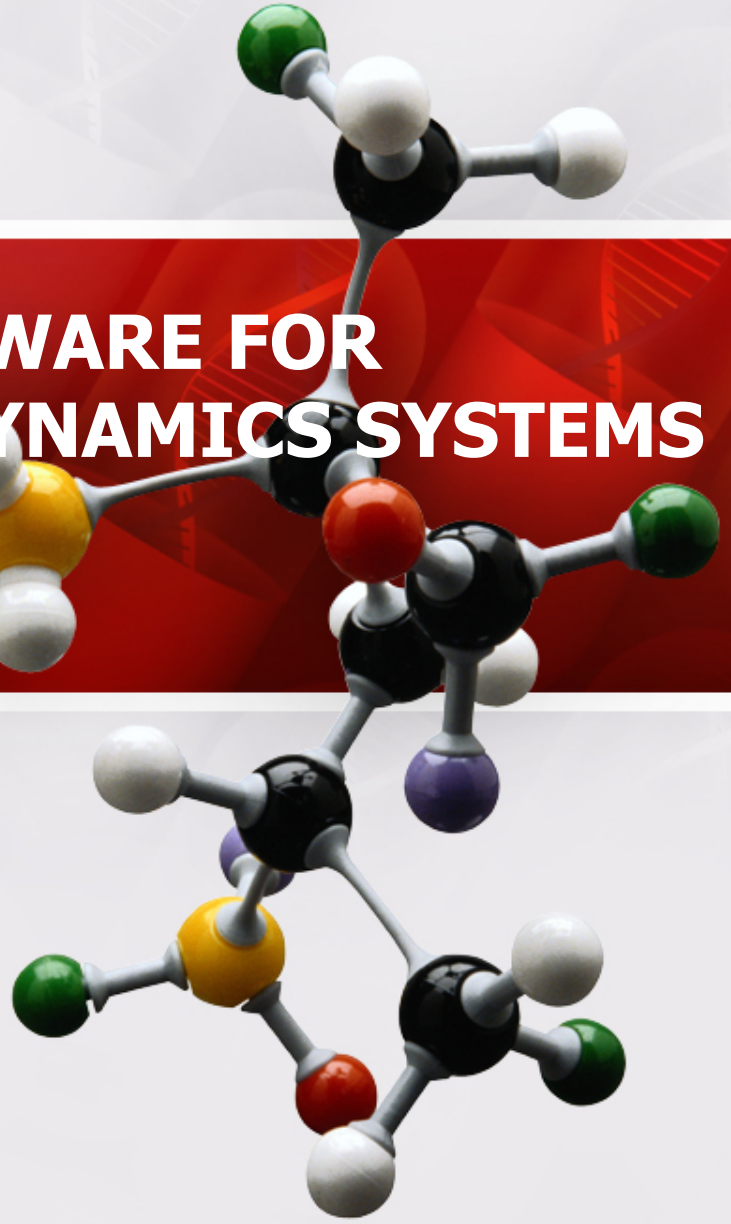
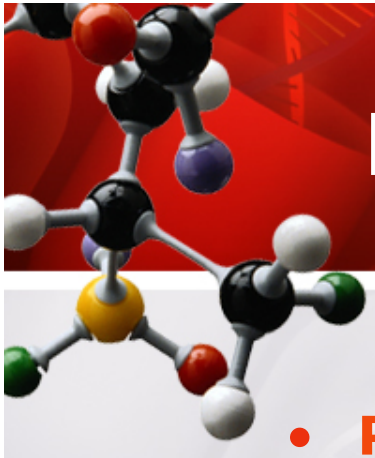
NEW OPEN SOURCE SOFTWARE FOR BUILDING MOLECULAR DYNAMICS SYSTEMS

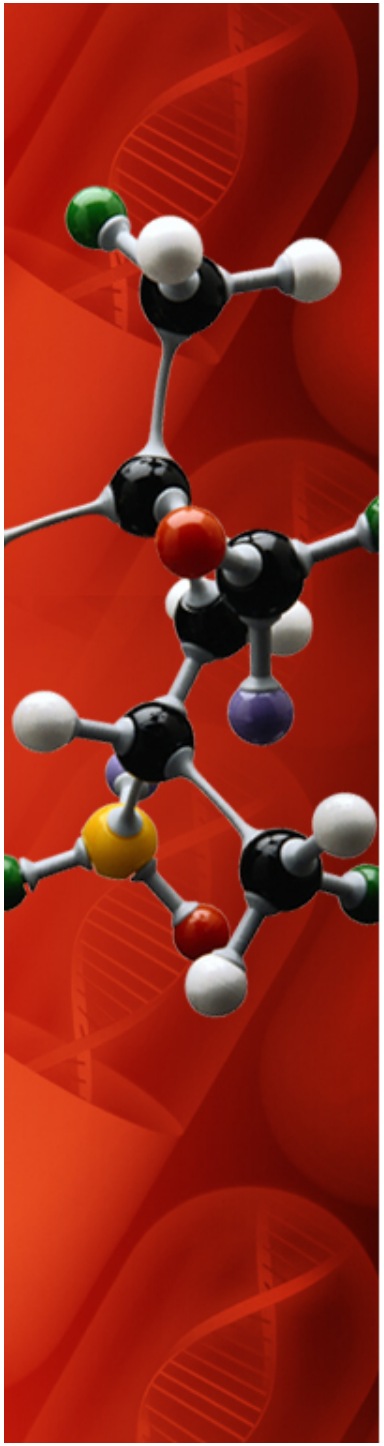
Welcome to MD Studio





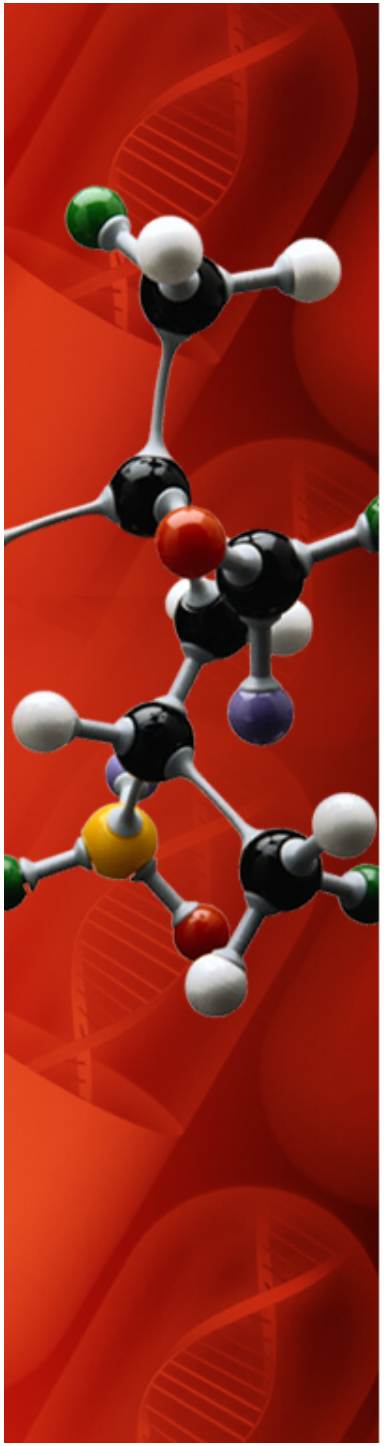
Background

- **PROBLEM SPACE**
  - **Molecular Dynamics (MD) Simulations are hampered by long build times for an initial MD cell.**
  - **Commercial software tools offer partial solutions at large costs in licenses and maintenance.**
- **SOLUTION SPACE**
  - **Created a prototype software (MD Studio) by refactoring existing open source software.**
  - **Allows Researchers to:**
    - Design molecule models
    - Build an MD cell from the molecule models
    - Generate a LAMMPS Geometry Input File (LGIF)
    - Run MD simulations with LAMMPS

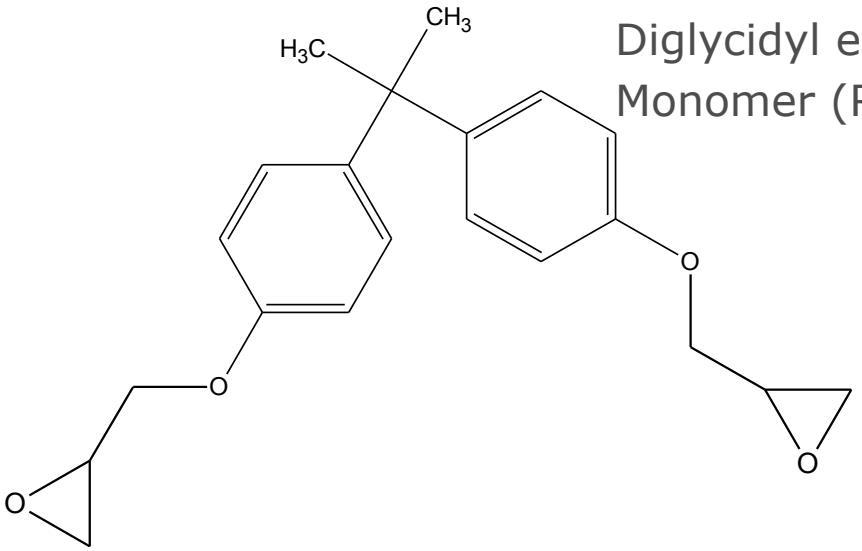


What is an MD Cell?

- A finite volume, usually a cube from 10Å to 100Å per side. Depends on number of atoms and force field
- Contains all molecules for a simulation
- Usually subjected to periodic boundary conditions (PBC) in one or more dimensions.
- PBC prevents loss of mass during a simulation
- Comes in two flavors: Initial and final

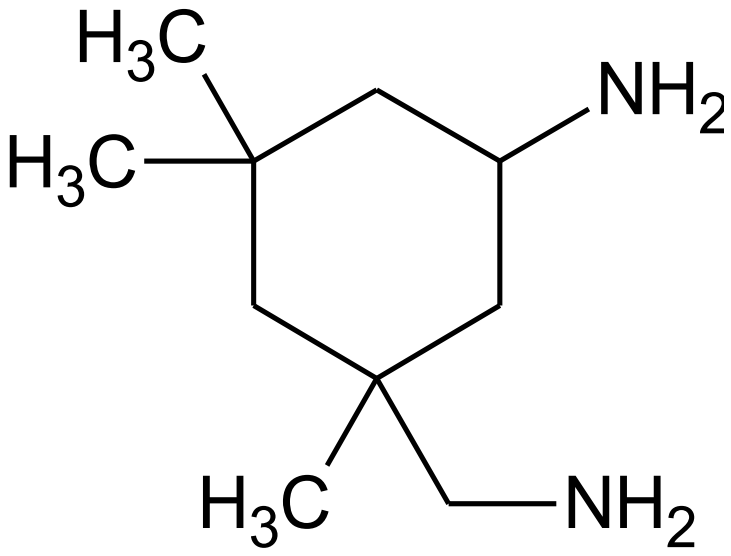


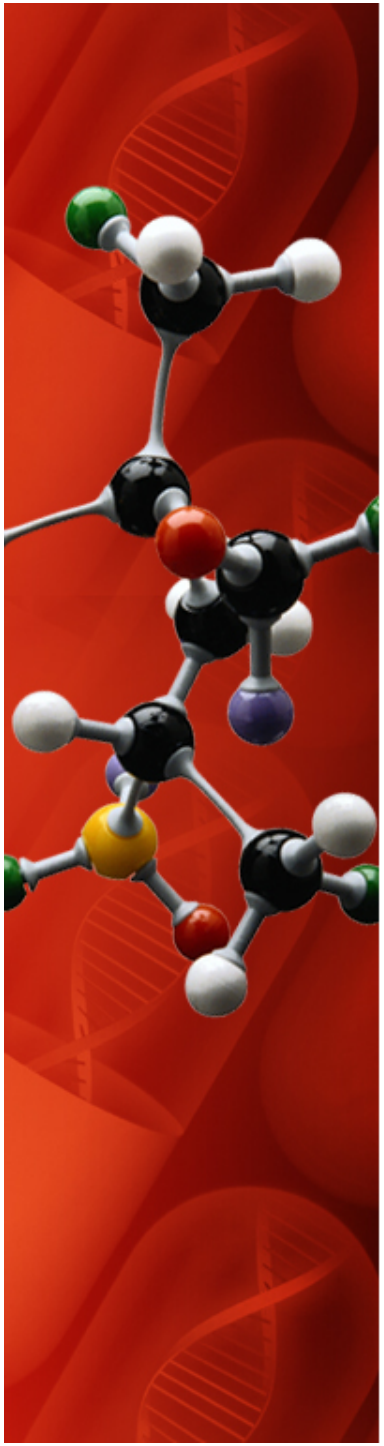
Molecule Models



Diglycidyl ether of bisphenol A (DGEBA)
Monomer (Resin)

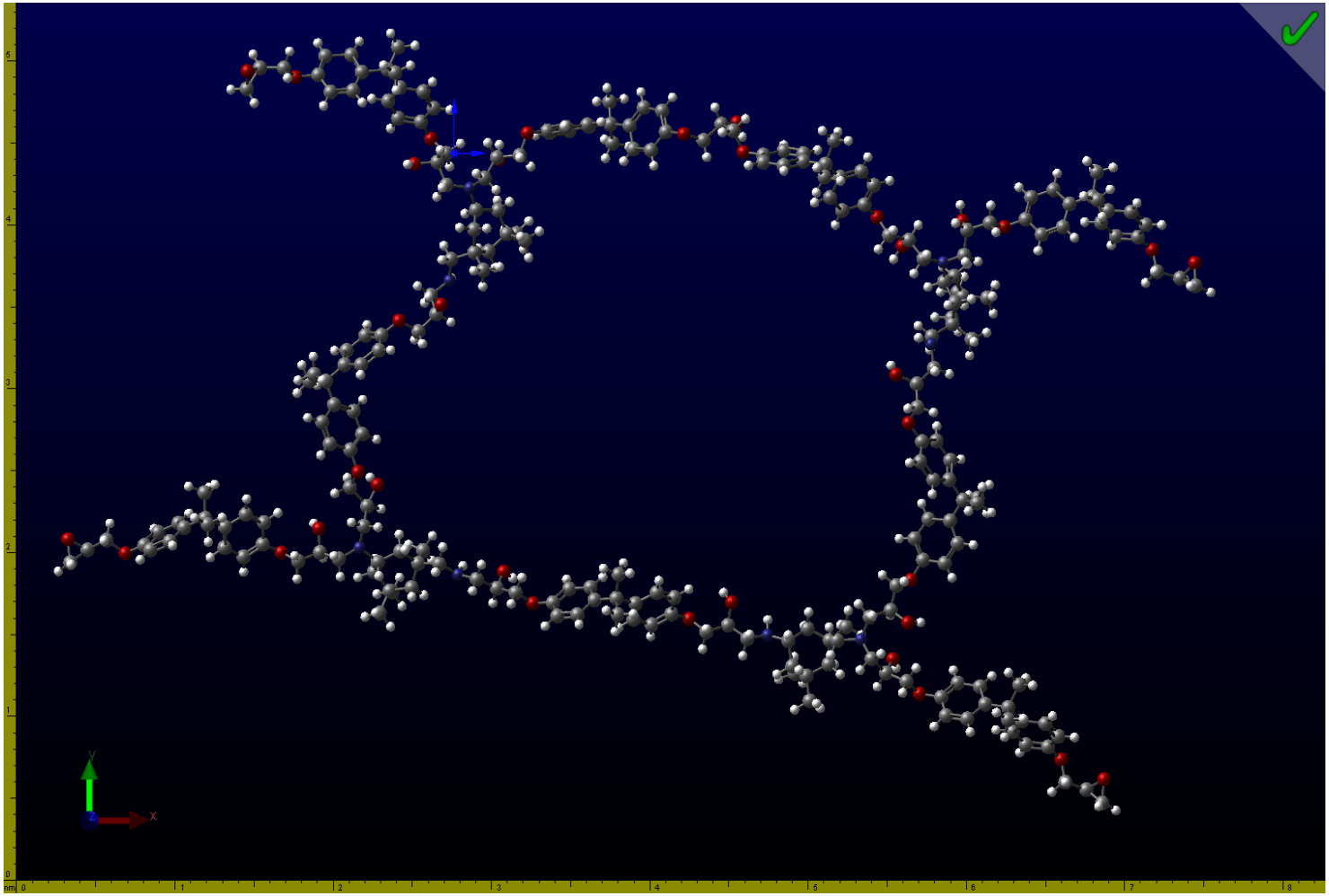
Isophorone Diamine (IPD)
Hardening Agent (Crosslinker)



