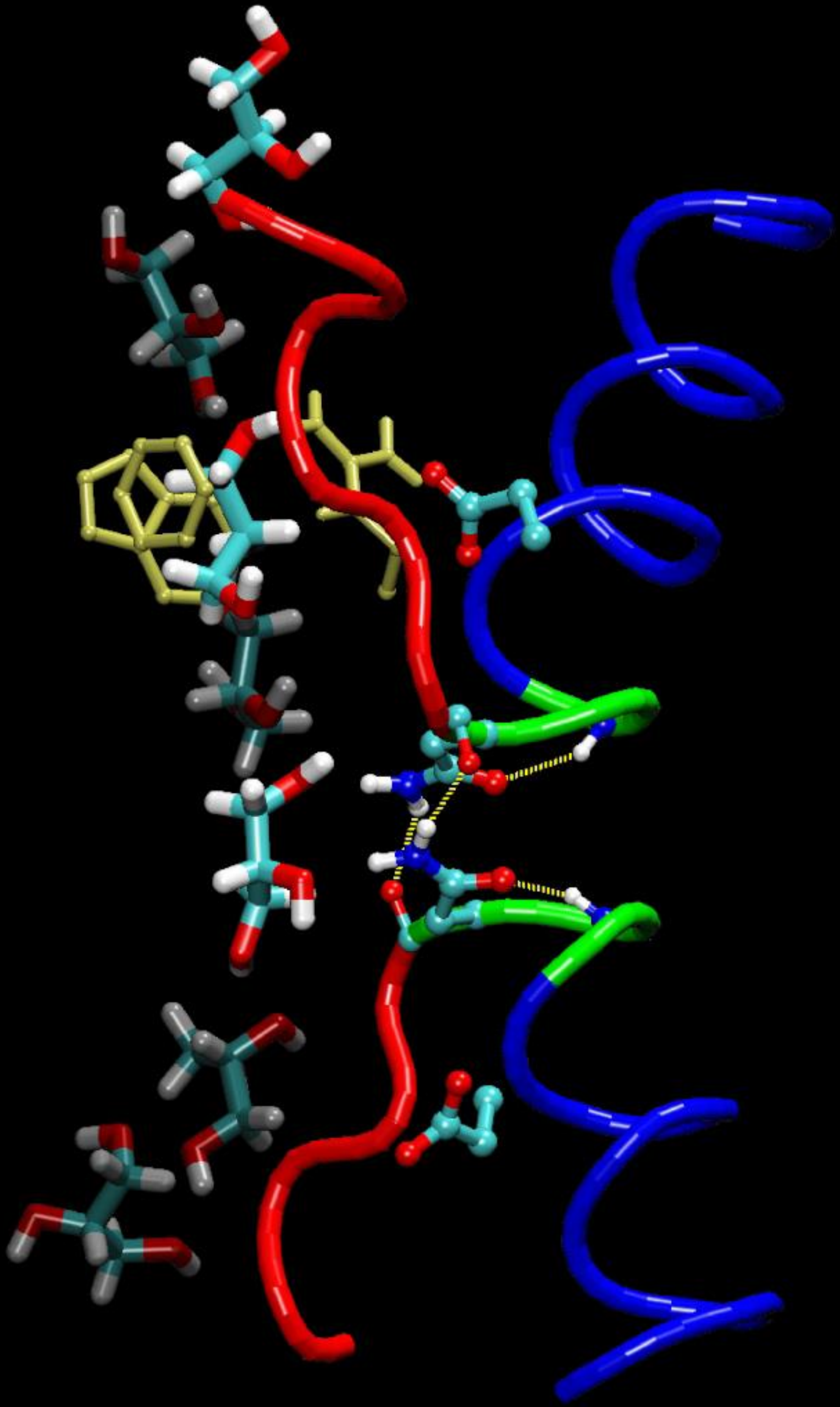
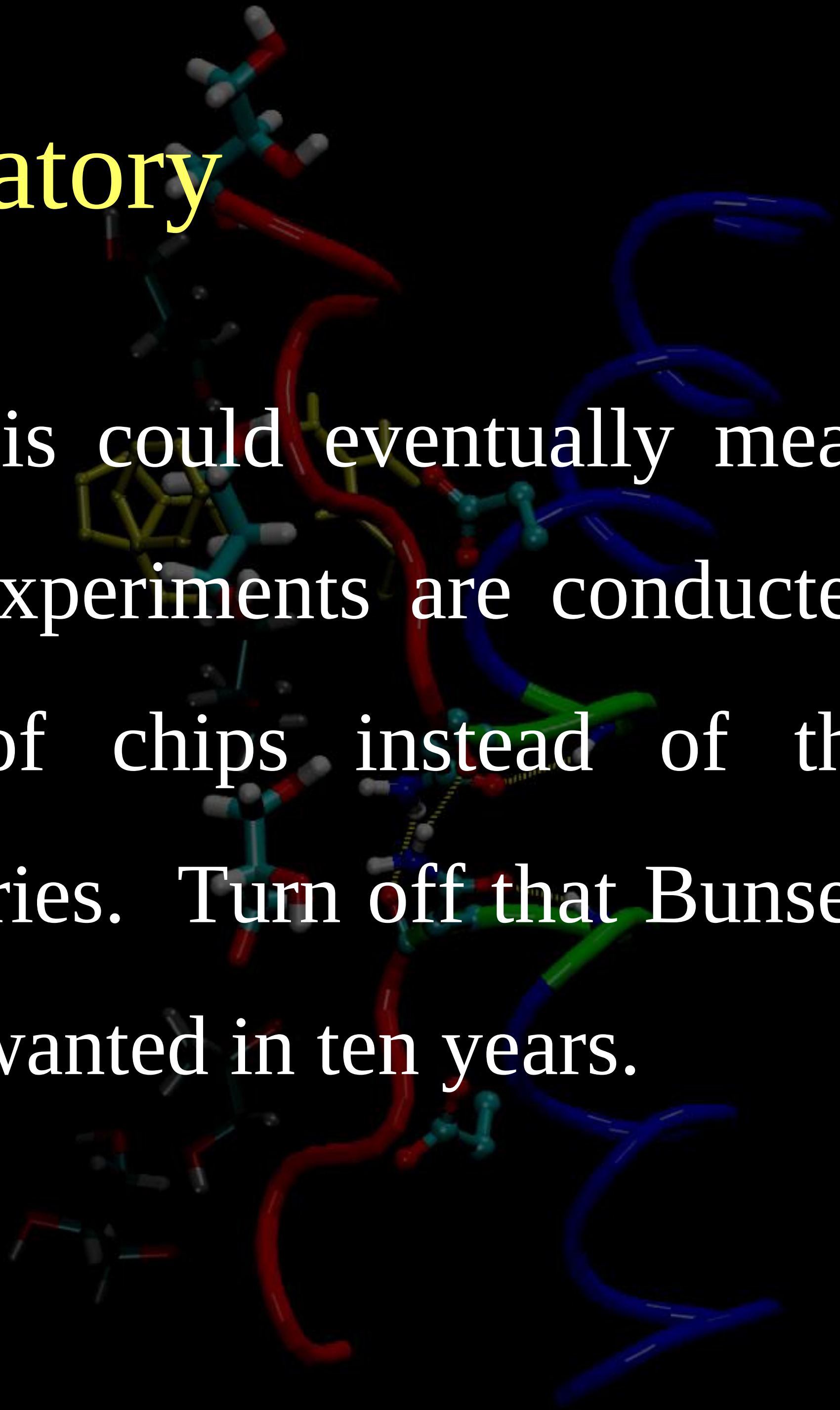
Molecular Dynamics Simulation



