 0.72

Mark Stevens
msteve@sandia.gov

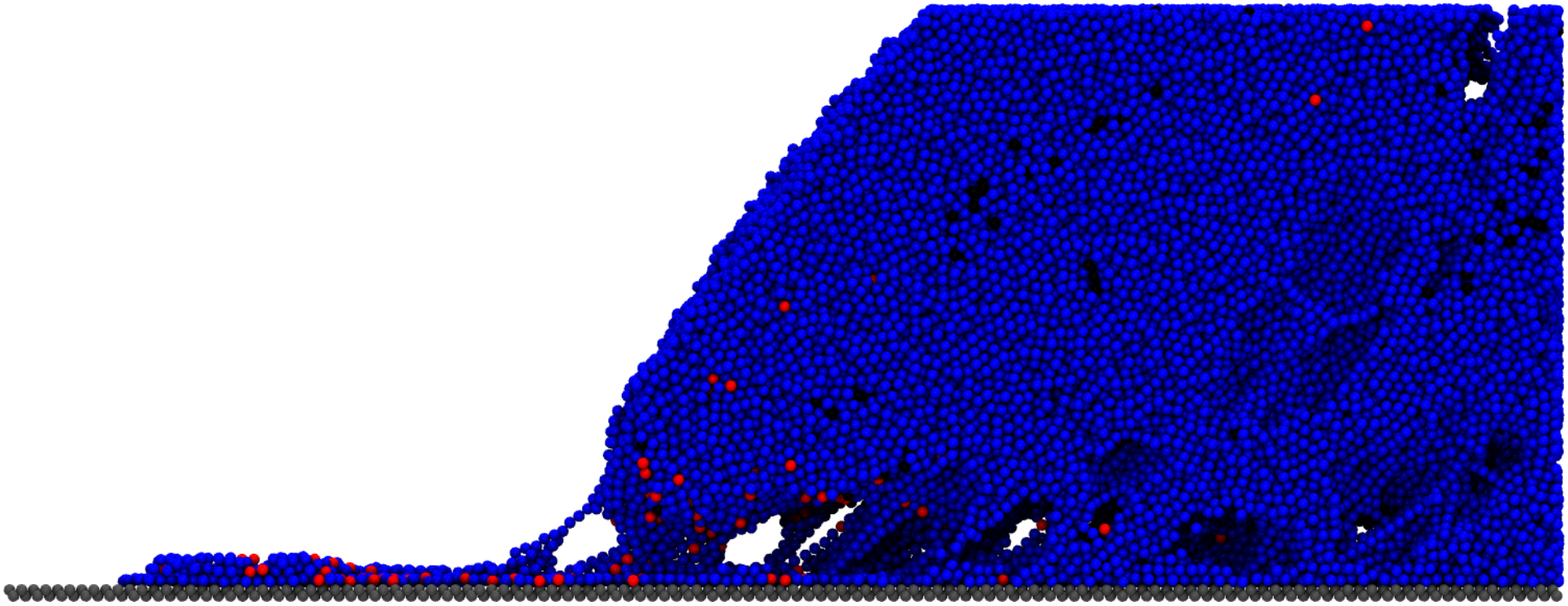


159 iconf=13



Mark Stevens
msteve@sandia.gov

r213 zoom iconf=57



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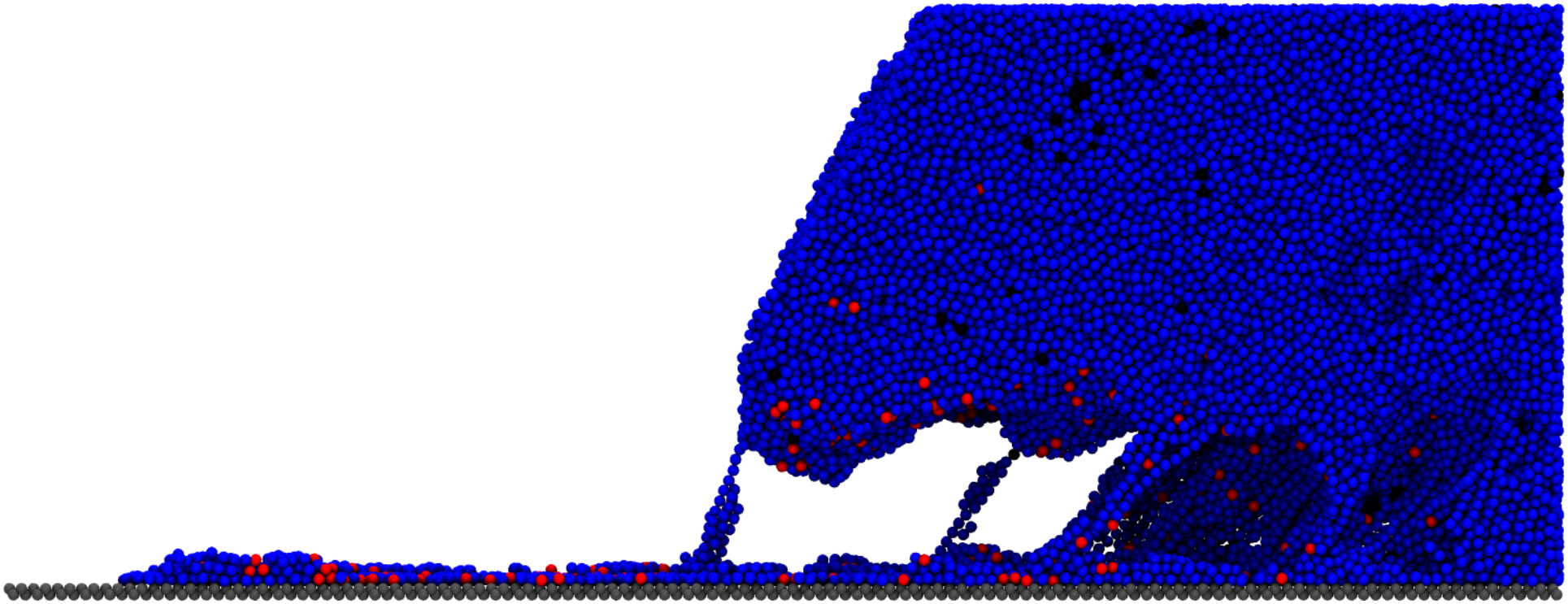
Mark Stevens
msteve@sandia.gov

r213 iconf=58



Mark Stevens
msteve@sandia.gov

Conclusions

Crack initiation at corners does occur within molecular simulation.

Failure strain is strongly system size dependent in these ‘small’ systems.

Stress is noticably concentrated at corners for small strain.

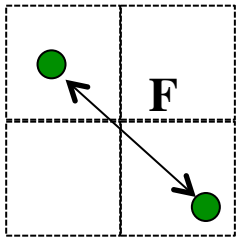
Shear stress in corner important because of pull-in at sides yields an acute angle of the polymer network surface in the corner.