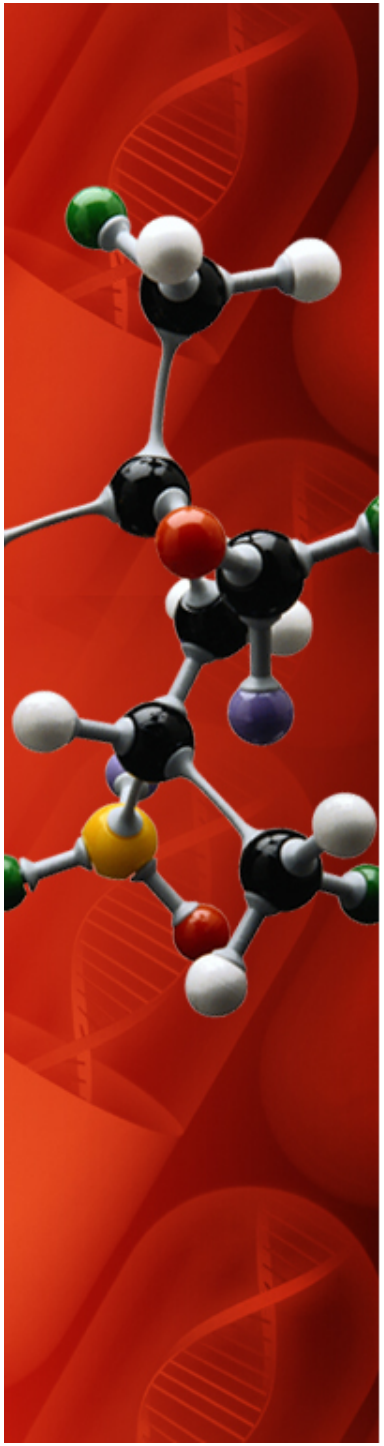


MD Cell Composition

- A cell is built by stuffing molecules into it
- Oligomer contains 569 atoms

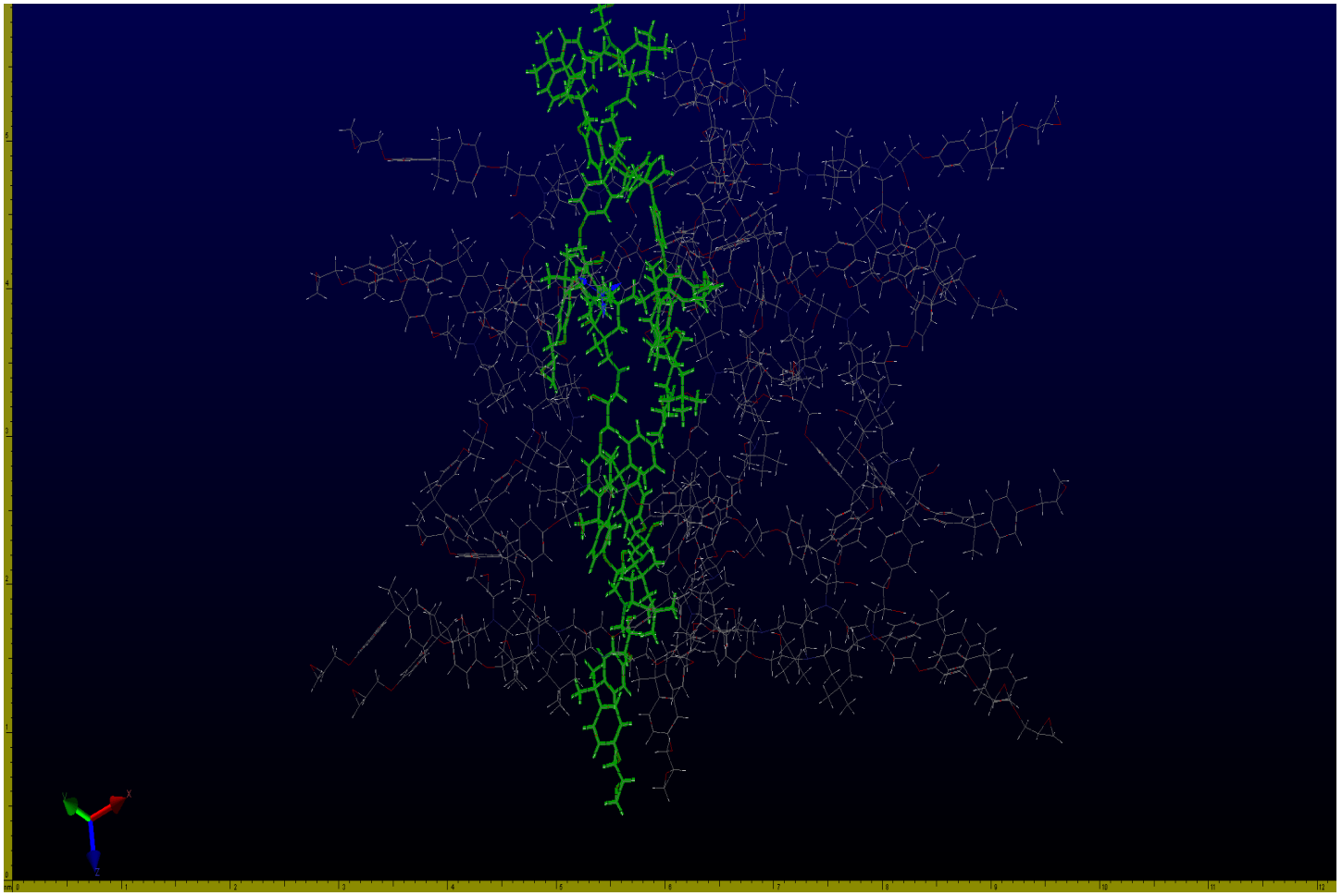


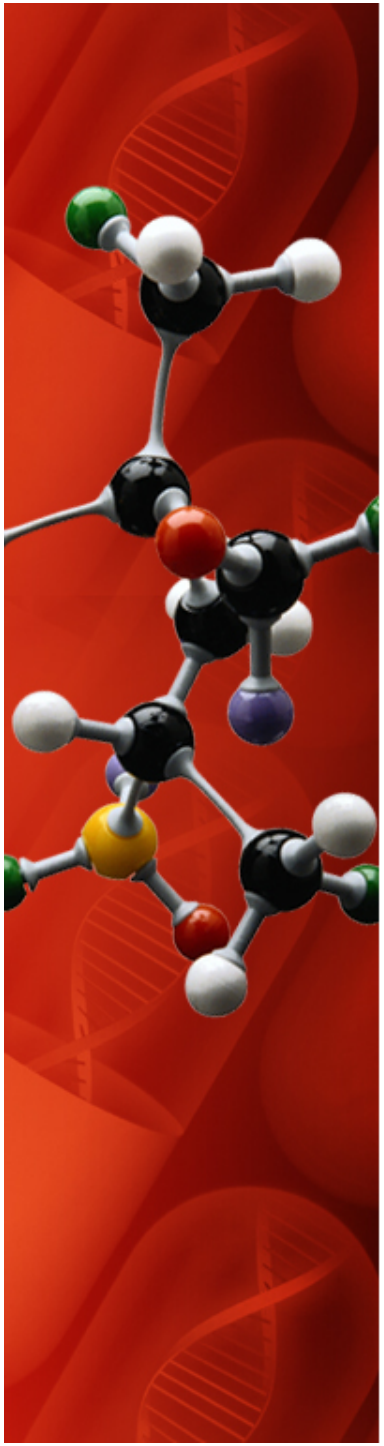
75% intra-crosslinked oligomer for constructing an MD cell



Initial MD Cell Geometry

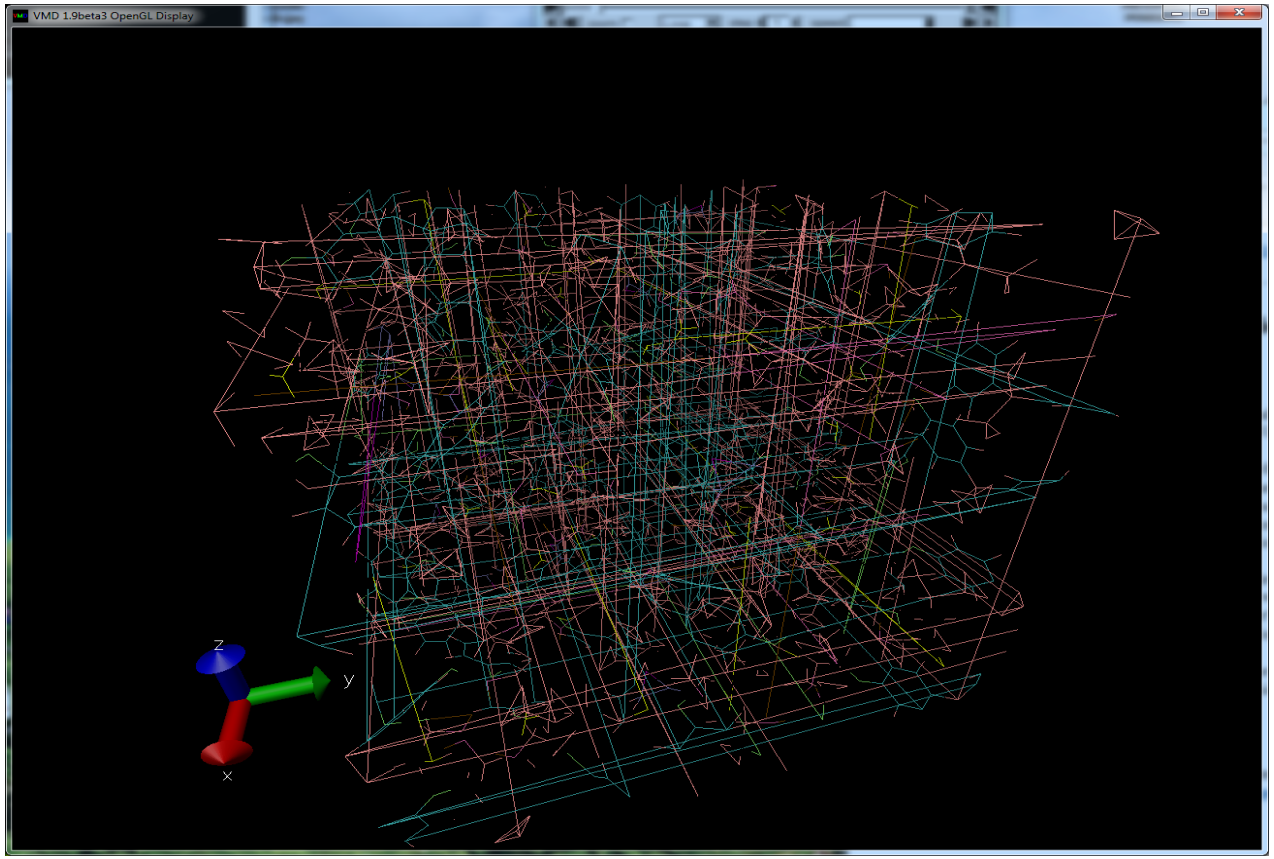
- Highlighted in green one oligomer in a system of five oligomers
- Shows intertwined oligomers
- Cubic cell 55Å per side

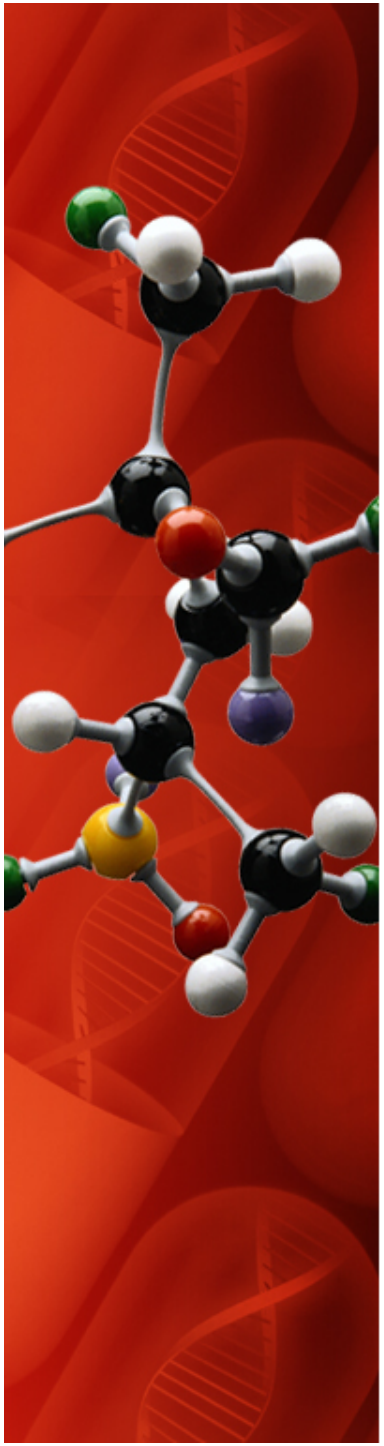




Final MD Cell Geometry

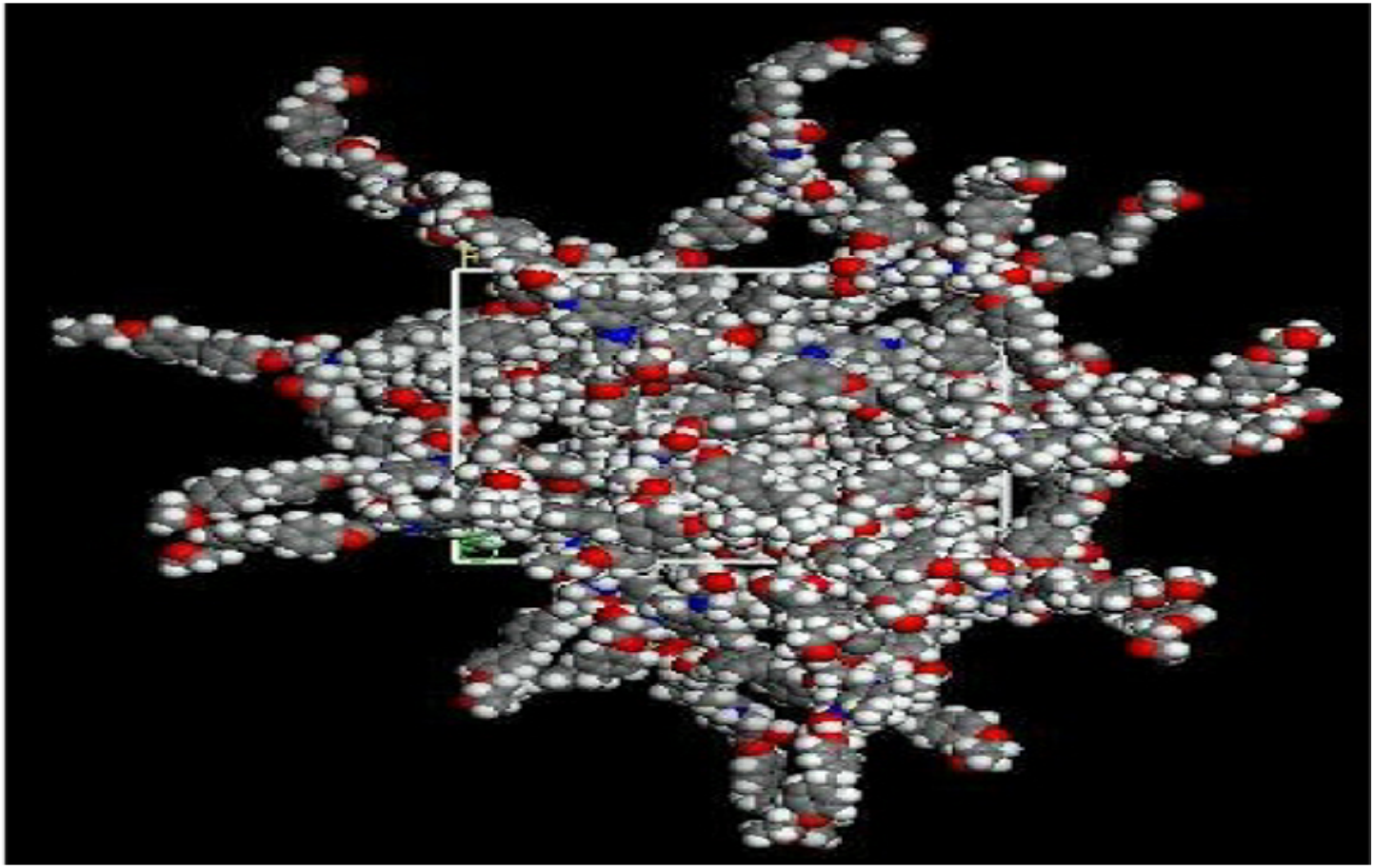
- Cell is shown under PBC
- Contains 2845 atoms
- Cubic ~30-32Å per side
- Cell preparation assumed isotropic behavior

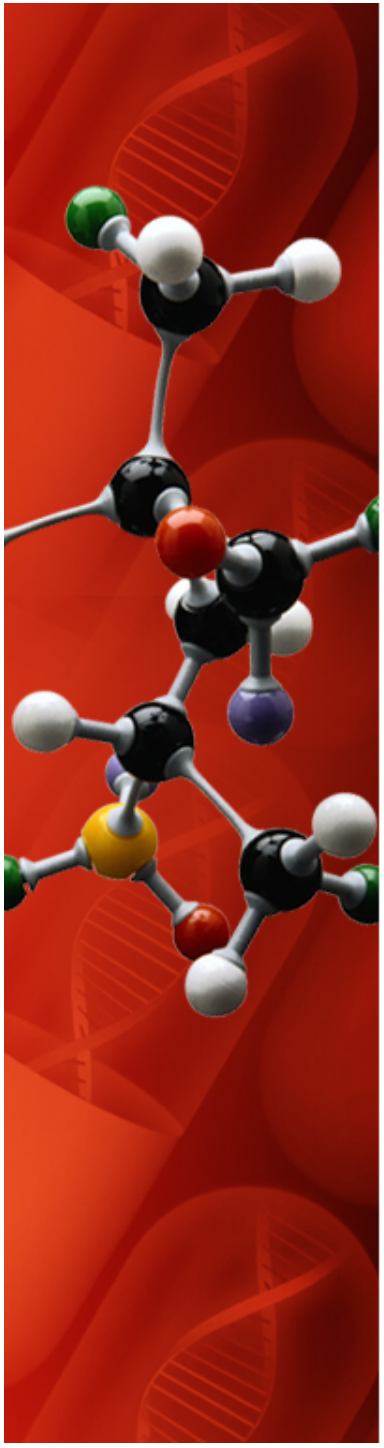




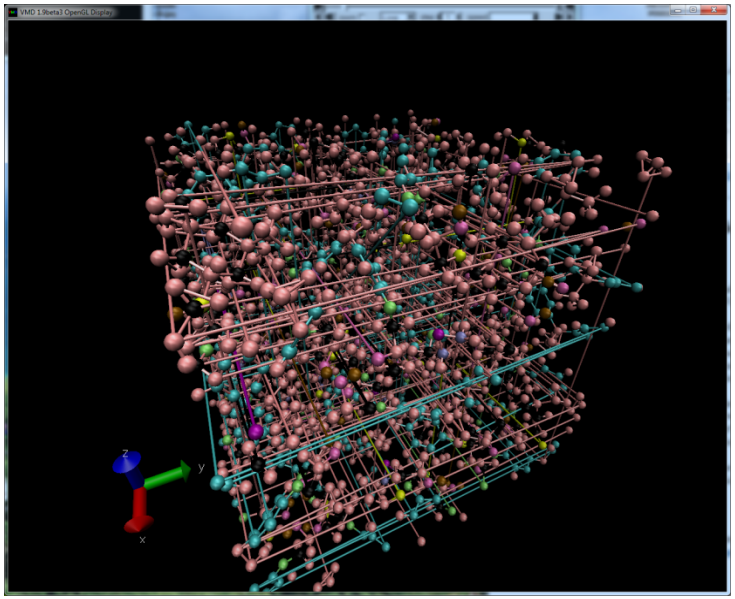
Final MD Cell Geometry

- Cell appears to be a sub-sample of all oligomers (White Box)
- Software decides which atoms are in the cell not the researcher
- DGEBF/DETDA system (Tack&Ford)



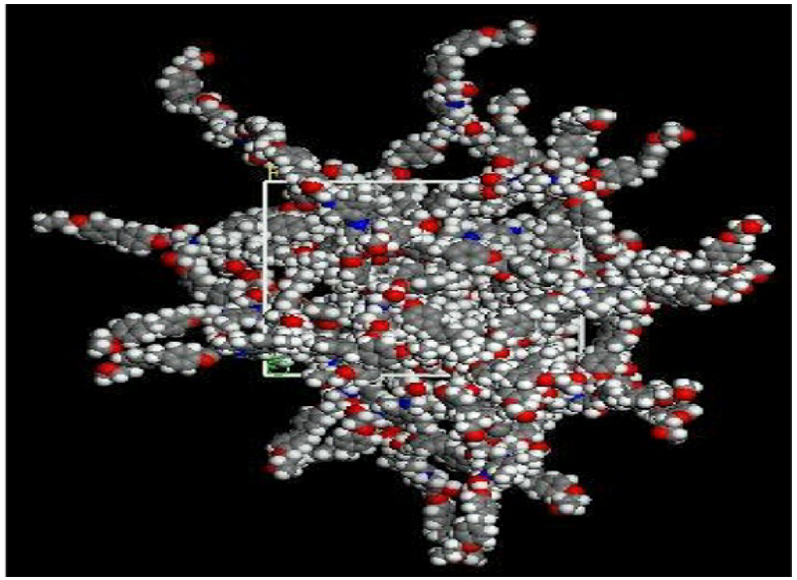


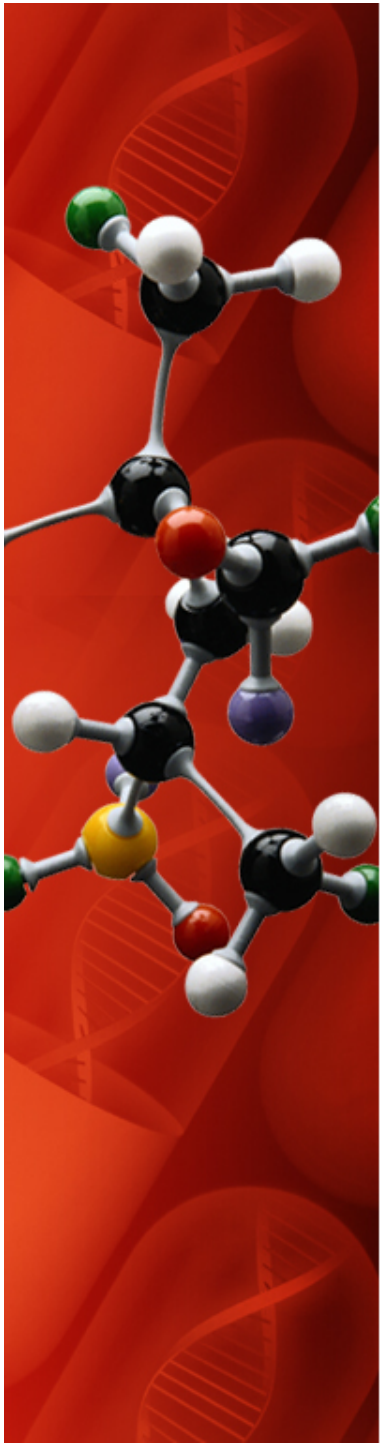
Final MD Cell Geometry



- Created using MD Studio
- Known chemical environment
- Requires researcher to run MM and MD to create final cell geometry.
- Cannot spear rings (PACKMOL)
- Builds pseudo-random cell
- Final cell size defined by conditioning
- PBC bond wrapping is an annoying feature of VMD