By Aqeel M. Ali
University of Basrah
Polymer Research Center
Dept. of Material Science

A Digital Laboratory

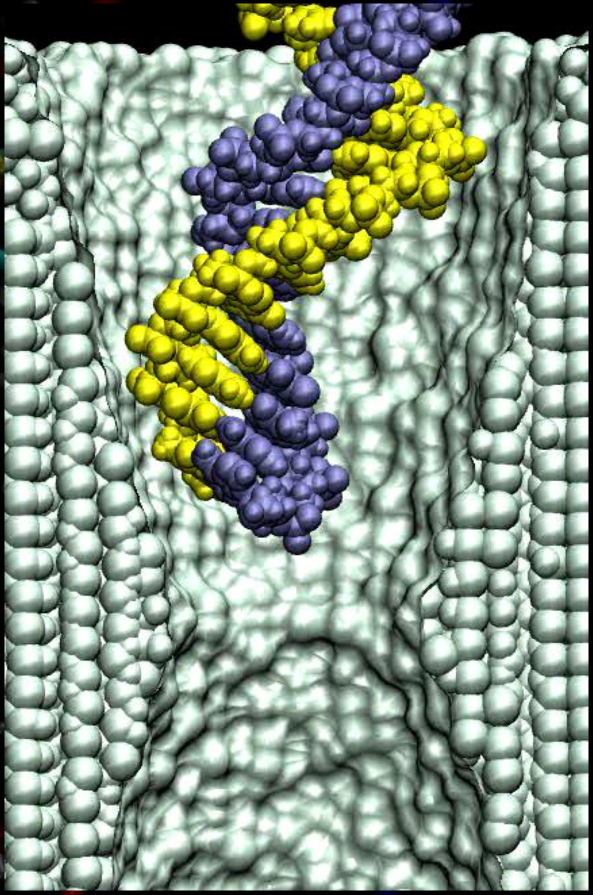


* In the real world, this could eventually mean that most chemical experiments are conducted inside the silicon of chips instead of the glassware of laboratories. Turn off that Bunsen burner; it will not be wanted in ten years.

A Different Type of Simulation

- Many Physically-Based Simulations model easily observable real world phenomena.

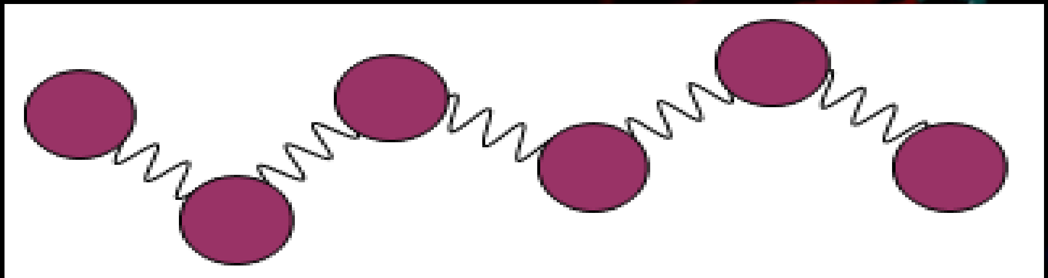
- Molecular Dynamics Simulations model things too small for us to observe directly.



Molecular dynamics (MD)

MD is a form of computer simulation in which atoms and molecules are allowed to interact for a period of time by approximations of known physics, giving a view of the motion of the particles.

In molecular dynamics a molecule is described as a series of charged points (atoms) linked by springs (bonds).