Mark Stevens
msteve@sandia.gov

Mark Stevens
msteve@sandia.gov

MD: local stress

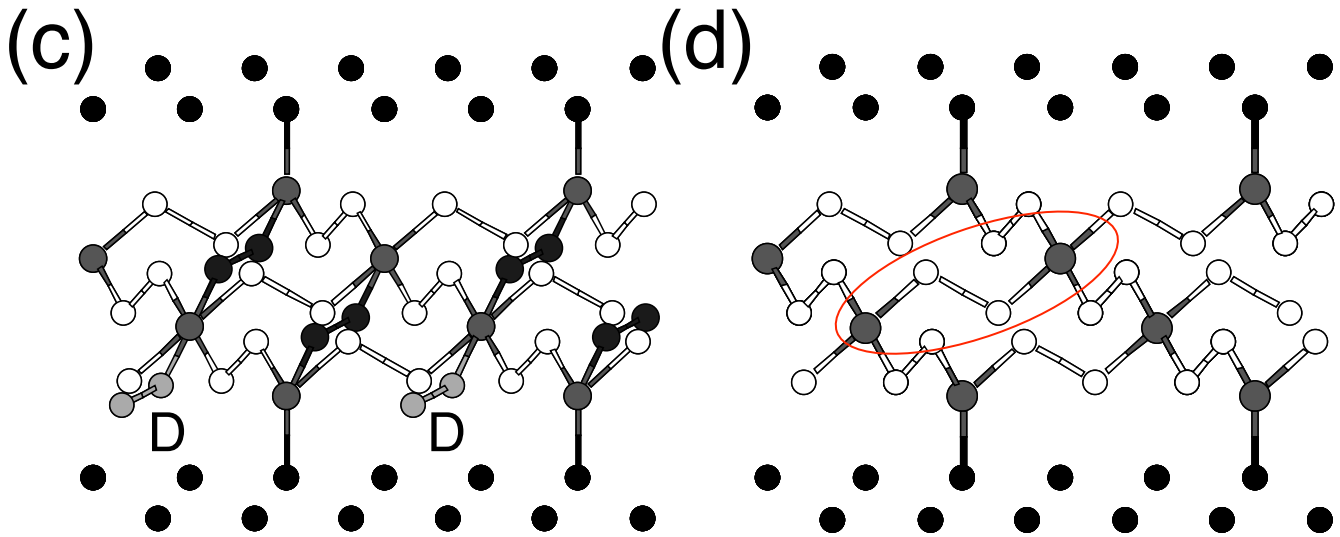
- Do MD with local stress calculation
  - large fluctuations?
- What does simulation say about traction-separation relation?
  - shape of the function
  - stress & structure at corners
    - can MD show stress divergence?



Force between particle pair: how much stress goes in each mesh volume?

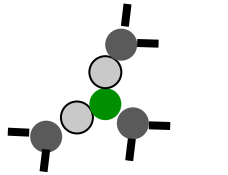
Mark Stevens
msteve@sandia.gov

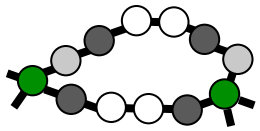
Network Structure



Original model

T403 model





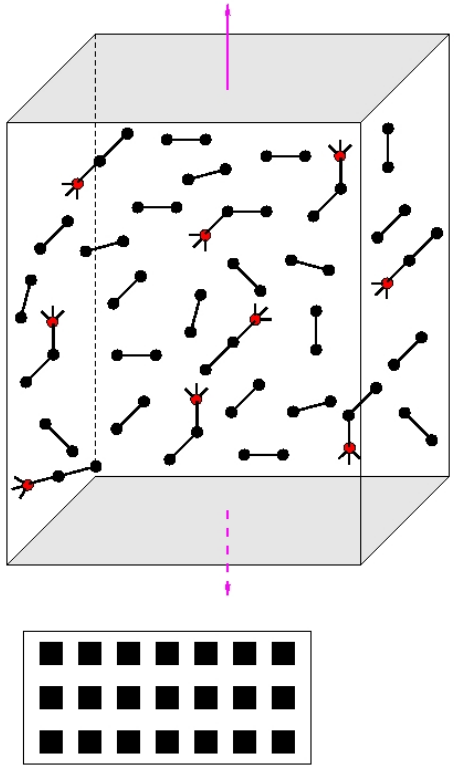
strands can
have 4, 5 or 6 beads
between junctions

- Every strand between junction has 2 beads in original model
- Random network formation
  - Start with binary liquid of crosslinker and resin
  - Crosslink to form network