- Created using Materials Studio
- Unknown chemical environment due to sub-sampling
- Most likely runs MM and MD during cell creation
- Spears rings and exits with errors
- Author confirmed short comings of Materials Studio at LAMMPS Workshop 2011
- Attempts to build isotropic cell (Tack&Ford)



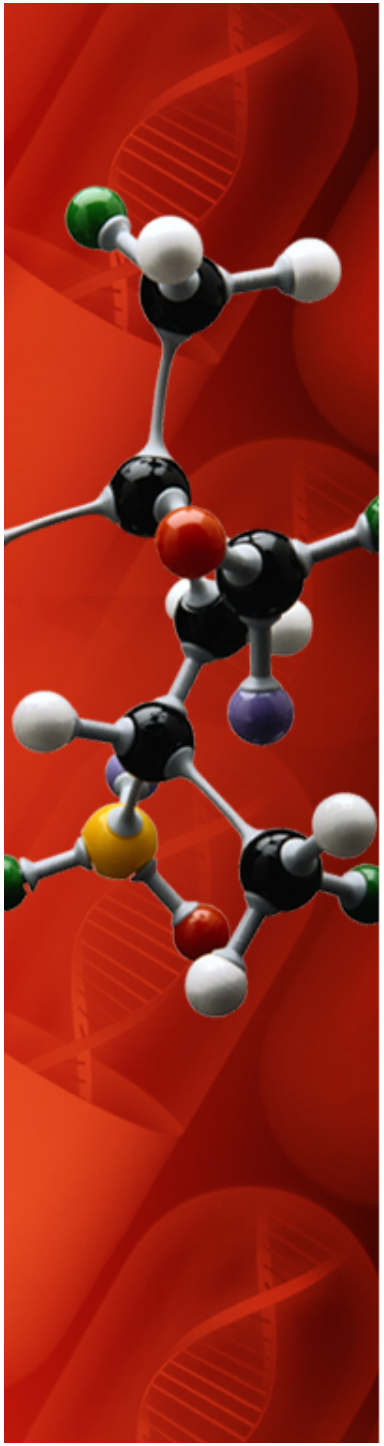


Spectrum of MD Cell Preparations

- Dynamic cell creation (done by several researchers in literature)
  - Populate a cell with resin monomers and hardener molecules
  - Run LAMMPS for some time, usually 1fs to 1000fs
  - Create bonds between amine and epoxide sites based on proximity, the closer the better which reduces stress
  - Minimize system energy
  - Repeat until the desired level of crosslinking is achieved
  - Requires running LAMMPS to run LAMMPS!!!
  - New SAW software will do this as well.

- Static cell creation I (e.g. Current SAW software)
  - Grow an epoxy molecule one atom at a time at multiple locations inside the cell
  - If the atom is a hotspot flip a coin to determine which molecule to attach to it and start growing that molecule too
  - Grow to a specific density or terminate if the density converges prior to target

- Static cell creation II (e.g. PACKMOL software)
  - Pick random attitudes for molecules
  - Packs molecules to minimize repulsive forces based on tolerance ($d_{tol} > 0$)

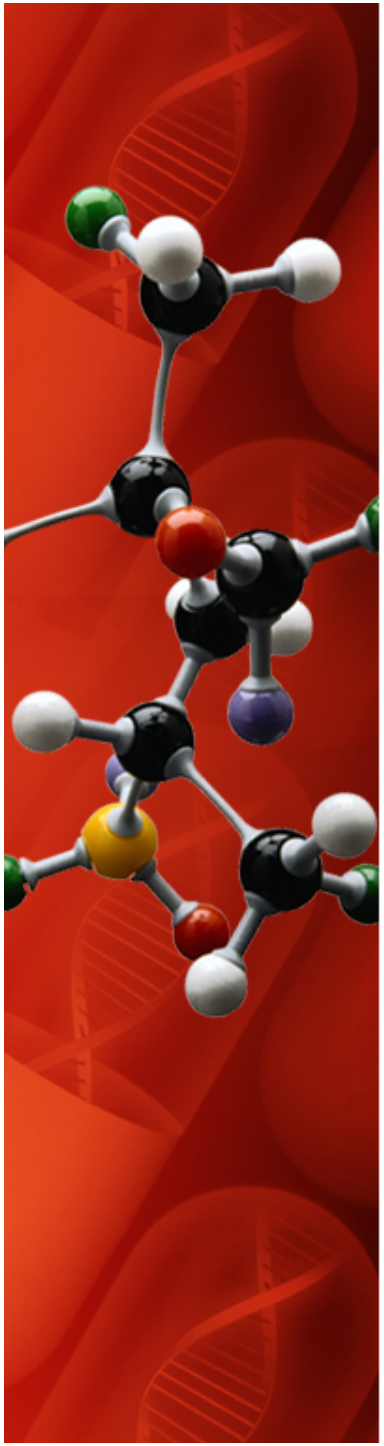


Commercial vs Open Source

Software Feature (aka Requirements)	Materials Studio	MD Studio
Draw Molecules via CAD	Integrated	NanoEngineer-1*
Manual Atom Typing	Integrated	Added to NanoEngineer-1*
Automatic Atom Typing	Integrated	Release 2†
Ring Perception	Integrated	Release 2†
MD Cell Creation	Amorphous Cell Module	PACKMOL* and MSI2LMP* SAW†
Molecular Dynamics Engine	Discover Module	LAMMPS
Cost	$20,000.00 + $2,000.00/year for maintenance (Academic pricing) companies pay much more!!!	Free Download (Summer 2012)
Technical Support	Red Carpet Service	User Community
Science Support	Red Carpet Service	User Community
Support for crosslinking	Limited/requires programming	Limited/requires programming
Better Crosslinking	N/A	SAW (see Appendix C) † New Open Source Software

***Software was significantly modified for thesis work**

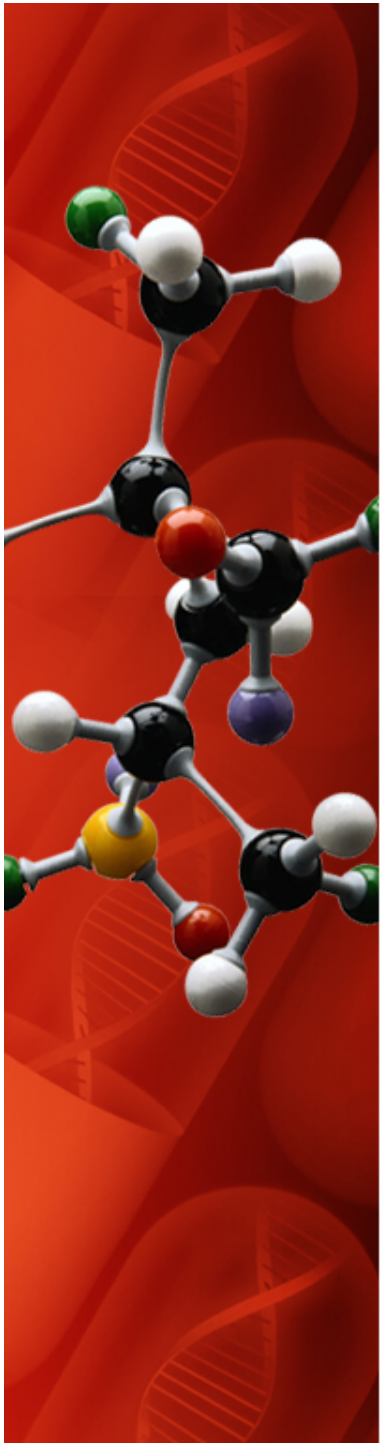
†Release expected: February, 2013



MD Studio Software Selection

Selection Criteria	NanoEngineer-1	PACKMOL	MSI2LMP	SAW*†
CAD	Draw and edit complex molecules			
Uses open MMP File Format	yes	no	no	Built to read and write
Uses PDB File Format	yes	yes	no	
Python	yes (250,000 LOC)			
FORTRAN		yes		
C	yes		yes	
C++/STL				yes
Creates initial MD cell		yes		yes
Creates solvated systems		yes		yes
Complex geometry Support	yes	yes	yes	yes
Creates LAMMPS Geometry Input Files			yes	
Reads CAR, MDF file pairs			yes	
Software Development tools available	Yes	Yes	Yes	Yes

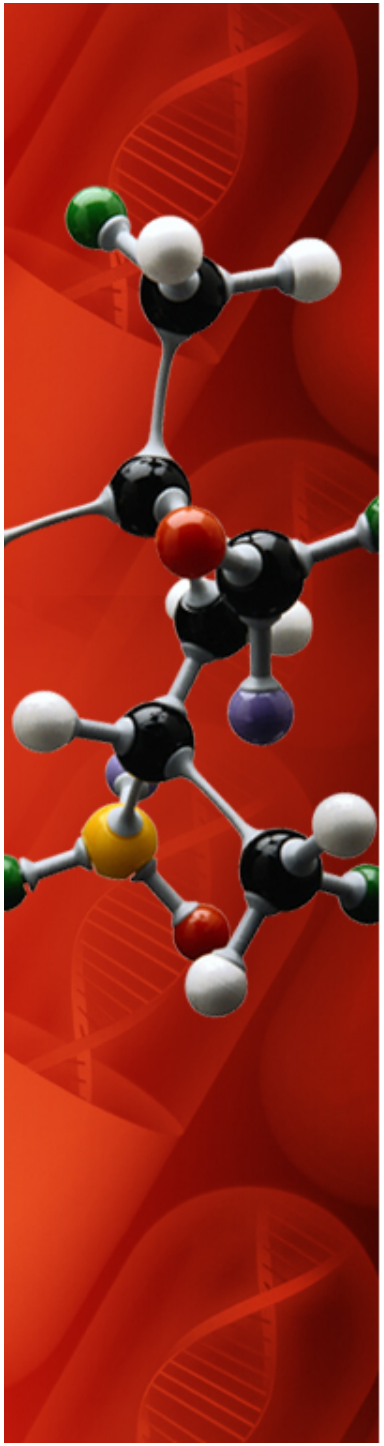
*** Partially functional vaporware**
† Release expected: February, 2013



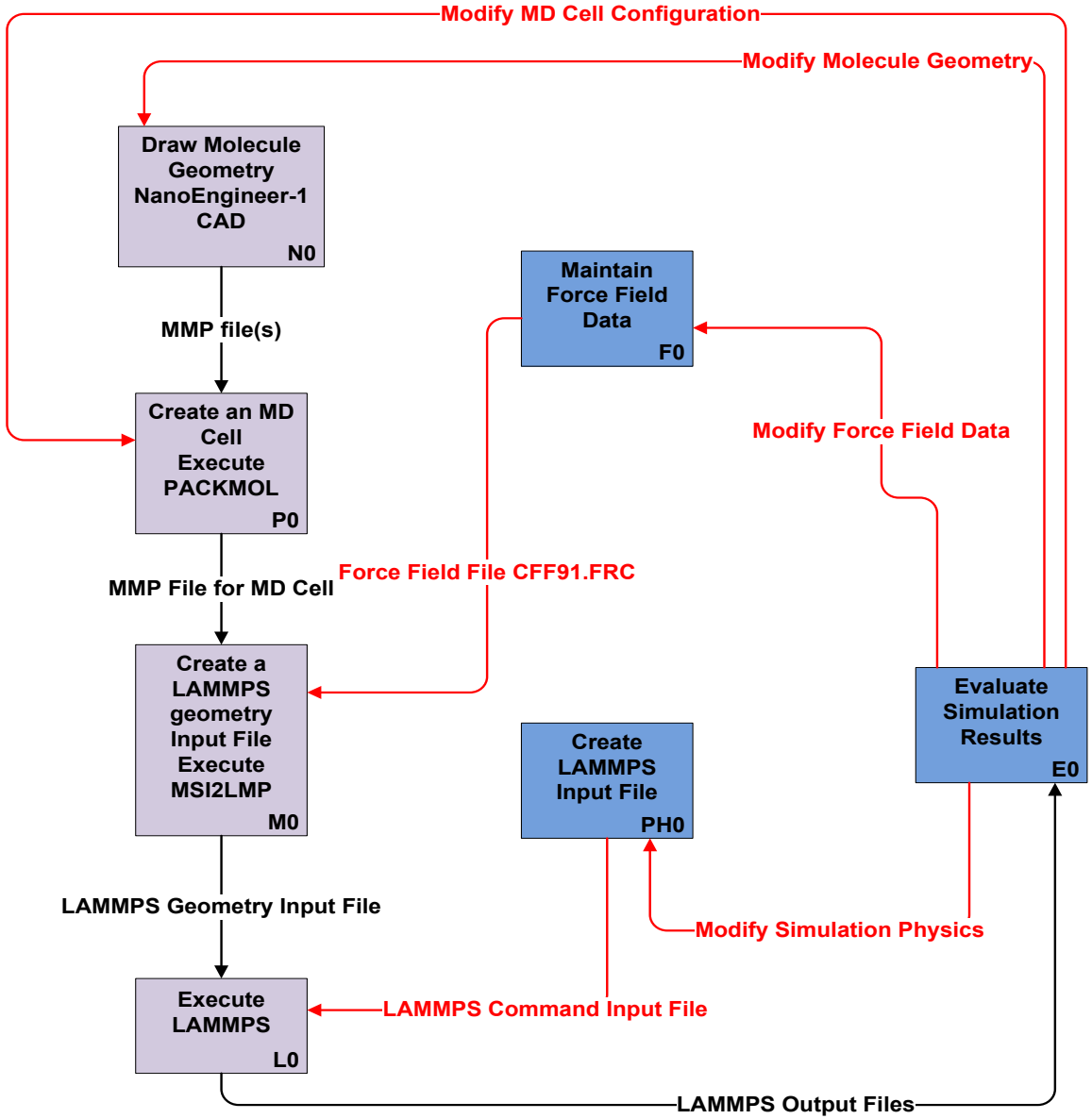
MD Studio Software Modifications

Software Modifications	NanoEngineer-1	PACKMOL	MSI2LMP	SAW*
CAD	Draw and edit complex molecules			
Uses modified open MMP File Format	yes	yes	yes	Built to read and write
Changes to MMP file for crosslinking and collision detection	yes	no	no	Yes Uses MMP file modifications
GUI Changes	yes			
Manual Atom Typing	yes			
Passes numeric force field data	yes	yes	yes	yes
Writes LAMMPS trajectory file			yes	
MMP file parser written in FORTRAN		yes		
Supports Intra-oligomer crosslinking	Requires oligomers to be pre-drawn	Does not crosslink but packs crosslinked oligomers	yes	Natively supports †
Supports Inter-oligomers Crosslinking	yes, but additional cell MM and MD required to remove stress	Changes to optimization algorithm in the works †	yes	Natively supports†

*** Partially functional vaporware**
† Release expected: February, 2013

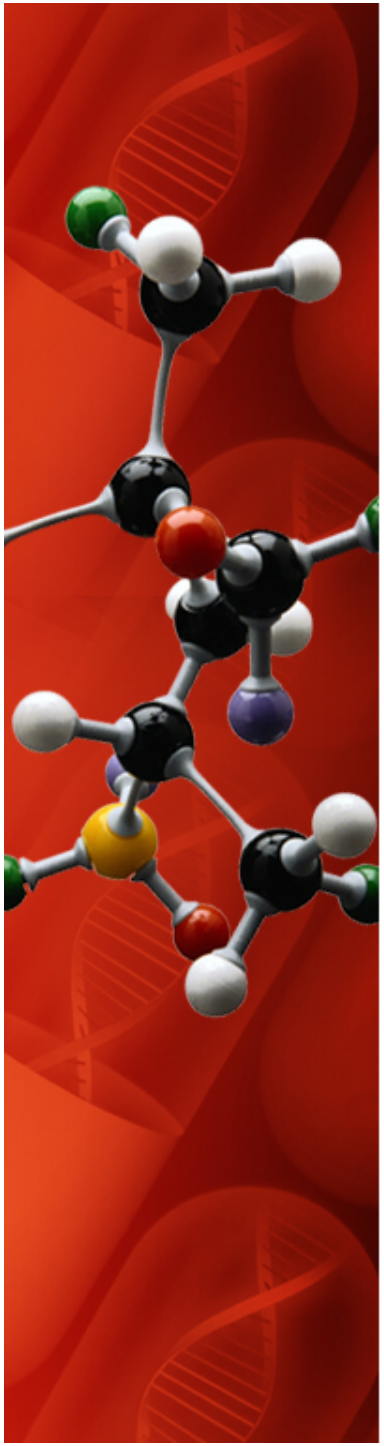


MD Studio Simulation Process Flow



Methods

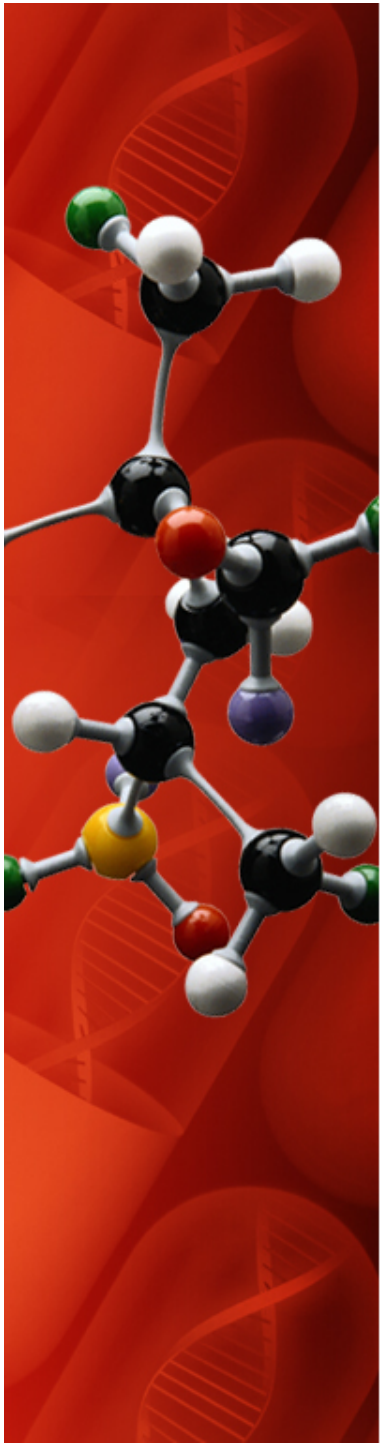
- **MD Studio Software Testing**
  - Software Requirements
  - Software Reliability
- **MD Cell Preparation for Simulations**
  - Initial cell creation
  - Final cell creation from initial cell
- **MD Simulations**
  - Ramping temperature
  - Equilibrating at temperature
  - Collection of cell volumes



NanoEngineer-1 Software Testing

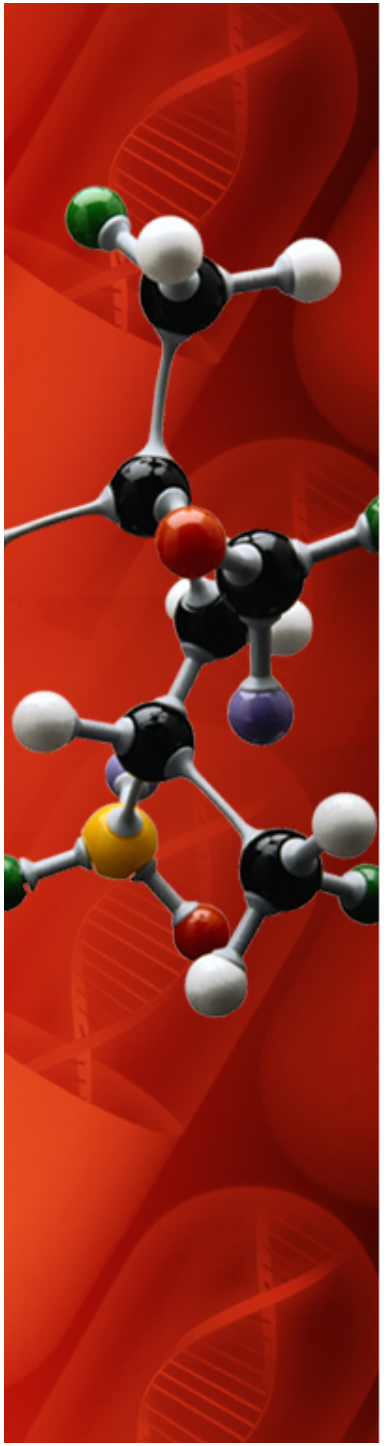
NanoEngineer-1 Software Feature	Test Method
Multiple Force Field Support	Atom types for CFF91 and COMPASS verified in GUI and in MMP file. The GUI force field Combo box allows a valid force field to be selected by the user.
Manual Atom typing	Atom types assigned in the GUI to atoms are written to the MMP file and read from the MMP file. Verification through ToolTips feature validates feature.
Collision detection*	Atoms are marked in threes by left-clicking in GUI – Triangle data is written to MMP file. GUI side bar displays a Triangle button for a created triangle. Triangle data is read from the MMP file and unhides triangle buttons in GUI.
HotSpot (crosslinker) *	**Two terminal atoms are highlighted via right-clicks to form a HotSpot. The first is male the second is female. A button is displayed in the GUI for the HotSpot. The HotSpot was successfully processed by SAW software to create long chain polymers from the DGEBA monomers.**
Delete Atom	When deleting an atom its triangle and hotspot attributes are checked and fixed. Triangles and HotSpots are deleted. The GUI is updated. Data written to the MMP file is written correctly.
Atom Selection	When selected in the GUI an atom will display a ToolTip balloon containing the chemical atom type and the numeric atom type.
Used WingIDE debugger	Visual inspection of variables and logical paths in software for above changes
ToolTip GUI Dialog	When created an atom must have a force field associated with it. The chemical and numeric force field is displayed in the tool tip balloon window. The ToolTip dialog box allows the user to turn the feature on and off. The Checkboxes were exercised and found to work as expected.