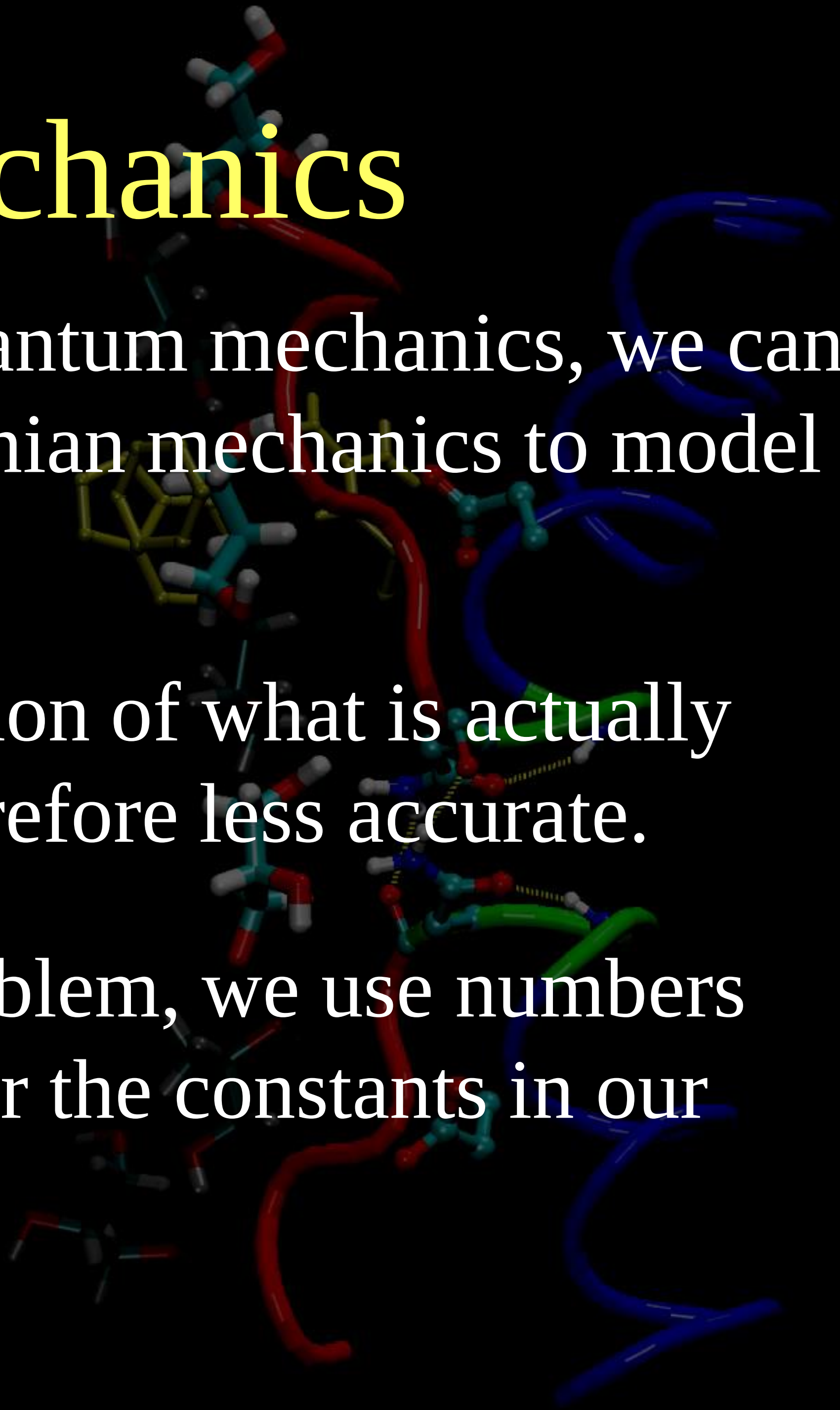


Richard Feynman once said that

"If we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that all things are made of atoms, and that everything