Mark Stevens
msteve@sandia.gov

Formation of Epoxy Adhesive

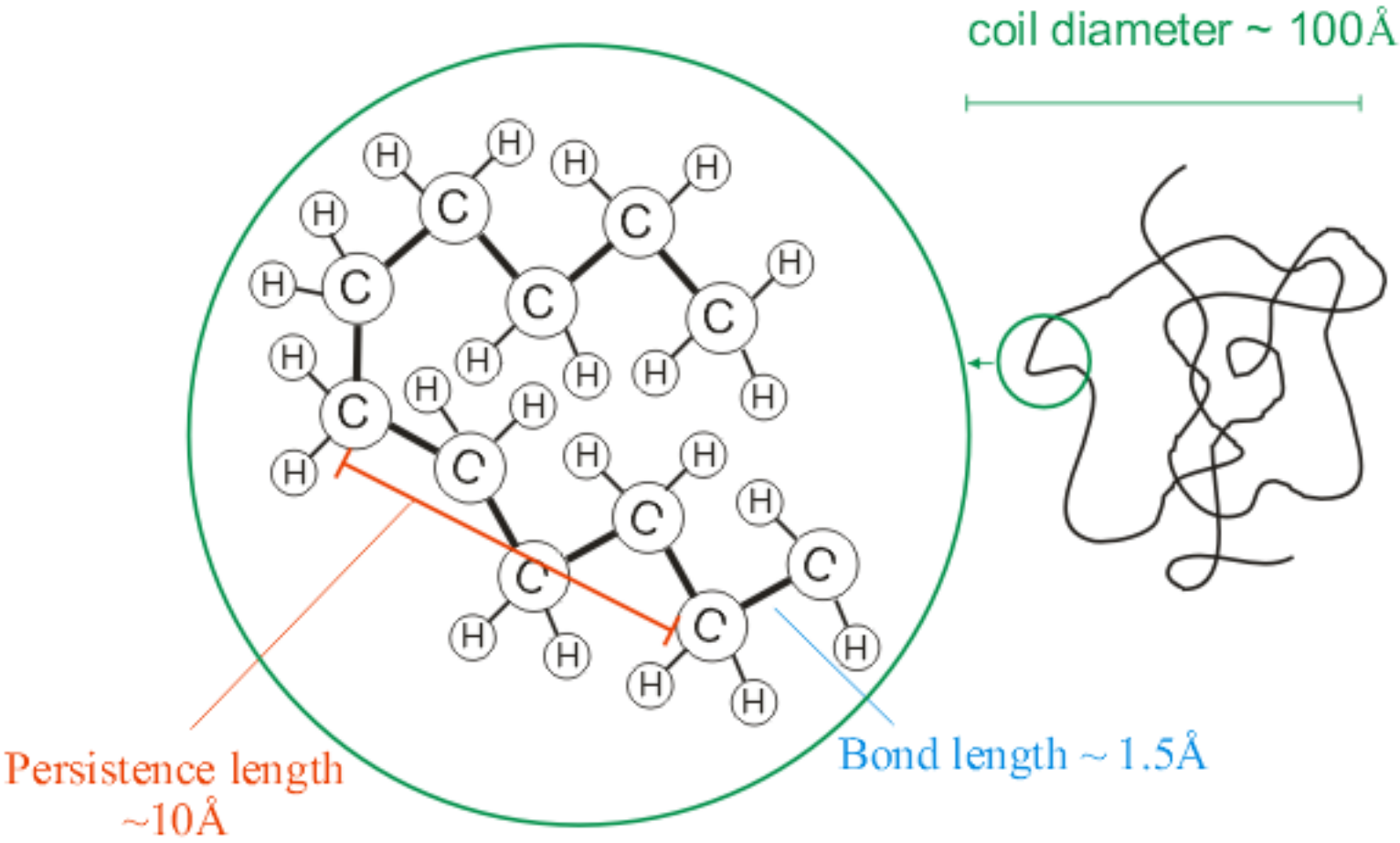
- Equilibrate binary liquid of crosslinker and resin
- Cure by dynamically crosslinking in simulation
  - obtain highly-crosslinked network with short strands
- Vary number of bonds allowed to bottom surface
  - mimics SAM treatment of experiments