*Features added to support SAW



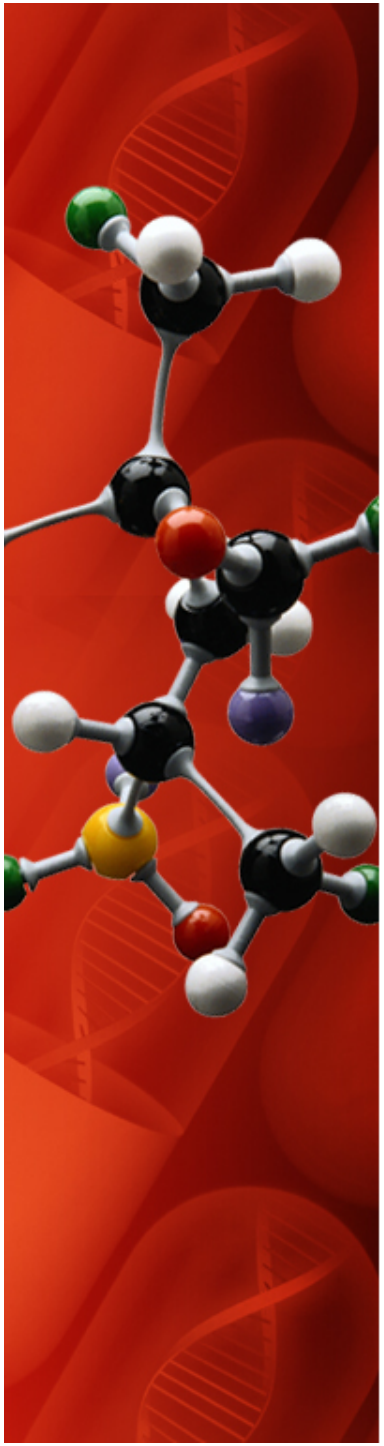
PACKMOL Software Testing

PACKMOL Software Feature	Test Method
Read MMP Files	Visually inspected data structures in core PACKMOL software to insure atom attribute data was populating spatial and force field variables in the software.
Write MMP Files	Visually inspected data structures containing the newly created molecules and compared the number of atoms per molecule and the number of molecules to the PACKMOL control file.
Used Dynamic Display Debugger (open source)	All FORTRAN code modified and written was visually inspected using the debugger



MSI2LMP Software Testing

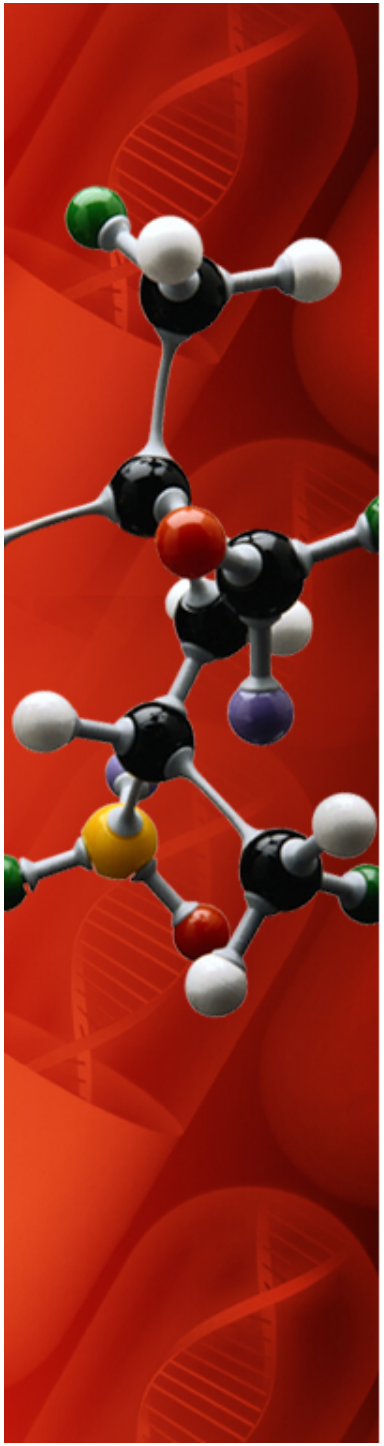
MSI2LMP Software Feature	Test Method
Read MMP Files	Visually inspected data structures in core MSI2LMP software to insure atom attribute data was populating spatial and force field variables in the software.
Write LAMMPS Trajectory File	Used VMD software to display cell of molecules and compared atom numbers to numbers in MMP file.
Used Visual Studio	All C language code modified and written was visually inspected using the debugger
Molecule identification	Visually inspected LAMMPS Geometry Input File and data structures to insure that every unique molecule created could be identified in LAMMPS.
Numeric Force Field Feature	Visually verified that the number of parameters in the modified force field files were being correctly read in and stored for use by the parameterization function in the software.
Atom numbers, atom types, number of bonds, angles, dihedrals and impropers	These were cross checked by inspection between the MMP and the LGIF file.



SAW Software Testing*

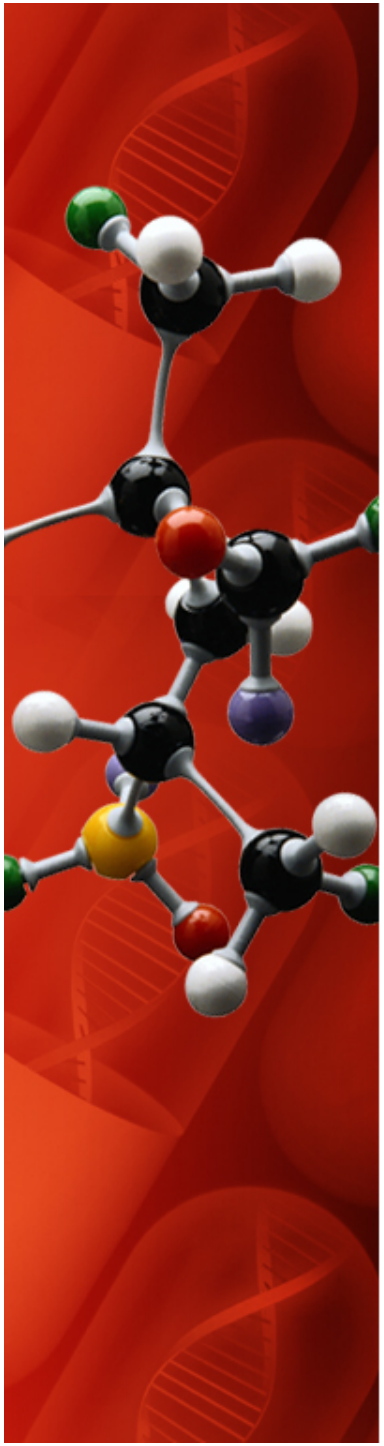
SAW Software Feature	Test Method
Read MMP Files	Compared MMP file contents to dynamic data objects created in the software to confirm the MMP file is being parsed correctly. Reads multiple MMP files, one for each molecule to be used in the MD cell creation.
Write MMP Files	Did the reverse of the Read test. Opened the MMP file created in NanoEngineer-1 to look for missing atoms, bonds and other problems.
Using Visual Studio	All C++/STL code is visually inspected and executed
Read SAW MCF File	Compared the file contents to dynamic data objects created in the software to confirm the MCF file is being parsed correctly. The number of molecules to be created and their locations are compared to the final MMP output file containing the final system.
Output MMP file	Contained linked DGEBA molecules forming a polymer structure. Checked for overlapped molecules and for spearing of ring structures.
Collision detection	Using the debugger checked all reported collisions to determine if collision detection algorithms were working.

*In progress



Software Quality/Reliability

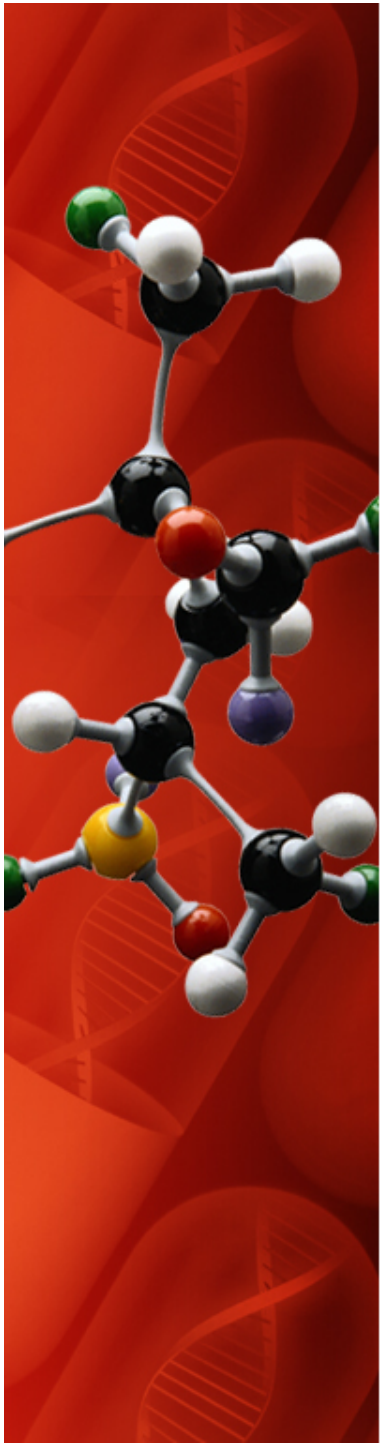
- Encountered many software bugs getting this far
- Fixed many bugs so far
- The software is still a proof-of-concept with Alpha release Summer 2012
- Peers are using MD Studio software to create systems
- Minor bugs exist with work-a-rounds
- Continuing to fix bugs as they occur



MD Cell Preparation

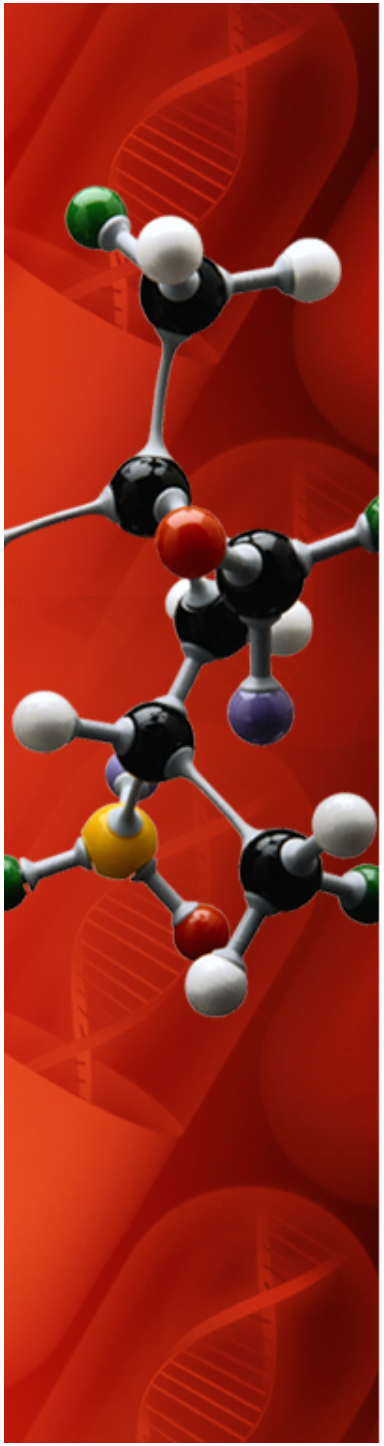
- **Equilibration of the cell is the goal**
  - Temperature
  - Volume
  - Many other definitions based on the simulation
- **MM Energy Minimization**
  - Lower potential energy
  - Decrease cell volume*
  - Set cell pressure to 1atm*
- **Quench**
  - NVE ensemble with velocity rescaling
  - Lowers potential energy
  - Remove bad contacts and atoms jumping processors
- **Simulated Annealing**
  - Helps find global energy minimum
  - NPT ensemble reduces system volume based on force field
- **Final MD cell is created for a specific temperature and pressure**

*LAMMPS Fix box/relax feature



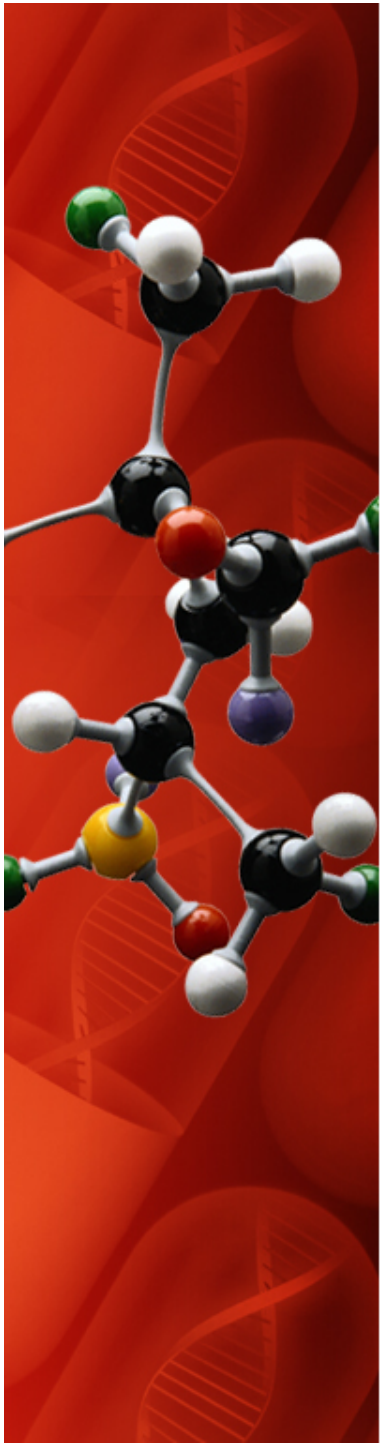
MD Cell Quench Schedule

NVE with Velocity Rescaling	
Time Step Duration (fs)	**Number of steps**
0.001	10,000
0.01	10,000
0.1	10,000
0.2	10,000
0.4	10,000



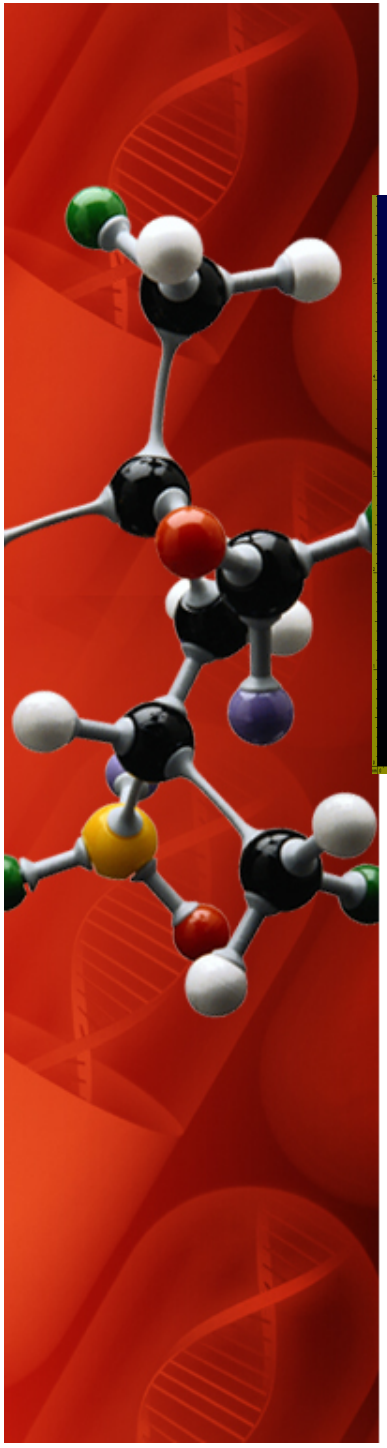
MD Cell Annealing Schedule

Simulated Annealing NPT Ensemble at 1atm			
Step	**Start Temperature (K)**	**End Temperature (K)**	**Duration (ps)**
1	298	298	50
2	298	600	50
3	600	600	200
4	600	298	50

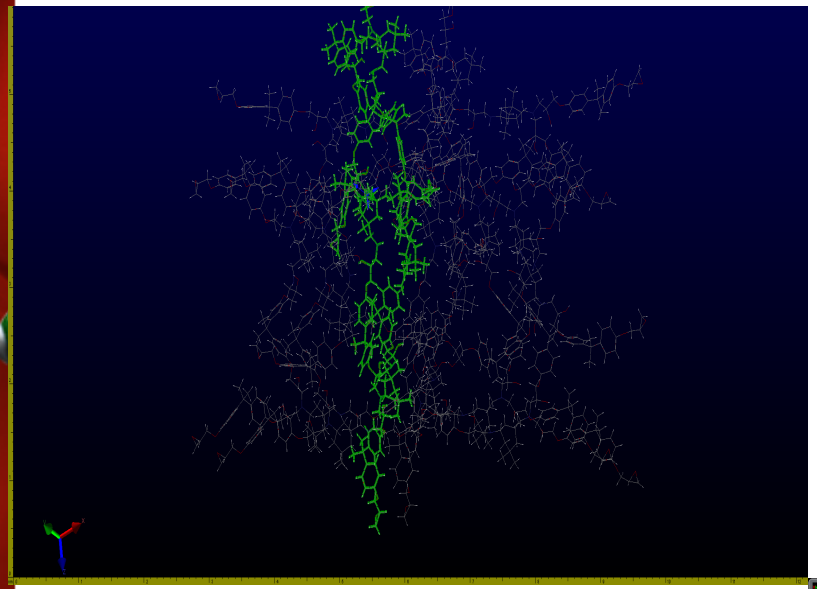


MD Cell Bulk Modulus Schedule

Bulk Modulus Data Collection at 298K, NPT Ensemble			
Step	**Start Pressure (atm)**	**End Pressure (atm)**	**Duration (ps)**
1	1.0	1.0	100
2	1.0	5001.0	100
3	5001.0	5001.0	100