that living things do can be understood in terms of the jiggling's (هزهزة) and wiggling's (تلوي) of atoms."

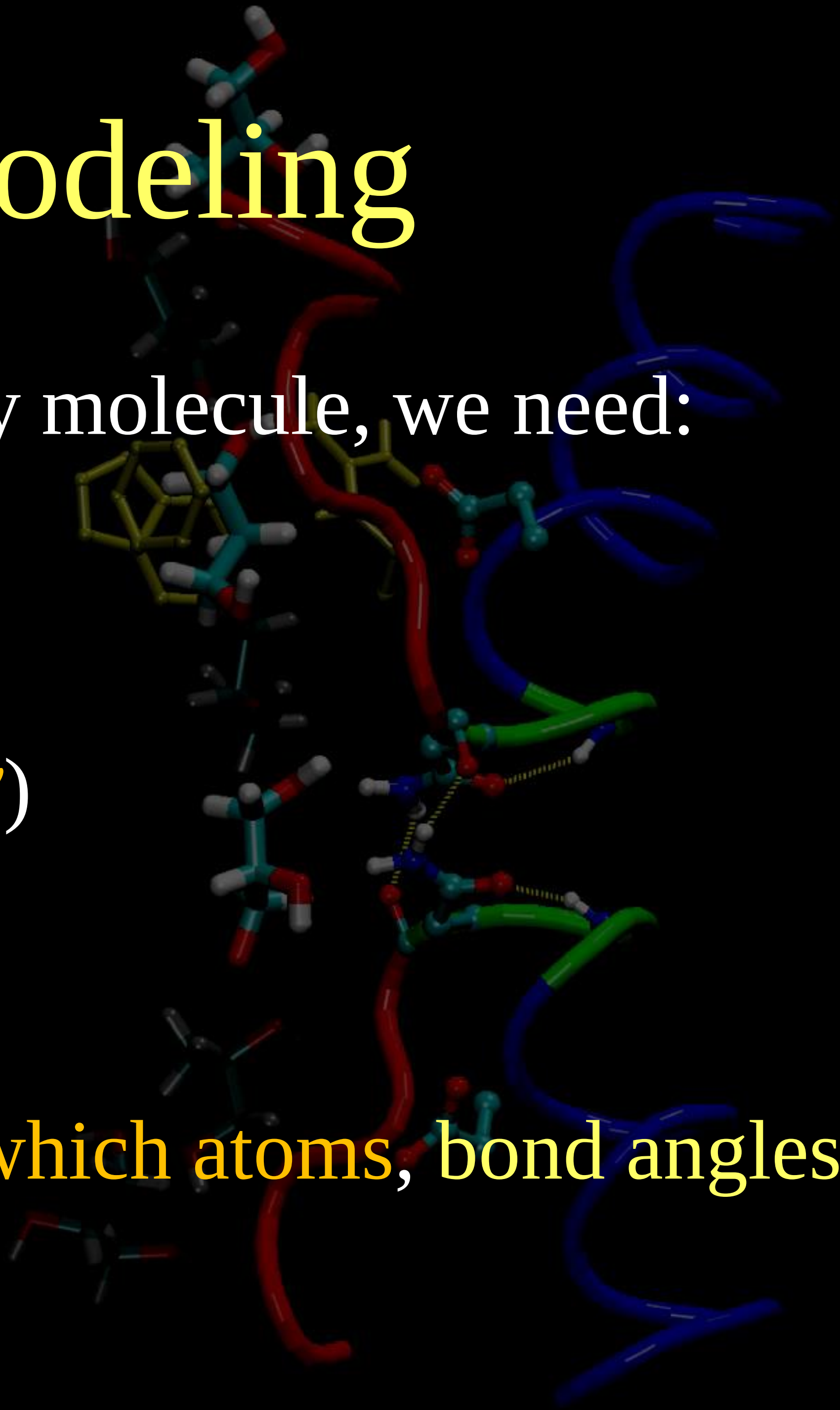
Richard Phillips Feynman (1918–1988)