model → network structure → stress-strain curves

Mark Stevens
msteve@sandia.gov

Polymer Modeling: Length Scales

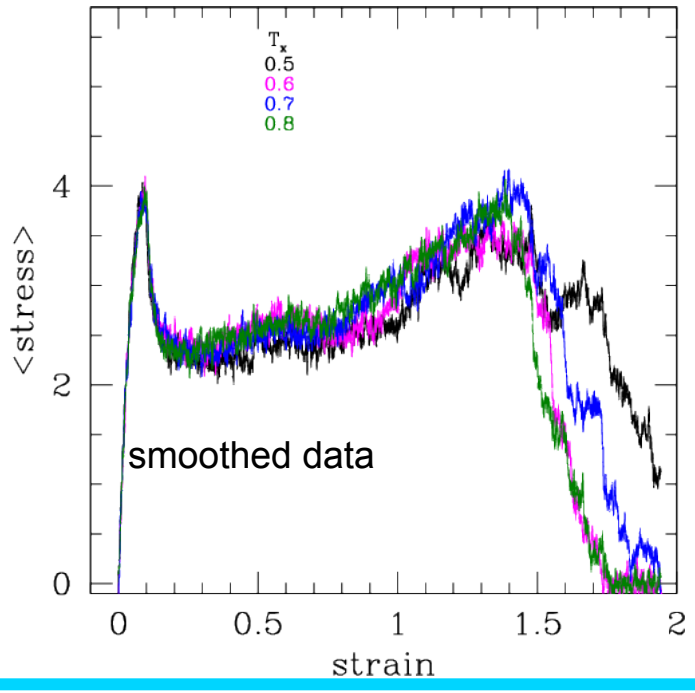


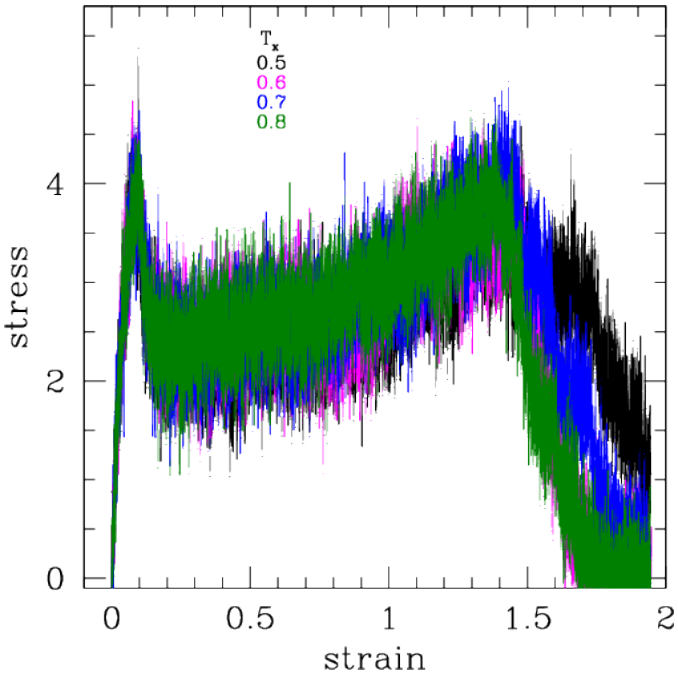
Mark Stevens
msteve@sandia.gov

Varying Crosslink Temperature

Created systems (very small, original model) crosslinked at different temperatures, T_x.
Performed tensile pull simulations.

- Large fluctuations in stress due to small system size
- yield stress independent of T_x
- only large strain data appears dependent on T_x
- But? need to have much longer crosslink times for lower T_x?



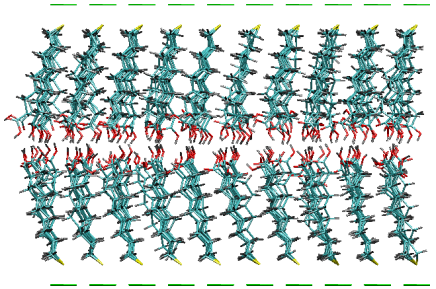


Sandia National Laboratories

Mark Stevens
msteve@sandia.gov

Units

- Mapping using SAMs
  - Stress to separate two SAMs with different endgroups
    - R. Thomas, *et al.,* JACS, 117, 3830 (1995).



Separation	Load
CH3-CH3:	320 ±160 MPa
COOH-NH2:	3400 MPa

vdW separation stress > measured bonded separation stress

Simulation:

bonded SAMs	112 u_0 / d^3
LJ SAMs	5.6

LJ maps: $1\ u_0 / d^3$ = 3400/112 = 30 MPa
= 320/5.6 = 57 MPa

$u_0 / d^3 \approx 40$ MPa
d = 0.5 nm

(This d value better matches new model)

Mark Stevens
msteve@sandia.gov