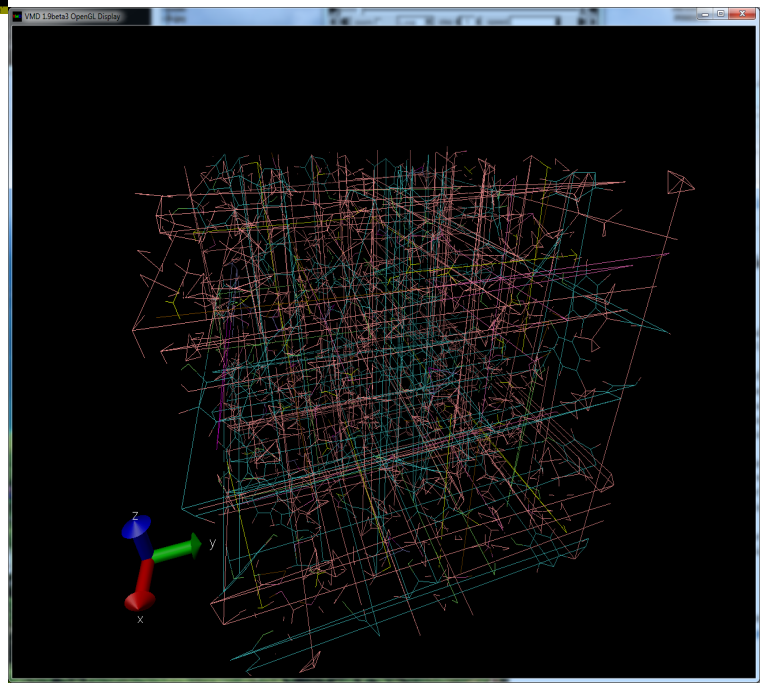


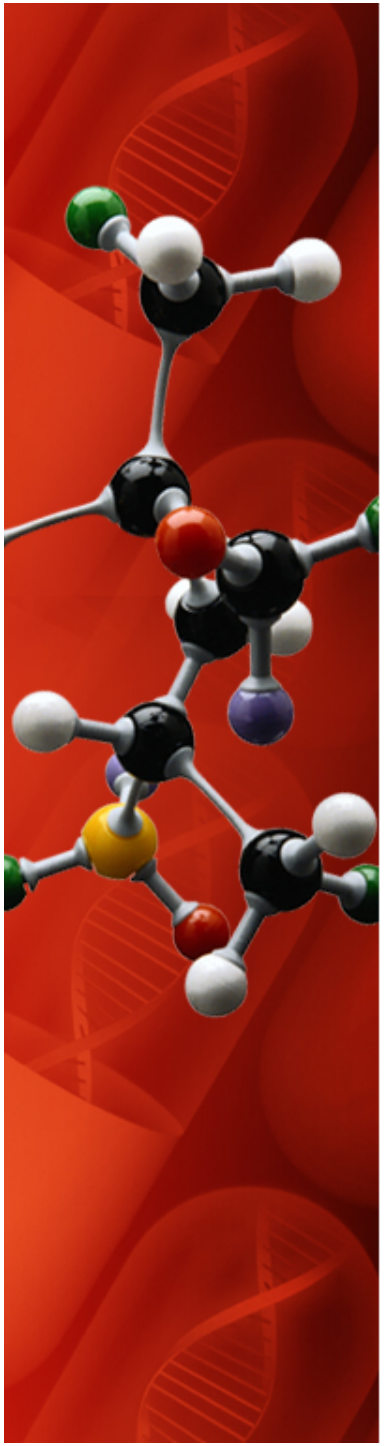
System Two: MD Cell



- Initial cell is 55Å per side
- Results of 3D Math

- Final cell is ~30Å to 32Å per side
- Results of cell preparation



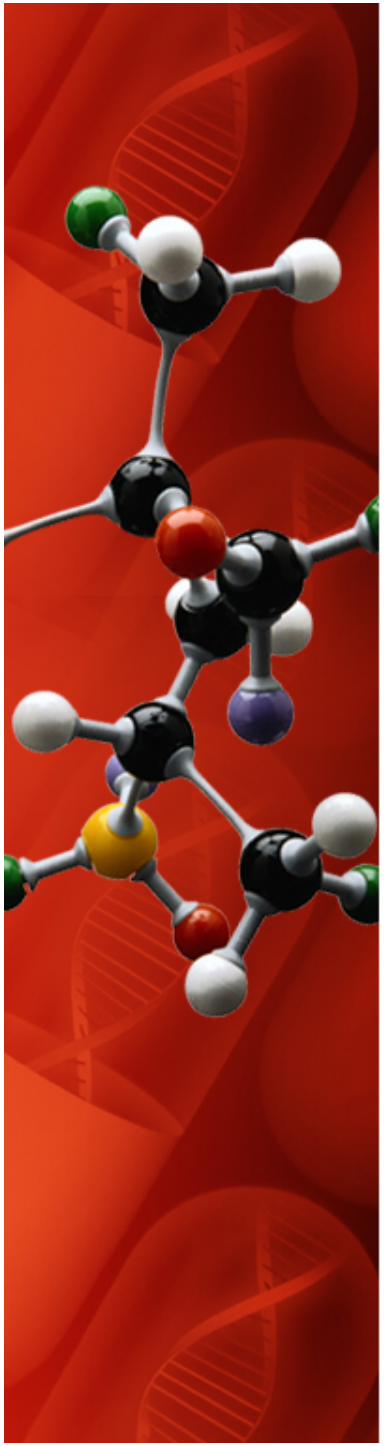


MD Simulations for Density

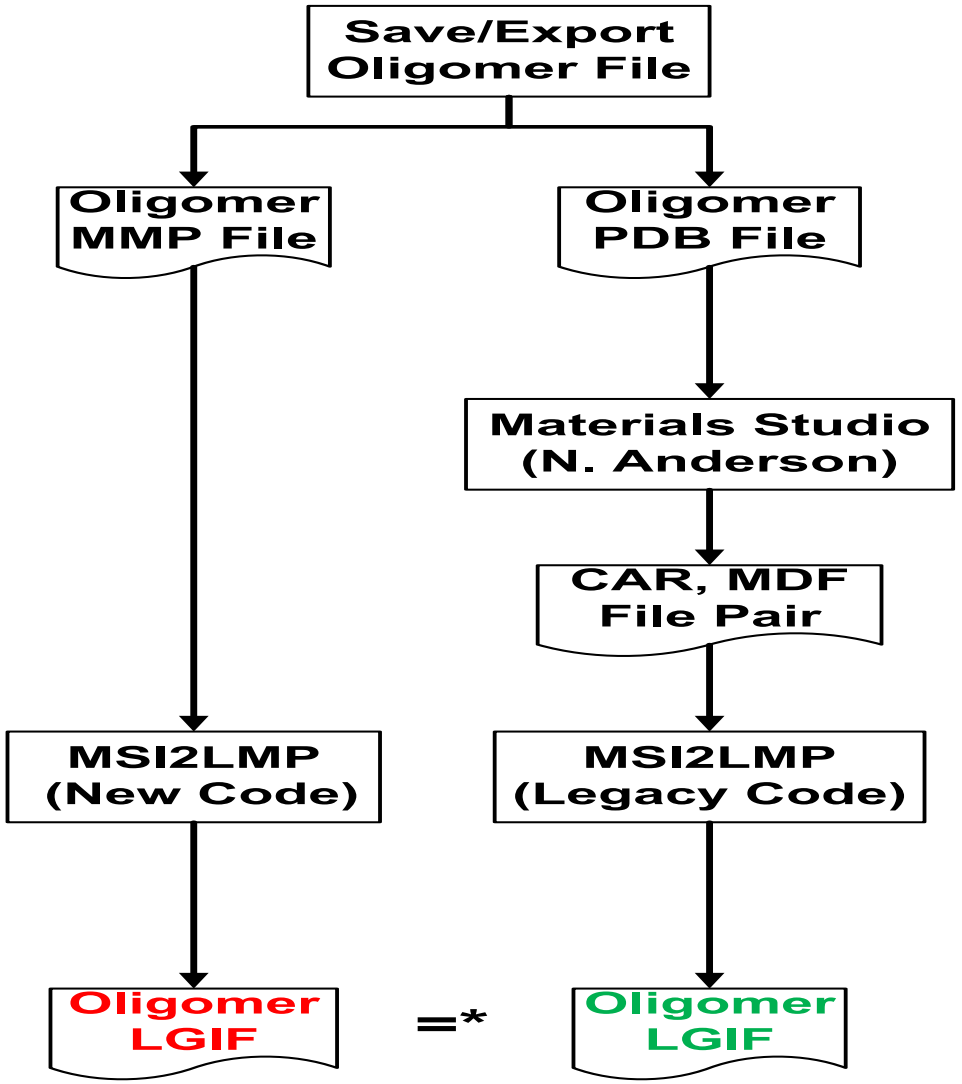
- **NPT ensemble used for densities at specific temperatures. All data collected at 1atm.**
  - **Temperature Ramp**
    - Fix 4 all npt temp 600.0 570.0 100.0 iso 1.0 1.0 1000.0 drag 2.0
  - **Temperature Equilibrium**
    - Fix 4 all npt temp 570.0 570.0 100.0 iso 1.0 1.0 1000.0 drag 2.0

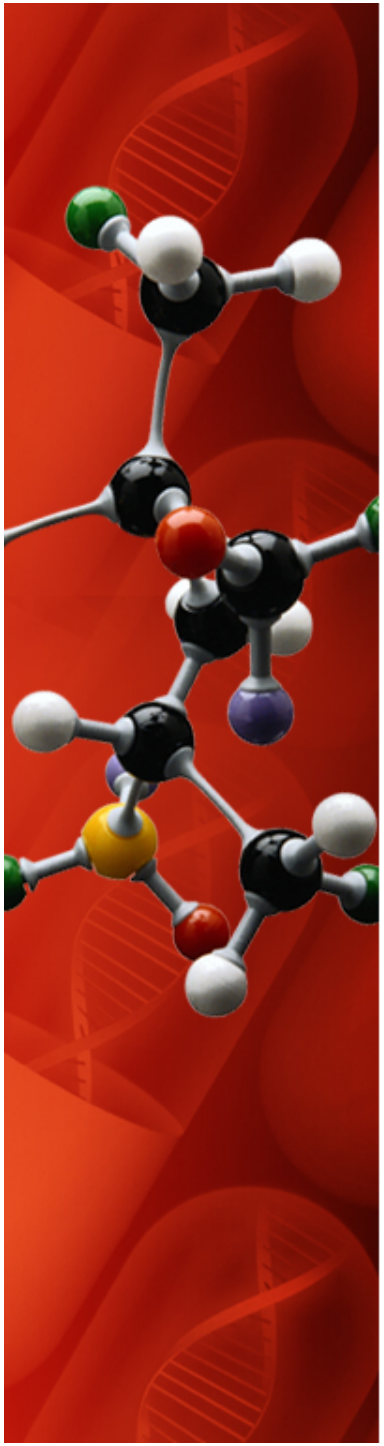
Results

- **Software Testing Results**
- **Simulation Results for the following DGEBA/IPD Systems:**
  - System One: Liquid system
  - System Two: Five 75% intra-crosslinked oligomers
  - System Three: Five 87.5% intra-crosslinked oligomers
  - System Four: Inter-crosslinked oligomers: 2/1



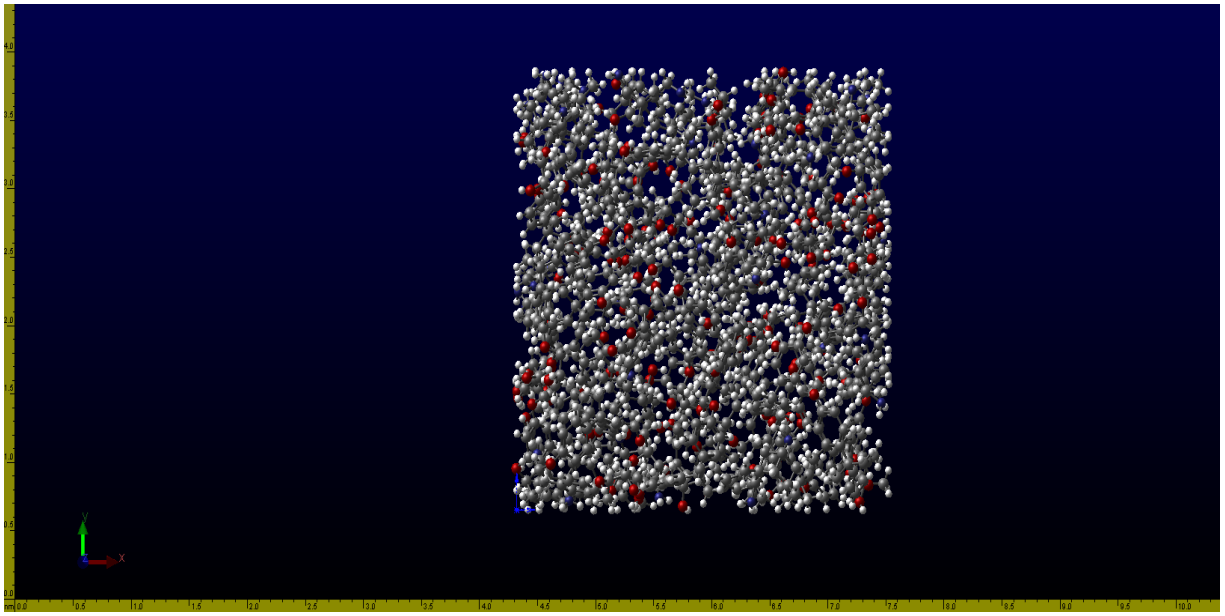
Software Parallel Testing (MSI2LMP)

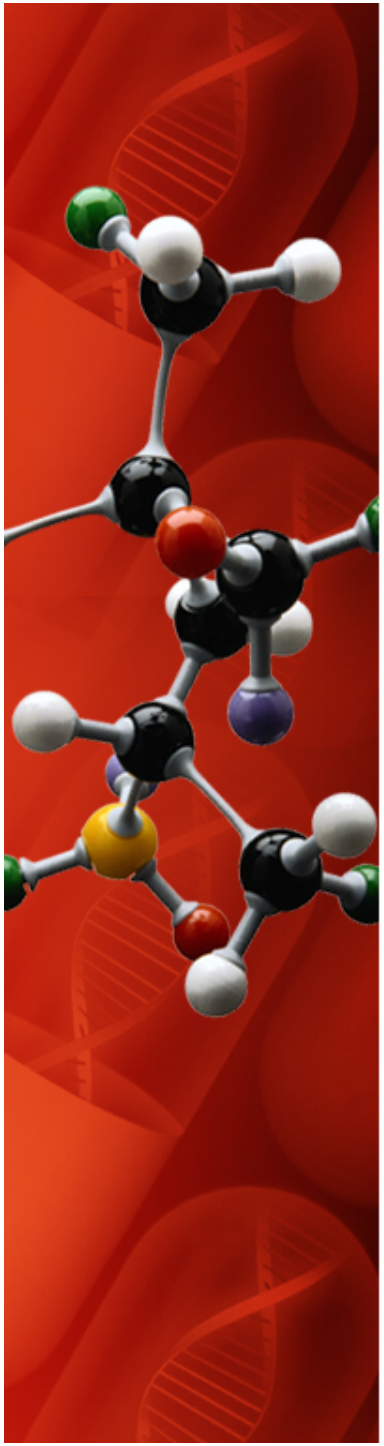




System One (No Crosslinking)

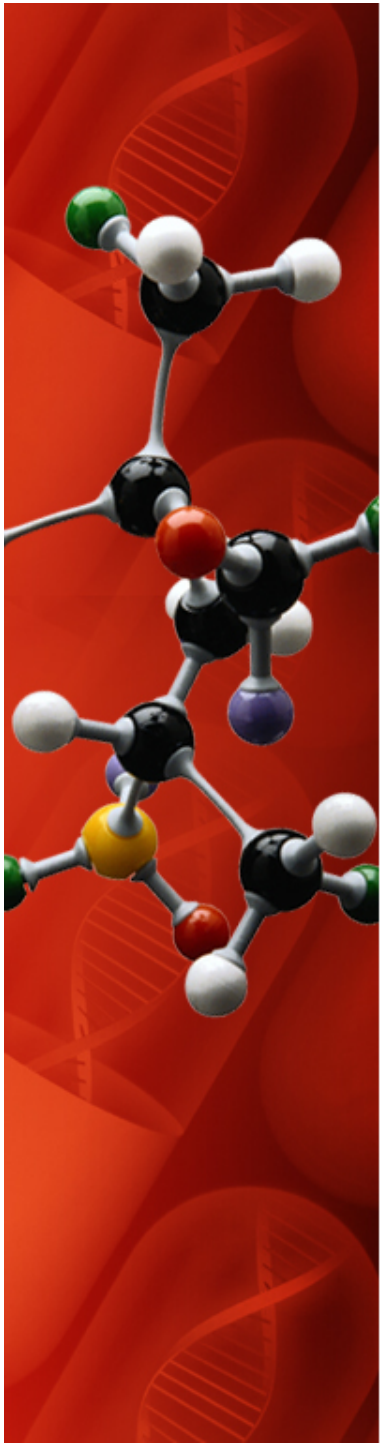
- 45 DGEBA & 20 IPD molecules
- Density: ~1 gm/cc at 298K and 1atm
- MD does not support reactions – this is a liquid
- Looks like the Borg Cube from Star Trek





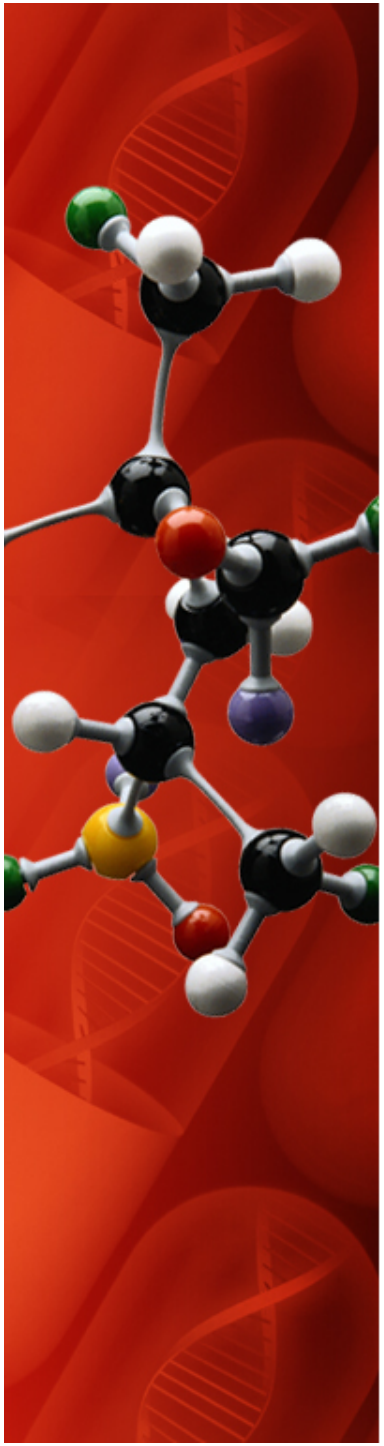
System Two (75% Intra-crosslinked)