Classical Mechanics



- Instead of using Quantum mechanics, we can use classical Newtonian mechanics to model our system.
- This is a simplification of what is actually going on, and is therefore less accurate.
- To alleviate this problem, we use numbers derived from QM for the constants in our classical equations.

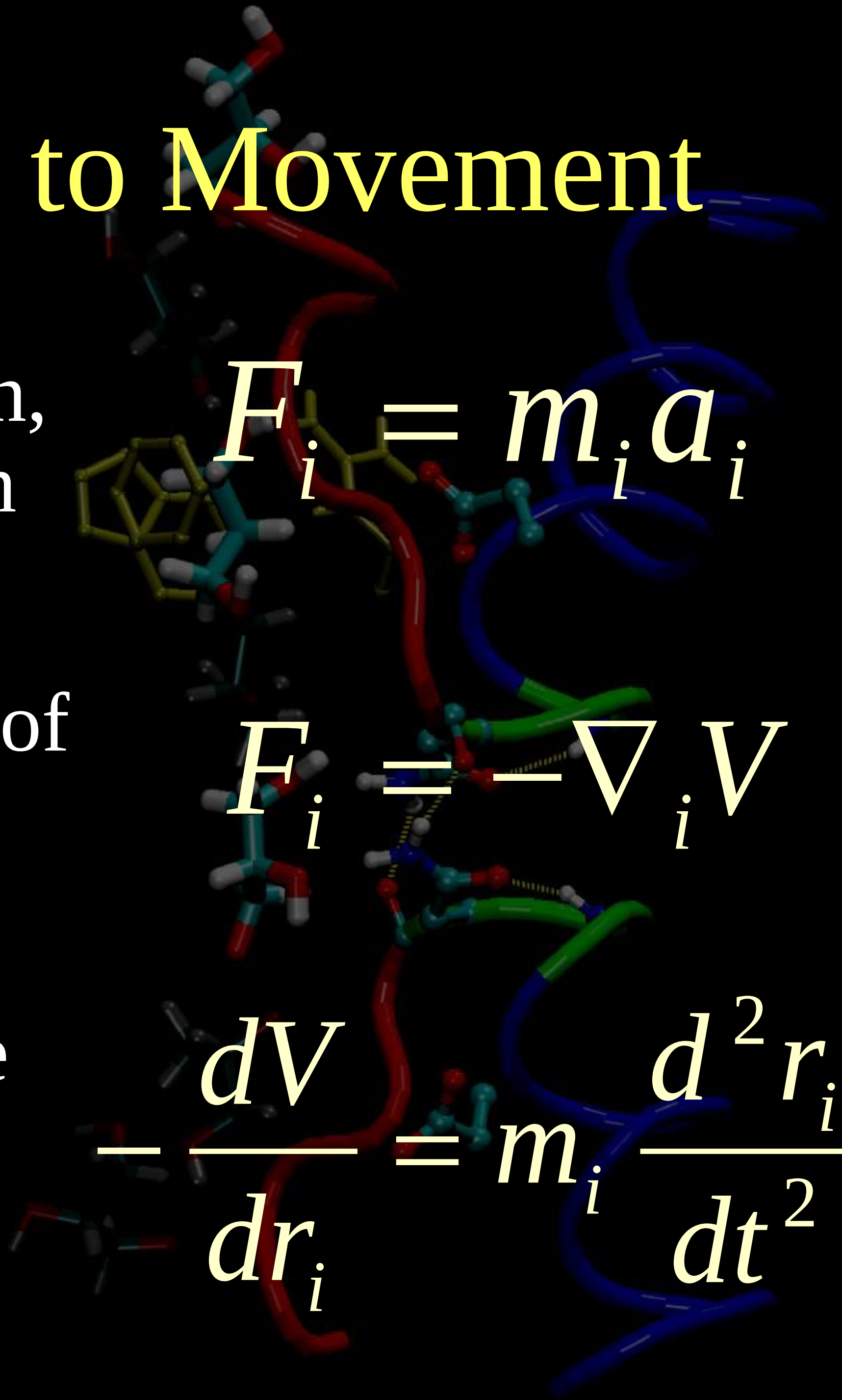
Molecular Modeling



For each atom in every molecule, we need:

- Position (r)
- Momentum ($m + v$)
- Charge (q)
- Bond information (which atoms, bond angles, etc.)

From Potential to Movement



To run the simulation, we need the force on each particle.

$$F_i = m_i a_i$$

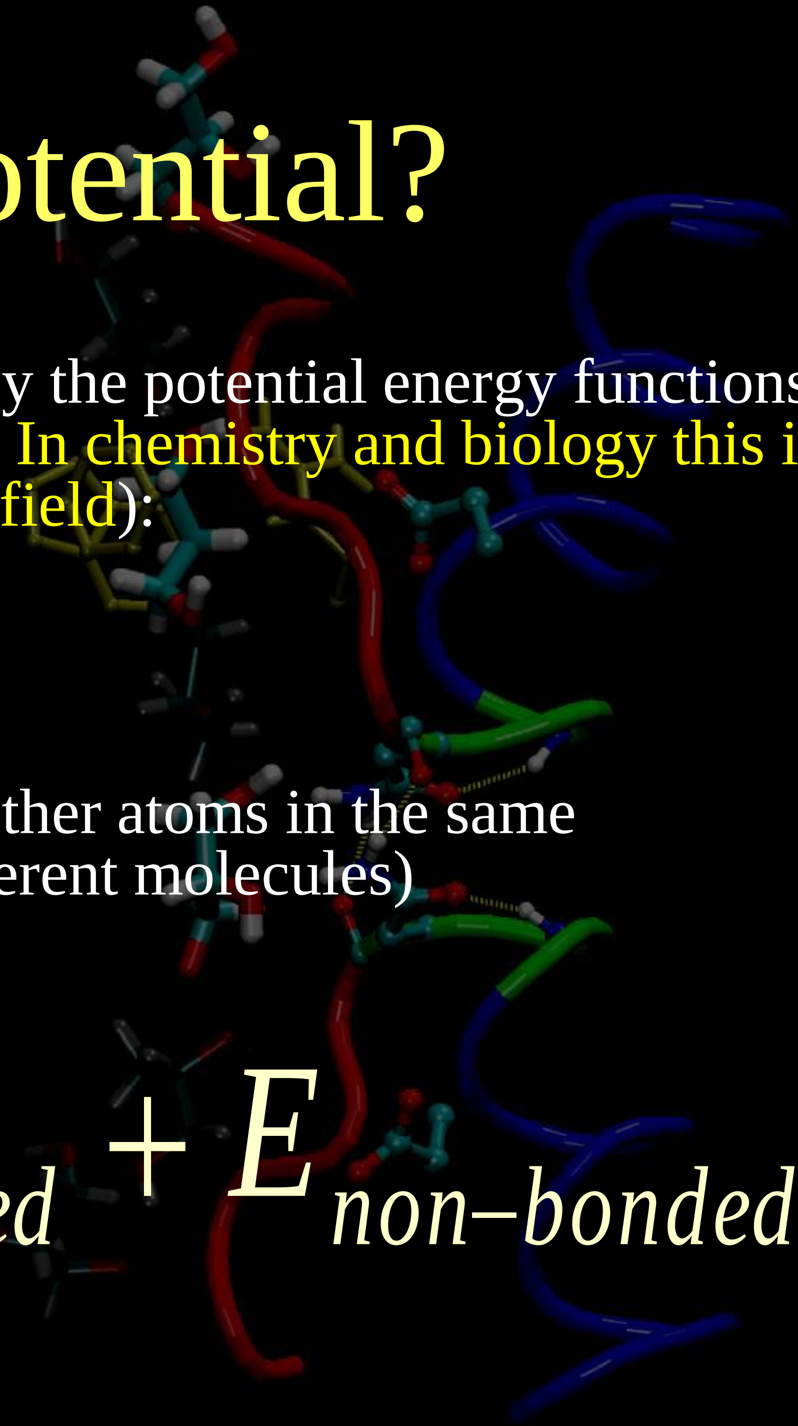
We use the gradient of the potential energy function.

$$F_i = -\nabla_i V$$

Now we can find the acceleration.

$$-\frac{dV}{dr_i} = m_i \frac{d^2 r_i}{dt^2}$$

What is the Potential?