System Two Temperature and Density Variation (Nose-Hoover Thermostat)				
Average Temperature (K)	**Maximum Temperature (K)**	**Minimum Temperature (K)**	**Maximum Density (gm/cc)**	**Minimum Density (gm/cc)**
298.26	307.81	288.82	1.060	1.025
328.05	340.21	317.27	1.067	1.035
358.47	368.88	346.28	1.062	1.032
388.72	406.61	374.03	1.061	1.024
418.93	432.50	402.7	1.052	1.007
449.12	469.56	433.77	1.035	0.989
479.44	495.73	463.58	1.032	0.990
509.72	527.25	491.7	1.02	0.980
540.02	557.47	520.94	1.01	0.963



System Two (75% Intra-crosslinked)

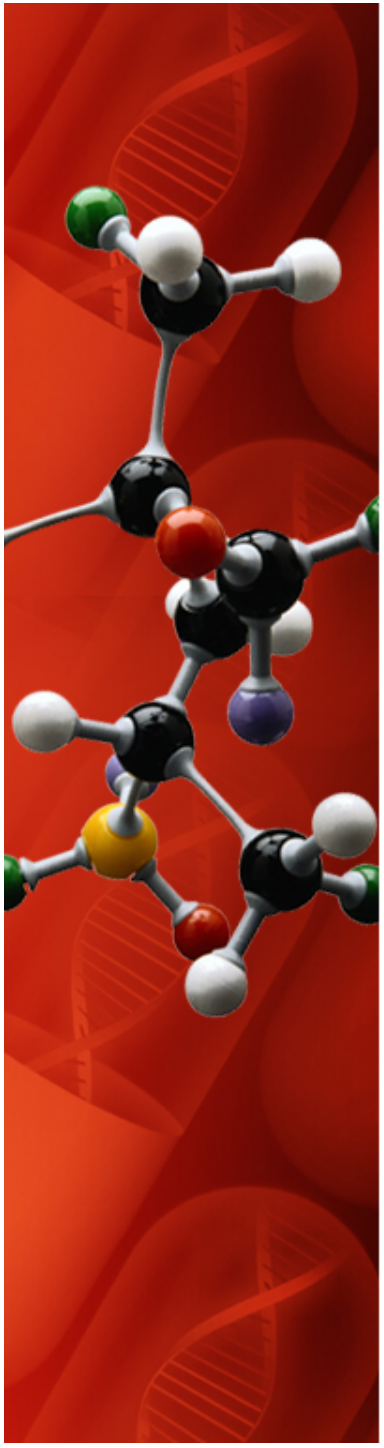
System Two Calculated Density by Temperature at 1atm					
Temperature (K)	**Lx (Å)**	**Ly (Å)**	**Lz (Å)**	**Volume (cc) X 1.0e20**	**Density (gm/cc)**
297.55	30.75	30.76	30.77	2.8954	1.056
328.02	30.74	30.76	30.77	2.9106	1.0510
358.12	30.78	30.79	30.80	2.9197	1.0458
388.63	30.83	30.84	30.85	2.9344	1.0427
418.66	30.79	30.80	30.81	2.9222	1.0470
449.02	30.93	30.94	30.95	2.9634	1.0325
479.55	31.07	31.08	31.09	3.0042	1.0185
509.85	31.39	31.14	30.42	3.023	1.0122
539.95	31.32	31.34	31.35	3.0783	0.99404
570.57	31.46	31.47	31.48	3.1164	0.98187
599.86	31.56	31.57	31.58	3.14645	0.9725



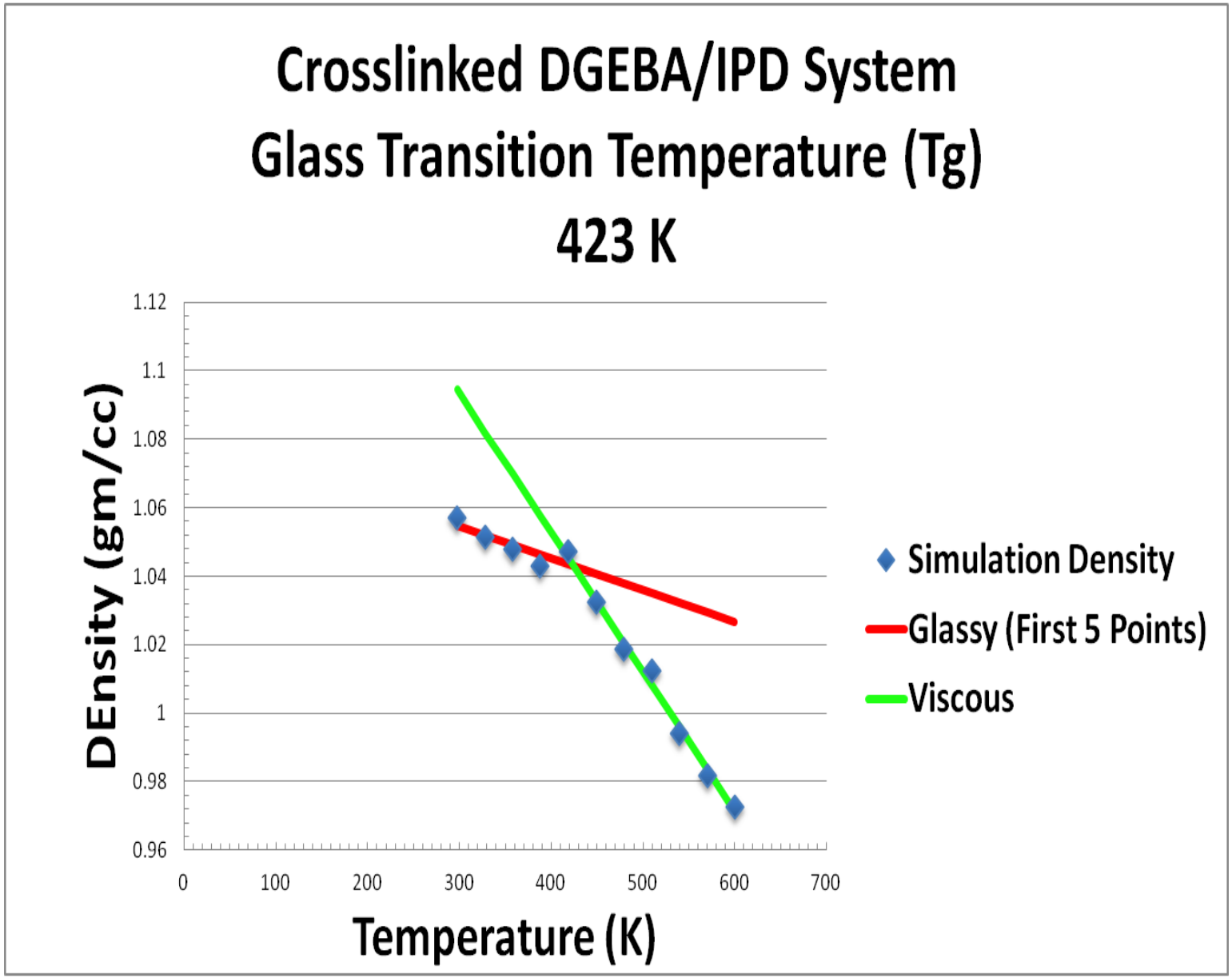
System Two (75% Intra-crosslinked)

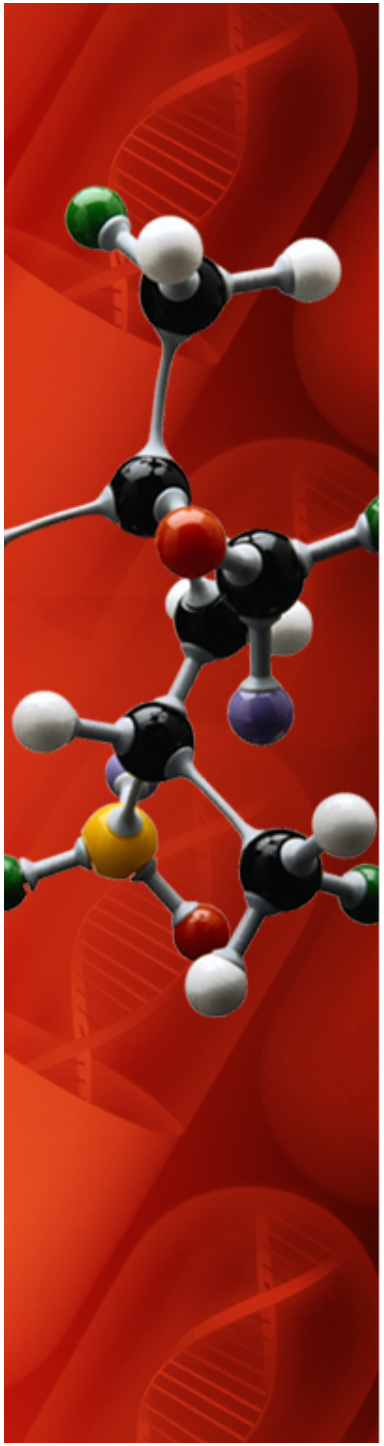
System Two: Bulk Modulus Raw Data				
Pressure (atm)	**Lx (Å)**	**Ly (Å)**	**Lz (Å)**	**Volume (cc)**
1.0	30.86	30.87	30.88	2.94e-20
5001.0	24.76	29.82	35.92	2.65e-20

System Two: Bulk Modulus for 5 Oligomer Rings				
ΔP (MPa)	**ΔV (cc)**	**V_0 (cc)**	**Simulated Bulk Modulus (GPa)**	**Experiential Bulk Modulus (GPa)**
506.6	2.90e-21	2.94e-20	**5.13**	**5.01**



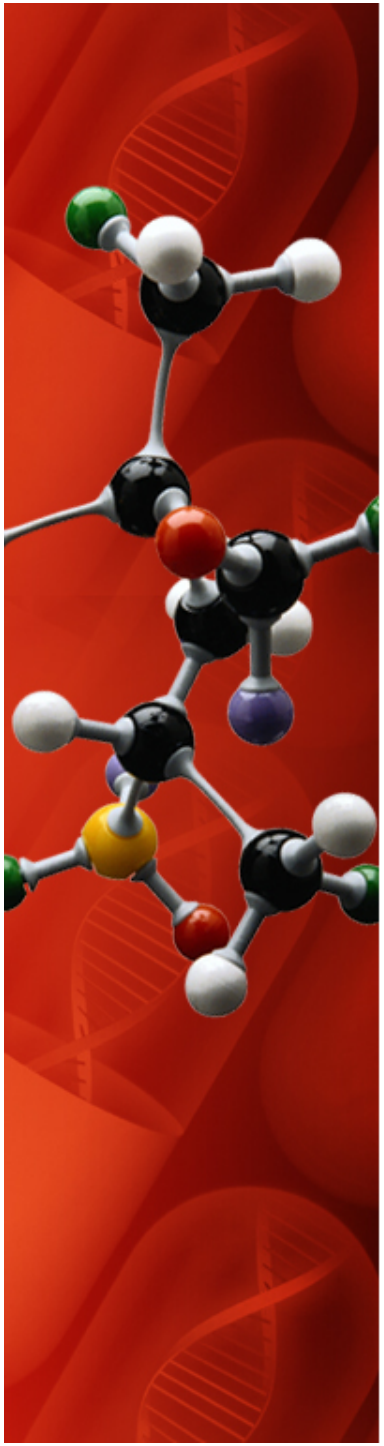
System Two (75% Intra-crosslinked)



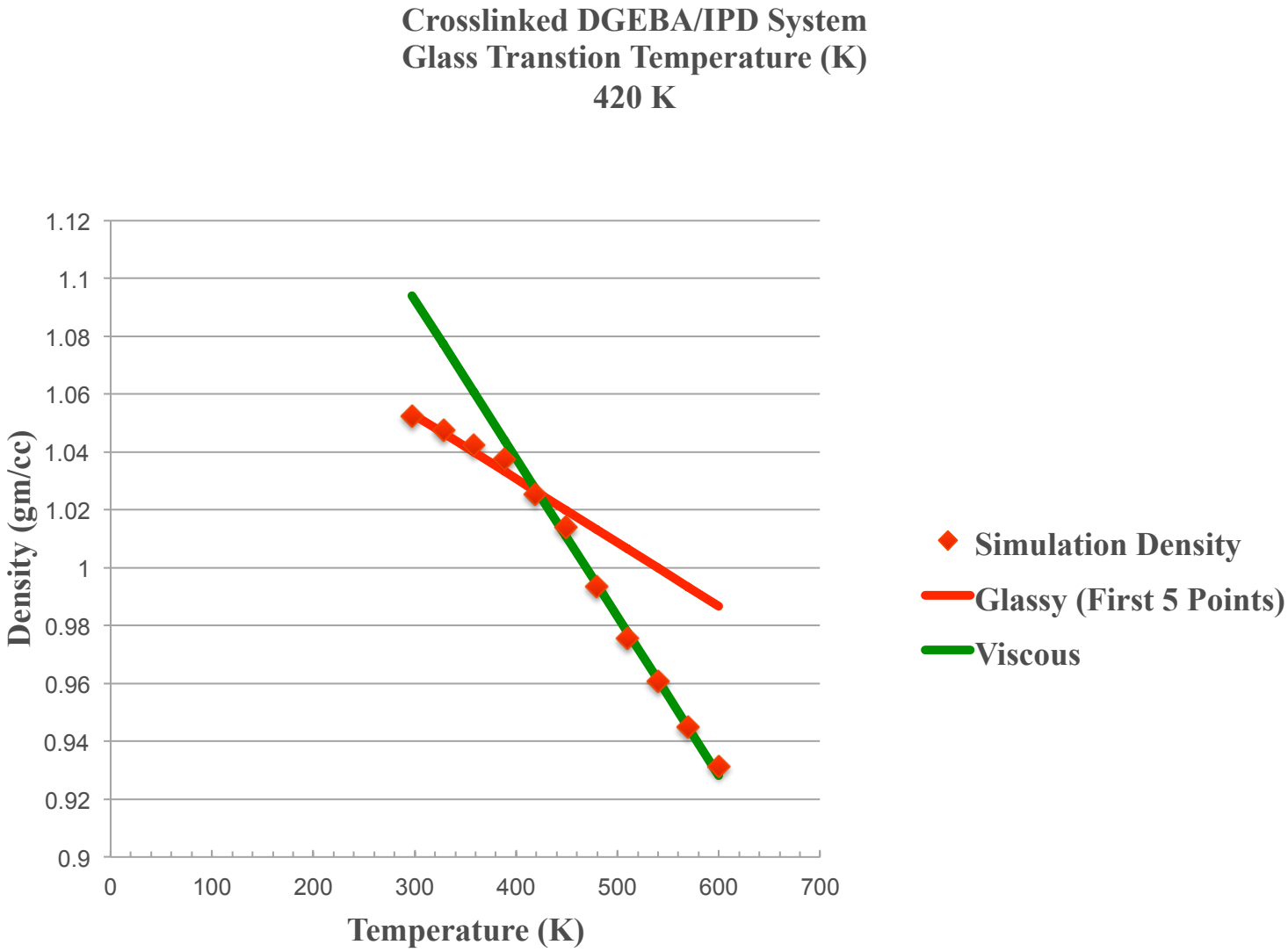


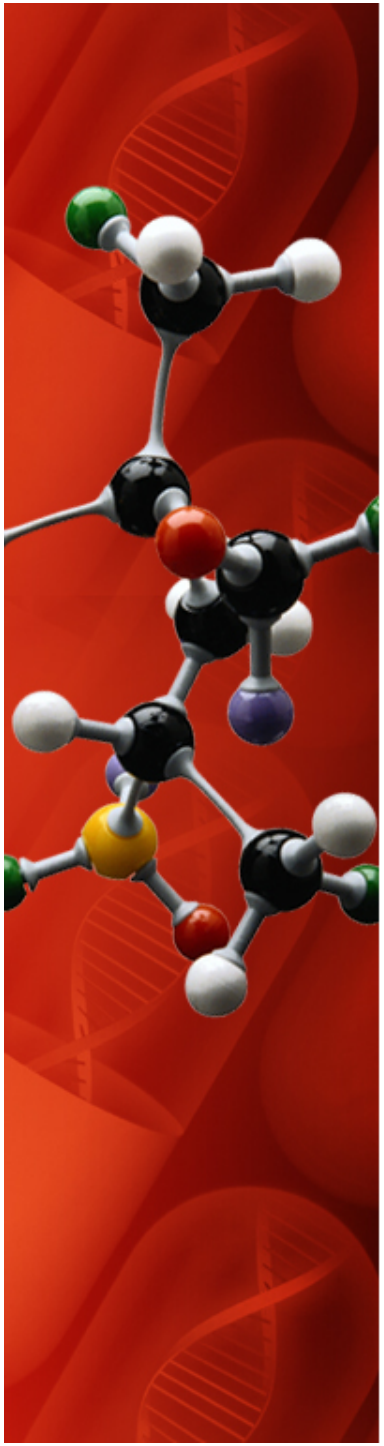
System Three (87.5% Intra-crosslinked)

System Three 87.5% Intra-oligomer crosslinked System Based on Average Volumes Mass: 3.6296e-20 gm					
Temperature (K)	Lx (Å)	Ly (Å)	Lz (Å)	Volume (cc) X 1.0e20	Density (gm/cc)
297.42	32.57	32.56	32.52	3.449	1.0523
328.07	32.62	32.61	32.56	3.4646	1.0476
358.47	32.68	32.67	32.62	3.48252	1.04225
388.71	32.72	32.72	32.67	3.4983	1.03754
418.99	32.85	32.85	32.80	3.5396	1.02544
449.40	32.98	32.928	32.92	3.5795	1.0140
479.40	33.20	33.19	33.14	3.65301	0.99361
509.56	33.40	33.39	33.35	3.72075	0.975518
539.72	33.57	33.56	33.52	3.77753	0.9608
569.80	33.76	33.75	33.70	3.84205	0.94472
600.18	33.92	33.92	33.86	3.89748	0.93128



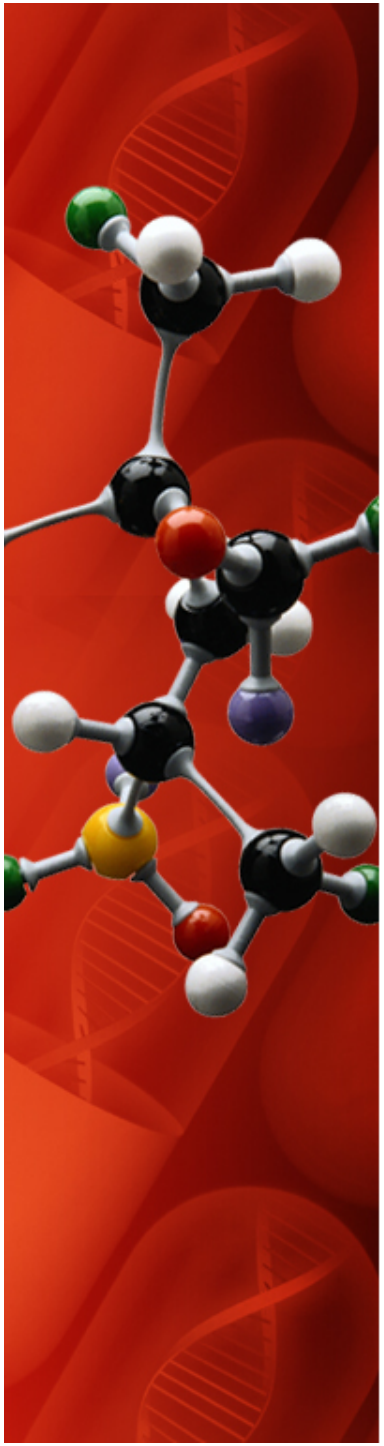
System Three (87.5% Intra-crosslinked)