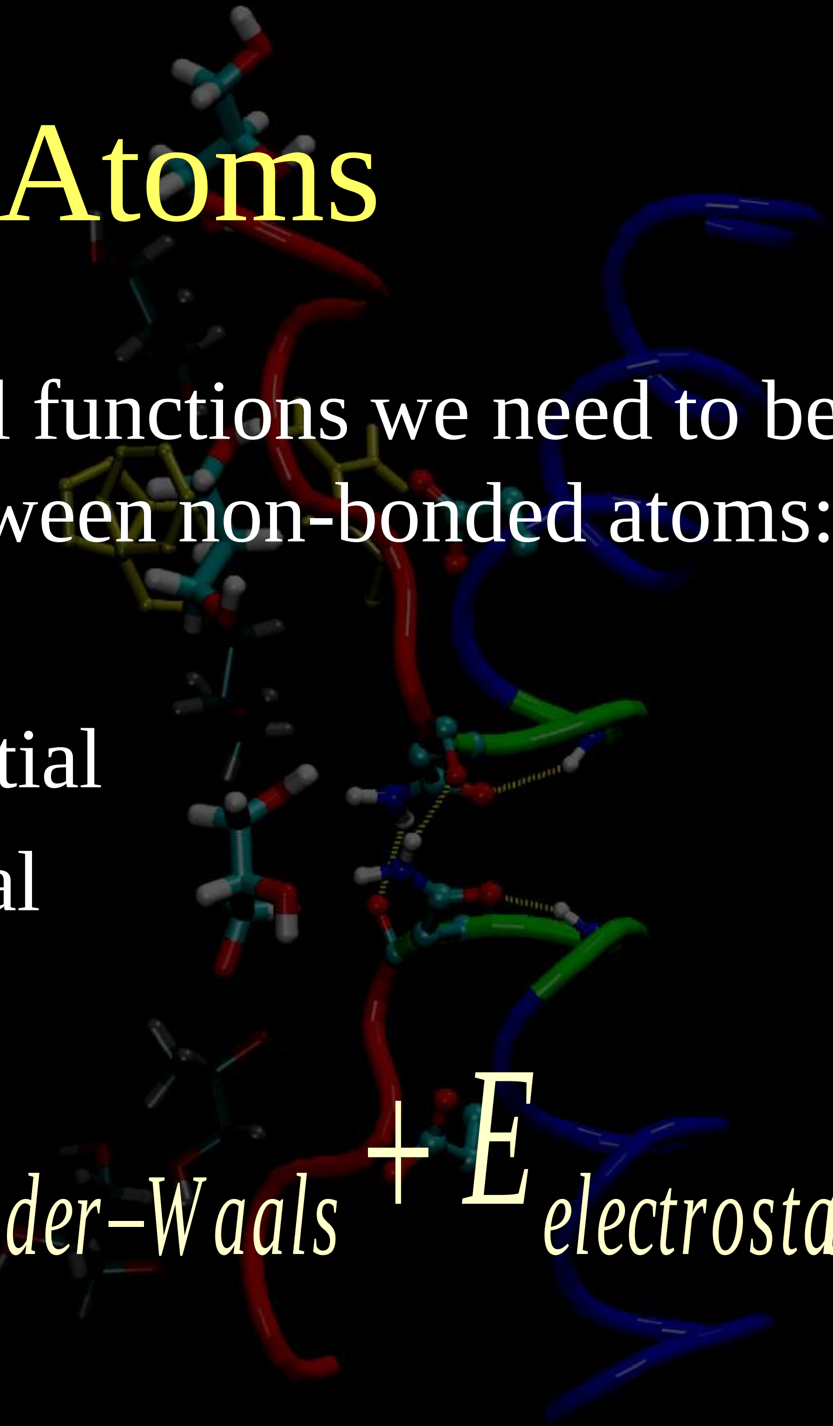


A single atom will be affected by the potential energy functions of every atom in the system (In chemistry and biology this is usually referred to as a force field):