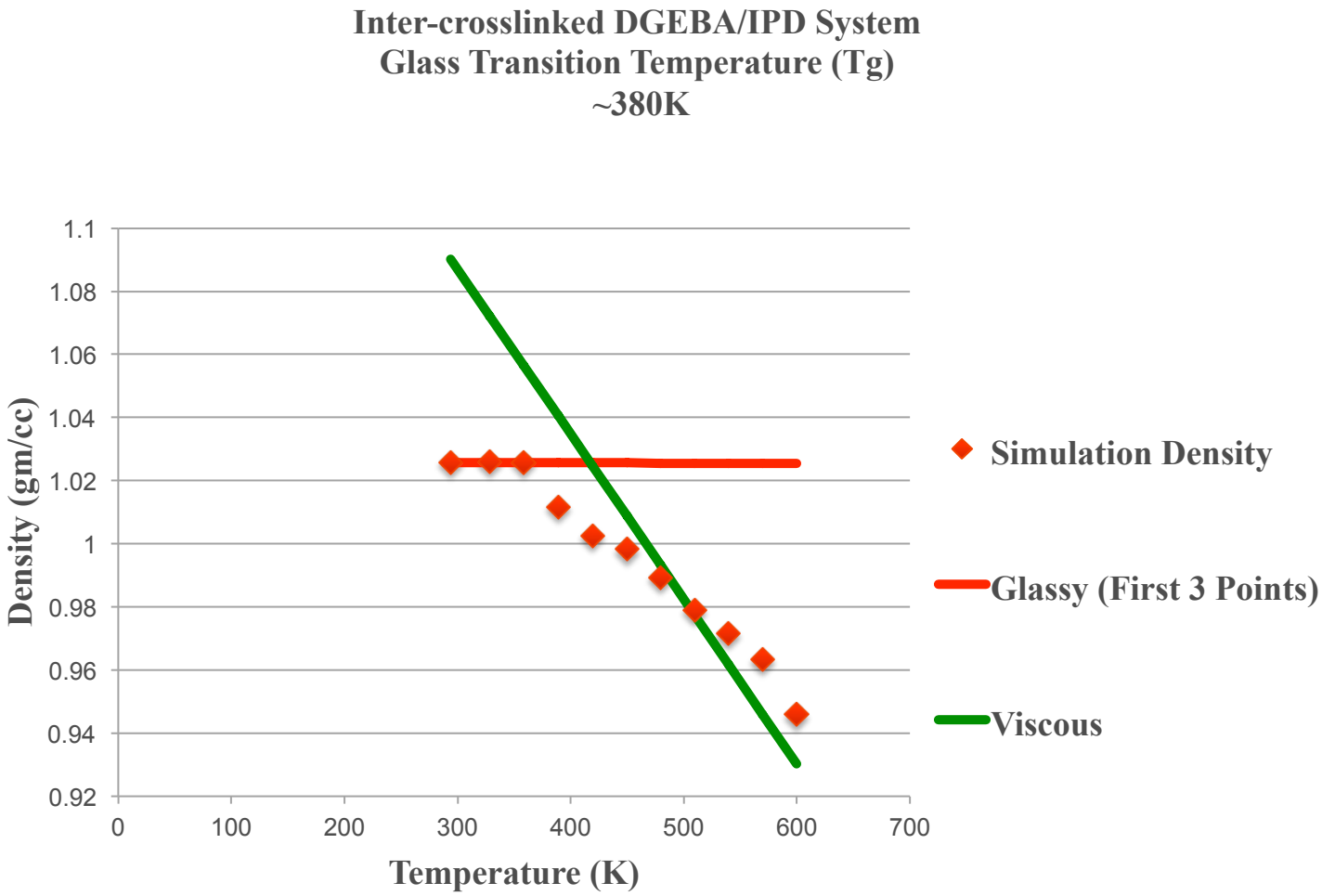


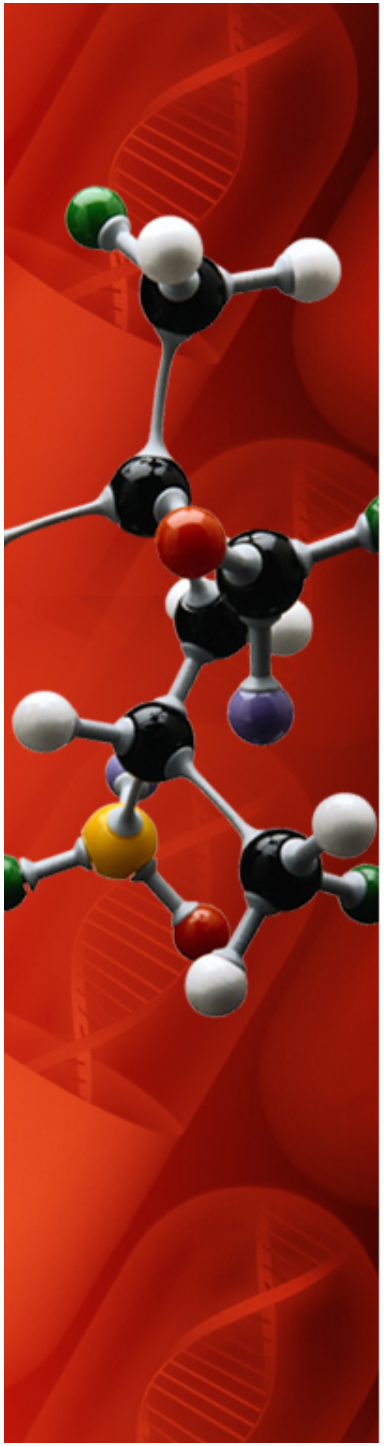
System Four (93.75% Inter-crosslinked)

System Four 93.75% Intra-oligomer crosslinked System Based on Average Volumes Mass: 3.06e-20 gm					
Temperature (K)	**Lx (Å)**	**Ly (Å)**	**Lz (Å)**	**Volume (cc) X 1.0e20**	**Density (gm/cc)**
294.18	31.12	31.13	30.79	2.9831	1.0257
328.20	31.11	31.13	30.78	2.9824	1.0260
358.30	31.11	31.13	30.79	2.9836	1.0255
388.86	31.26	31.28	30.93	3.0250	1.0115
419.02	31.35	31.37	31.02	3.0519	1.0026
448.92	31.40	31.42	31.07	0.9836	0.9983
479.32	31.49	31.51	31.16	3.0931	0.9892
509.62	31.61	31.62	31.27	3.1260	0.9788
539.78	31.68	31.70	31.35	3.1495	0.9715
569.92	31.77	31.79	31.44	3.1762	0.9633
599.91	31.96	31.98	31.63	3.2347	0.9459

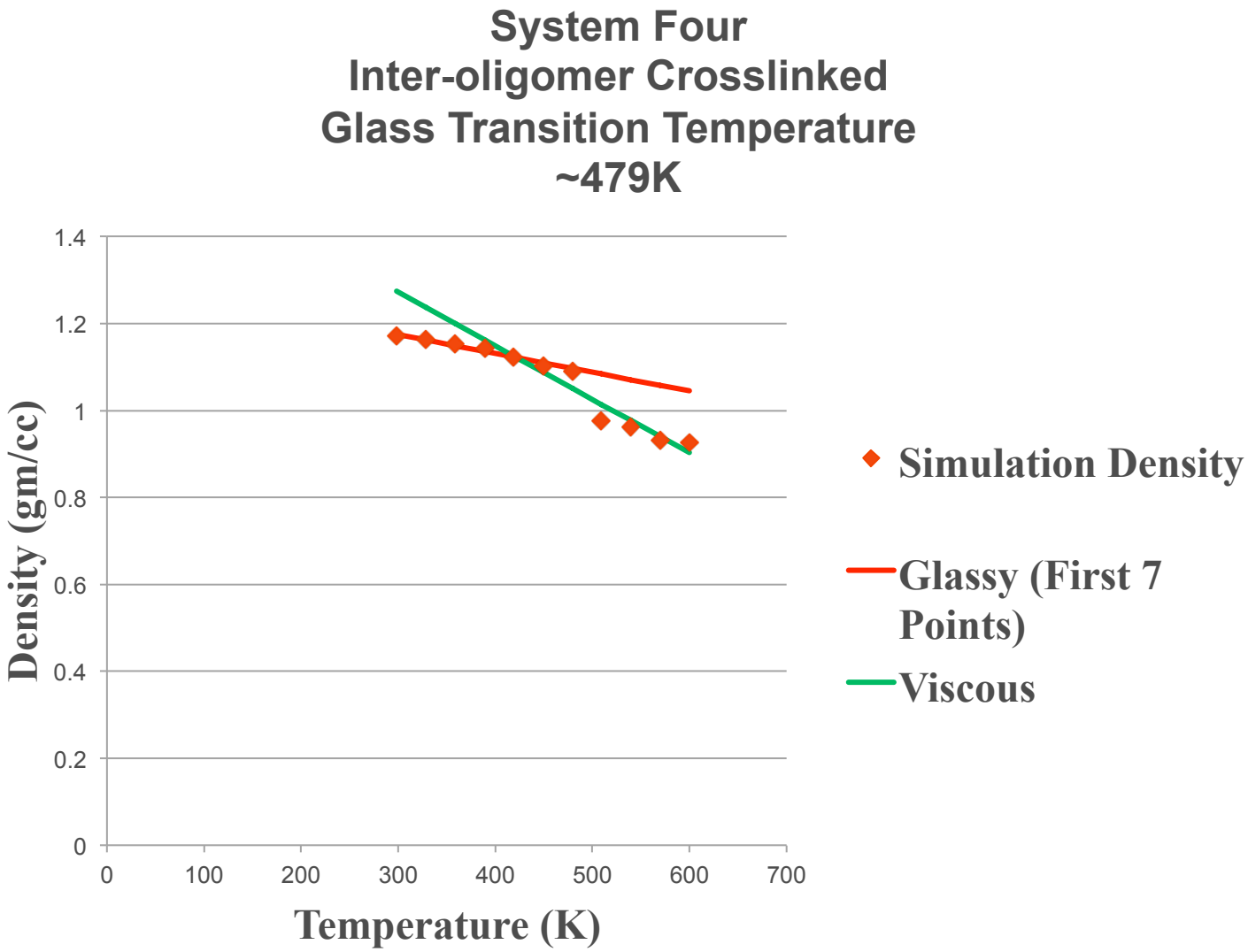


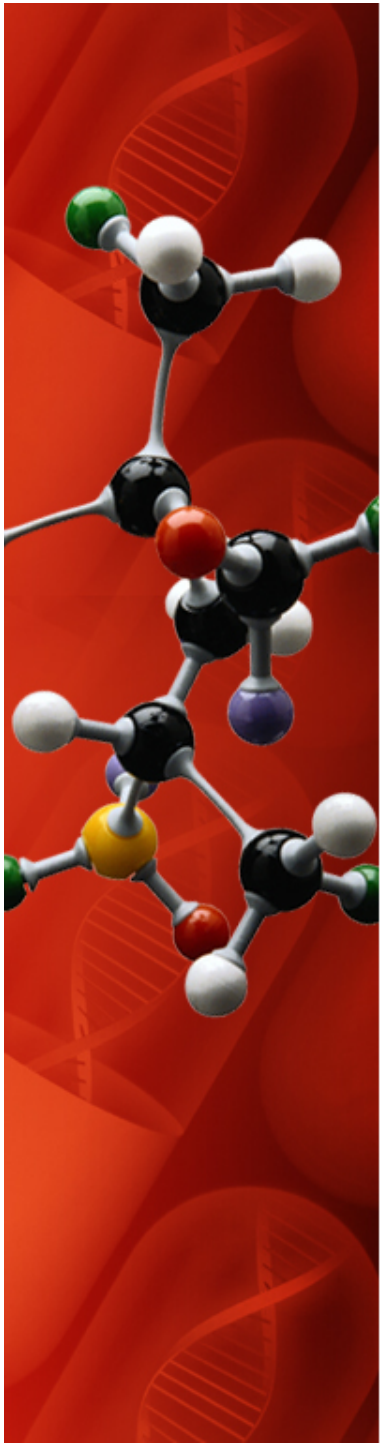
System Four (93.75% Inter-crosslinked)





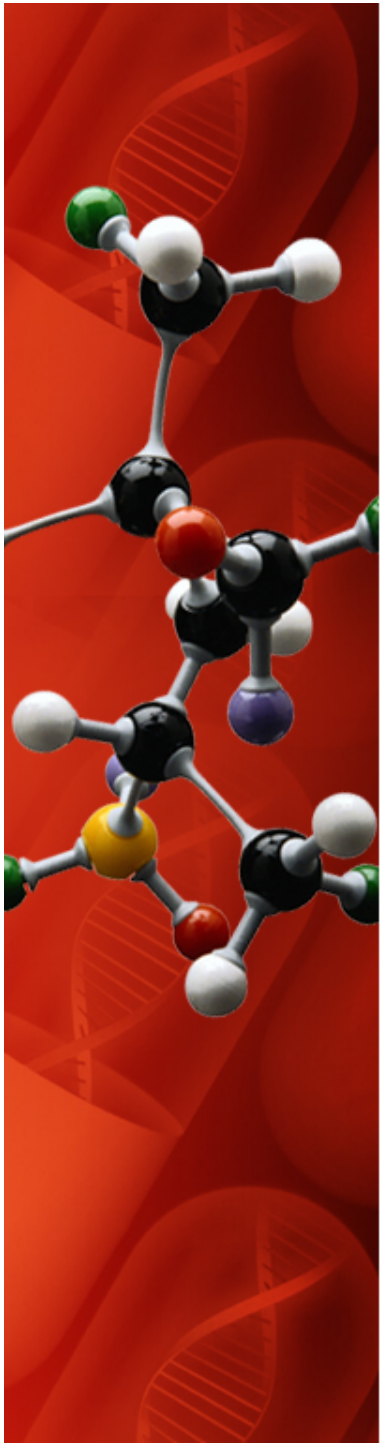
System Four (93.75% Inter-crosslinked)





Simulation Honorable Mentions

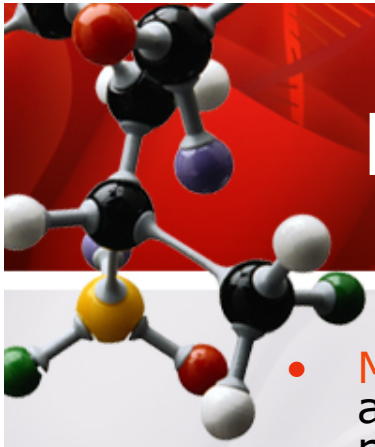
- Using the same simulation parameters:
  - Substituted DGEBF for DGEBA for system two
    - Density increased from 1.05 gm/ccto 1.11 gm/cc
    - Removing two Methyl groups per DGEBA increased Density
  - Opened epoixde rings, (Methyl & hydroxyl), did not affect density for system two.
  - Cut the (n=1) DGEBA dimer at the hydroxyl group for system two
    - Oligomer ring structure was done away with
    - Density did not change



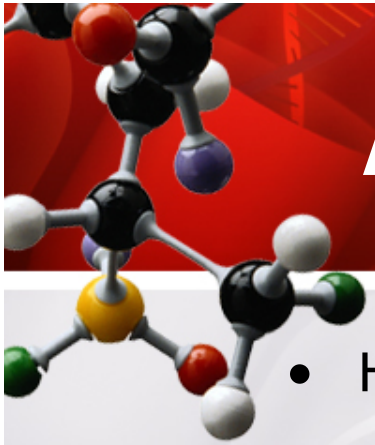
Simulation Results Summary

- Crosslinking does increase density as shown by system one and two results and thereby increases the glass transition temperature
- System three shows that intra-oligomer crosslinking alone is not the controlling factor
- System four has two different results based on the methods used to create the final MD cell. This is clearly the result of how the cell was created and not a reflection on the software.
- SAW, once complete, will allow automated construction of inter-oligomer crosslinked systems
- PACKMOL, once the new crosslinking software is added, will support better Static MD cell construction

Discussion



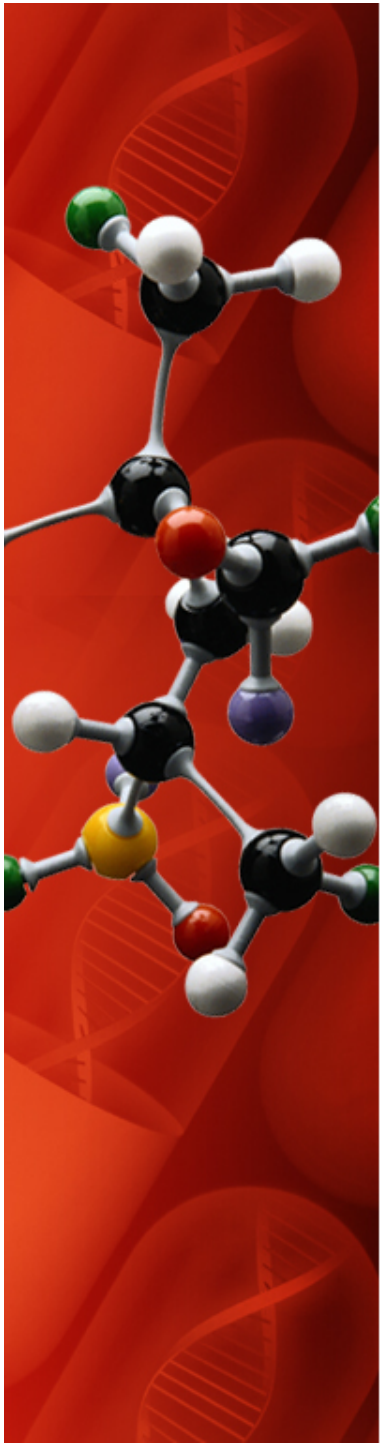
- MD Studio software allows researchers to quickly assemble an MD cell from any set of molecules that can be represented by a force field
- MD Studio software can be modified to support additional force fields
- MD Studio software capabilities compare well against Materials Studio on a basic functionality level
- Simulation results for intra-oligomer crosslinked systems are inline with published experimental and simulated results



Anticipated Questions*

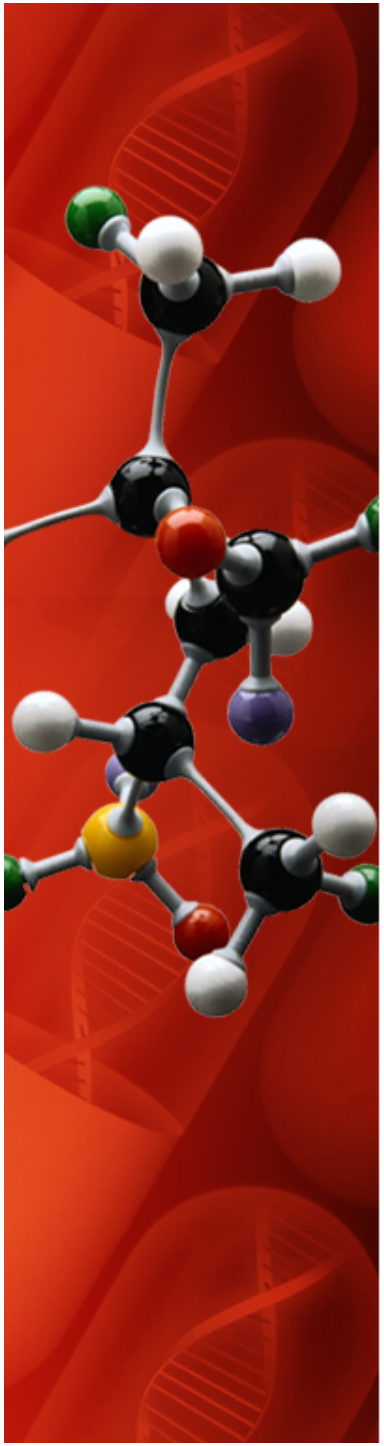
- How LAMMPS Works
- Long-range Nonbonded Forces
- System Equilibrium
- PACKMOL Space Partition and Cost Function
- Pressure Fluctuations
- SAW Software
- Thermostats

Note: Ancillary data sources are used in this section for informational purposes only. Your Copyright belongs to you and not to me.



HOW LAMMPS Works

- **Large-scale Atomic/Molecular Massively Parallel Simulator**
- **Time step**
  - 1 femtosecond duration based on vibration of C-H bond
  - Verlet time integration method is the default
- **Neighbor Lists**
  - Keep track of nearby atoms
  - Optimized for atoms that are repulsive at short distances in order to keep the local density of atoms low
- **Spatial Decomposition Methods**
  - Assigns sub-spaces of the MD cell to one of multiple processors if available
  - Most efficient with uniform density systems
  - Maintains "ghost atoms" for boundary atoms
- **Conservation of Energy**
  - Potential Energy
  - Kinetic Energy
  - Floating point arithmetic can cause system to lose energy about 1.5ns into a simulation
- **Isotropic and anisotropic simulations are allowed**

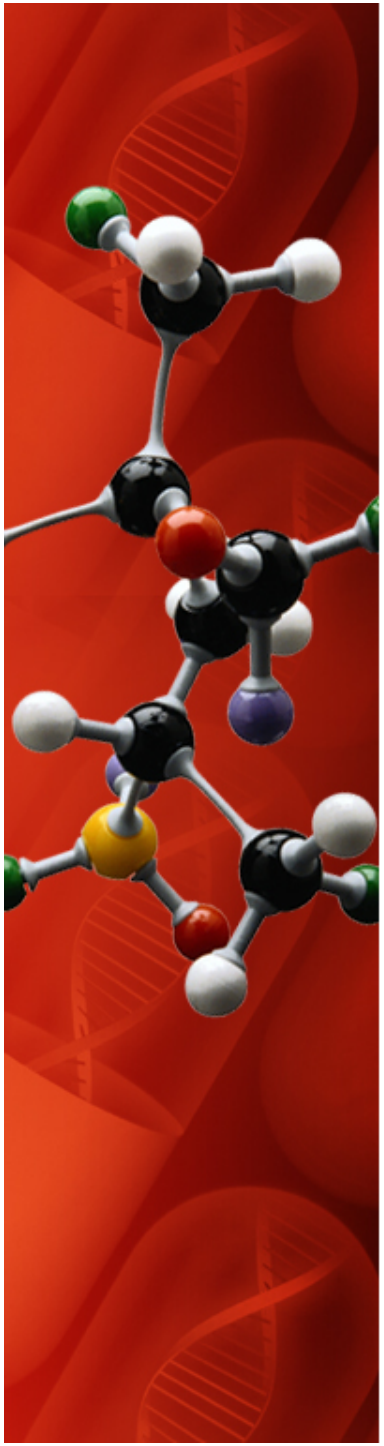


Long Range Nonbonded Forces

- Applied to Coulombic and Van der Waals solutions

- Ewald – "The *ewald style performs a standard Ewald summation as described in any solid-state physics text.* The cost of traditional Ewald summation scales as N^(3/2) where N is the number of atoms in the system.*" (LAMMPS User Manual)*
  - ***Maintains atom charges on every processor***
  - ***Easier environment for bad dynamics***
  - ***Longer simulation times***

- PPPM – "The *pppm style invokes a particle-particle particle-mesh solver (Hockney) which maps atom charge to a 3d mesh,*uses 3d FFTs to solve Poisson's equation on the mesh, then interpolates electric fields on the mesh points back to the atoms. It is closely related to the particle-mesh Ewald technique (PME) (Darden) used in AMBER and CHARMM. The PPPM solver scales as Nlog(N) due to the FFTs, so it is almost always a faster choice (Pollock)." (LAMMPS User Manual)
  - **Maintains atom charges on the processor maintaining said atoms**
  - **Easier environment to detect bad dynamics**
  - **Shorter simulation times**

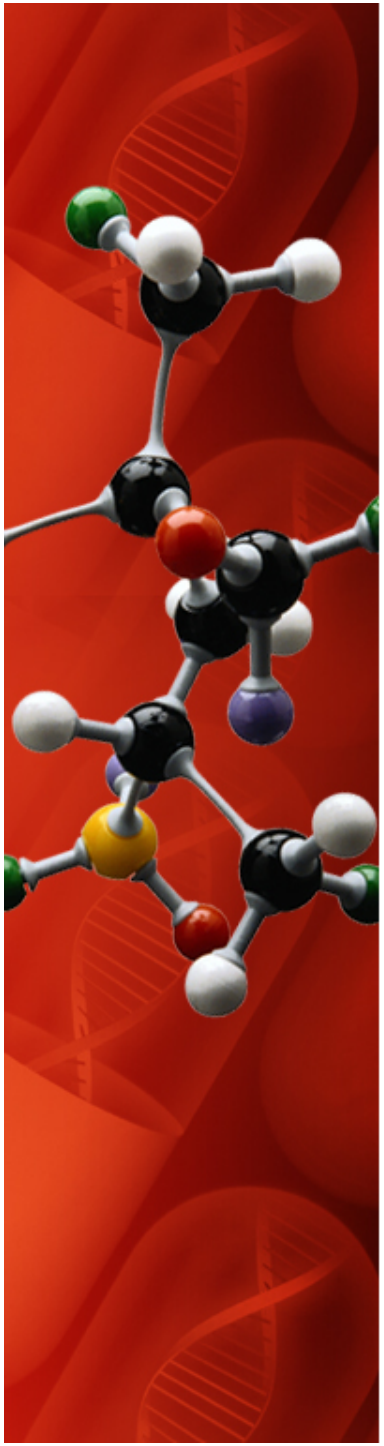


System Equilibrium

- How to:
  - **Run simulation for a long time and see how long you need to run it based on the change to time average instantaneous state values**
    - Pressure
    - Temperature
    - Volume

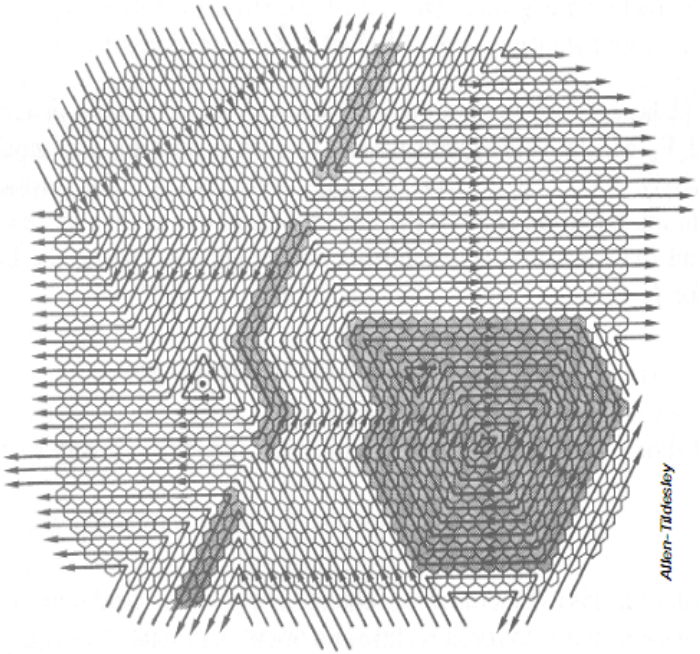
$$P = \frac{Nk_bT}{V} + \left(\sum_i^N r_i \cdot f_i\right)/3V$$

  - **Attempt to create a system with a zero valued virial (Wu & Xu)**
  - **Attempt to determine the system time constant for transient behavior. Run the simulation longer and time average instantaneous values not in the transient regime**
  - **Is the system ergodic?**



Ergodicity

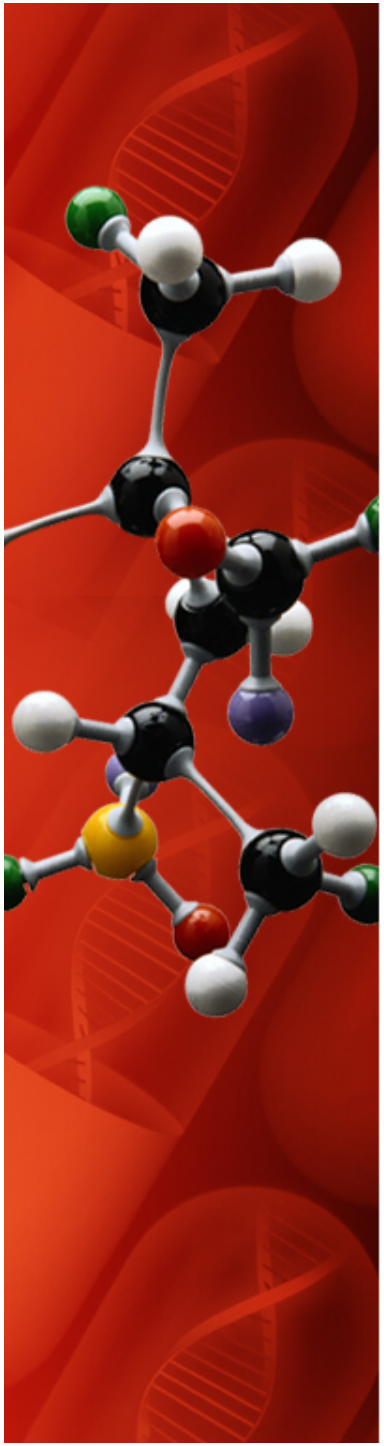
- In an ergodic system a long enough simulation will go through all points in phase space $\{\mathbf{q}_i, \mathbf{p}_i\}$.
- An example of a *non-ergodic* system (each hexagon represents one point phase space $\{\mathbf{q}_i, \mathbf{p}_i\}$):
  - In the darker area, the simulation moves in a close path, and can never get out of this area ⇒ the simulation does not test all of phase space, i.e. is non-ergodic.
  - In case there would be a single path which would go through the whole system, the system would be ergodic.



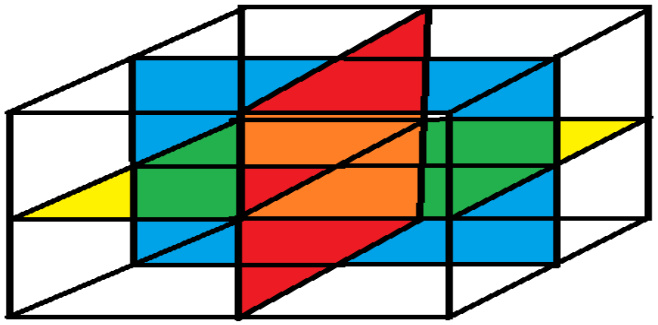
- Is it possible to prove that some system is ergodic? Not in the general case, and even for a given system it is usually very difficult in practice.
- In practice the system may not only have regions which are impossible to reach, but also regions which are surrounded by a high potential energy barrier so that reaching them in a finite simulation may be very unlikely (such a barrier is illustrated by the grey thin regions in the figure). This may distort the simulation averages badly.

(Dr. Antti Kuronen, University of Helsinki, Department of Physics)

(Allen, Tildesley: "Computer simulation of Liquids" (Oxford University Press, Oxford, England, 1989))



PACKMOL Space Partition and Cost Function



$$f(c,\theta)=\sum_{i=1}^{n\,mol}\sum_{j=1}^{n\,atom(i)}\left(\sum_{l=i+1}^{n\,mol}\sum_{m=1}^{n\,atom(l)}max\left\{0,d_{tol}^{2}-\left\|p^{ij}-p^{lm}\right\|^{2}\right\}^{2}\right)$$

$$+\sum_{i=1}^{n\,mol}\sum_{j=1}^{n\,atom(i)}\left(\sum_{z=1}^{r^{ij}}max\left\{0,g_{z}^{ij}\left(p^{ij}\right)\right\}^{2}\right)$$

Soft System Size Requirements

$$\left\langle \delta\sigma^2 \right\rangle \sim \frac{kT}{V\beta} \sim \frac{1}{N}$$

, where b is the compressibility, which is RMS of roughly 100 bar for a 10,000 atom biomolecular system. Much larger fluctuations are regularly observed in practice." (NAMD manual)

$$E = \left(\Delta\sigma / \Delta\varepsilon\right)_{meas}$$

To accurately and precisely measure elastic modulus: $\sqrt{\left\langle \delta\sigma^2 \right\rangle} << \Delta\sigma$

(stdev << magnitude)

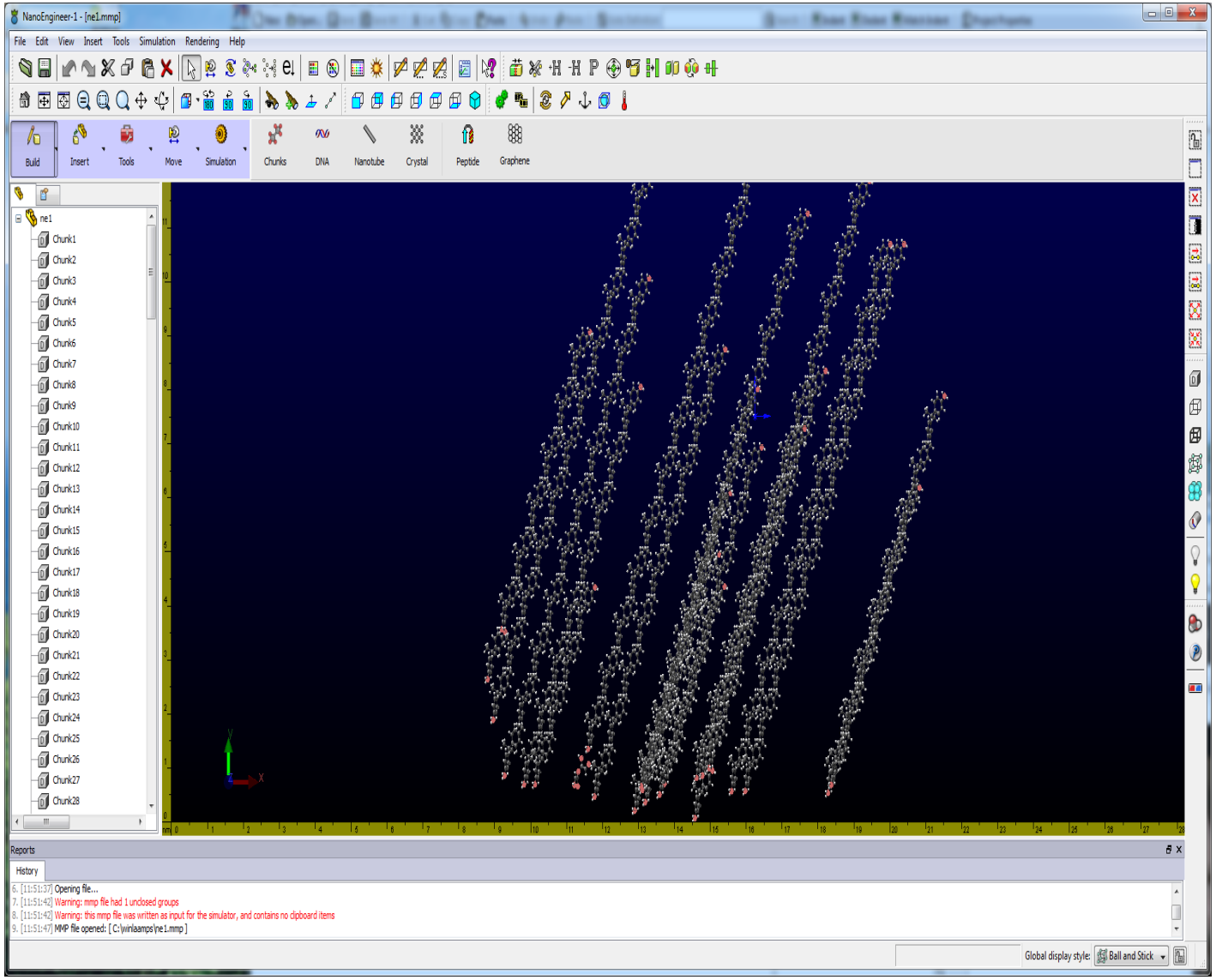
Epoxy rubbery E < ~10 MPa, so … $\Delta\sigma = E \cdot \Delta\varepsilon = (\sim 10MPa)(\sim 0.01) = 1bar$

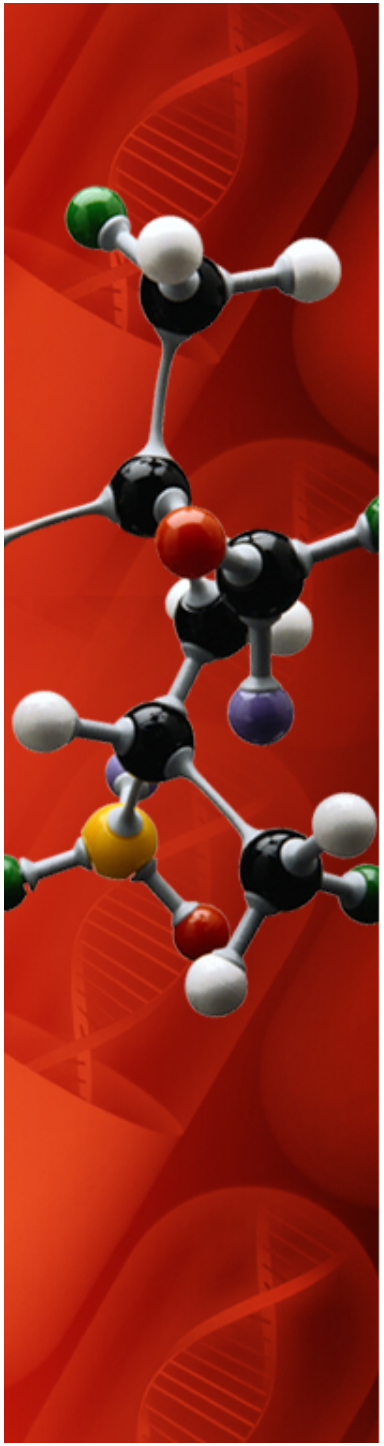
For ~60K atoms, we measure: $\sqrt{\left\langle \delta\sigma^2 \right\rangle} \sim 30bar$

$$\sqrt{\left\langle \delta\sigma^2 \right\rangle} \le \Delta\sigma \quad \text{if} \quad N = \frac{\left\langle \delta\sigma^2 \right\rangle_0}{\left\langle \delta\sigma^2 \right\rangle} \cdot N_0 = \frac{(30bar)^2}{(1bar)^2} \cdot (60Katoms) = 54Matoms!$$

"The instantaneous pressure [or stress tensor] of a simulation cell… will have mean square fluctuations (according to David Case quoting Section 114 of Statistical Physics by Landau and Lifshitz) of

Self-avoiding Walk Software MD Cell





Thermostats

•Andersen's Method (aka Velocity Scaling or Rescaling) (Ruhle, 2007)

- •$\lambda = (T_{setpoint} / T_{current})$ applied to all atom velocities
- •Does not support temperatures in canonical ensemble (NVT)

•Berendsen (Ruhle, 2007)

- •$\lambda^2 = 1\ \delta t/\tau\ ((T_{setpoint} / (T_{current}\ (t - \delta t/2)))-1)$
- •τ is a coupling parameter for the temperature bath to the system. As $\tau \rightarrow \infty$ the thermostat is inactive and NVE is restored.

•Nose-Hoover introduces an extra degree of freedom into the Hamiltonian to include the heat bath into the system. (Wikipedia)

$$\mathcal{H}(P, R, p_s, s) = \sum_i \frac{\mathbf{p}_i^2}{2ms^2} + \frac{1}{2}\sum_{ij, i\neq j} U(\mathbf{r_i} - \mathbf{r_j}) + \frac{p_s^2}{2Q} + gkT \ln(s),$$

$$R' = R,\ P' = \frac{P}{s} \text{ and } t' = \int^t \frac{\mathrm{d}\tau}{s}$$