- Bonded Neighbors
- Non-Bonded Atoms (either other atoms in the same molecule, or atoms from different molecules)

$$V(R) = E_{bonded} + E_{non-bonded}$$

Non-Bonded Atoms

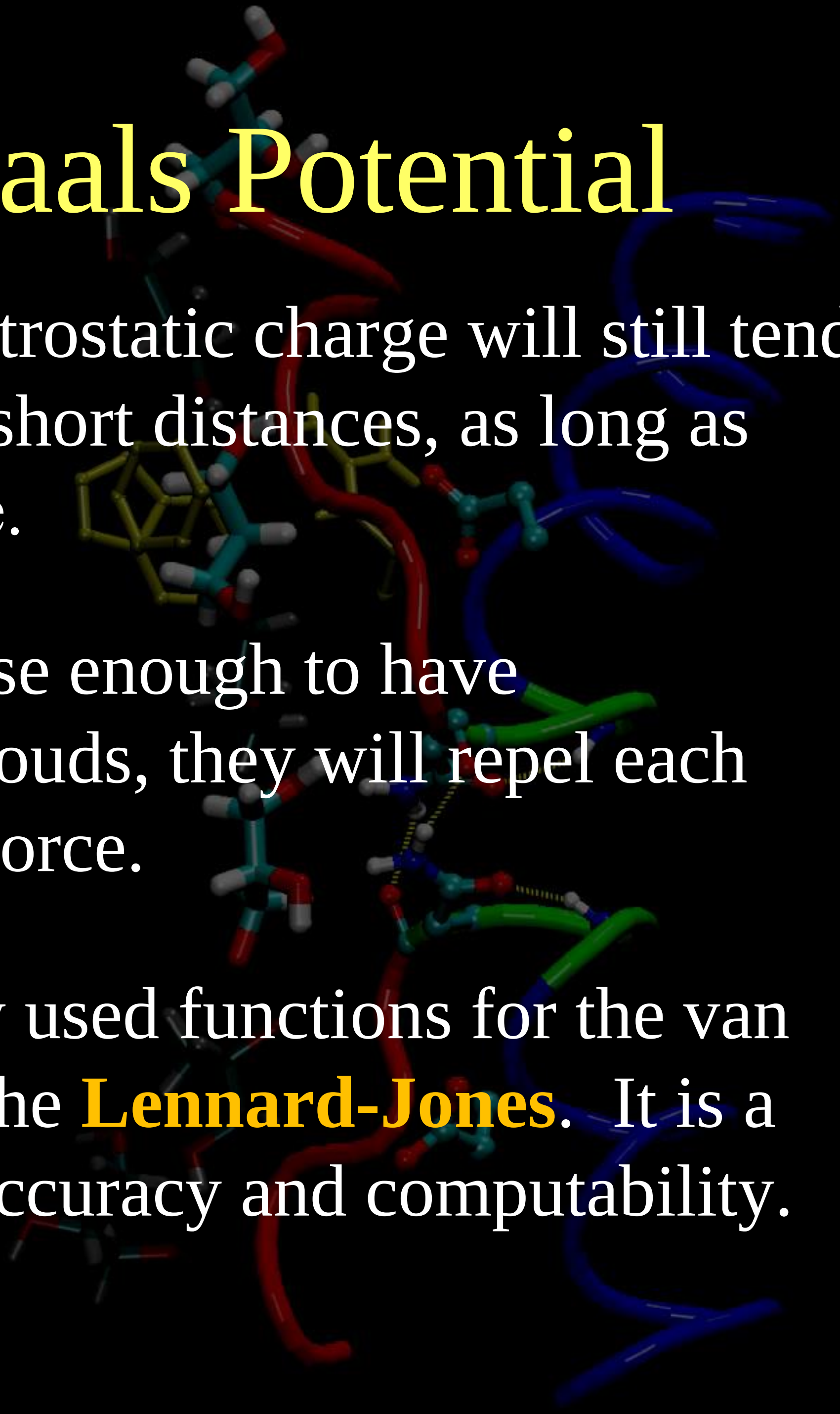


There are two potential functions we need to be concerned about between non-bonded atoms:

- van der Waals Potential
- Electrostatic Potential

$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}$$

The van der Waals Potential



- Atoms with no net electrostatic charge will still tend to attract each other at short distances, as long as they don’t get too close.
- Once the atoms are close enough to have overlapping electron clouds, they will repel each other with astounding force.
- One of the most widely used functions for the van der Waals potential is the **Lennard-Jones**. It is a compromise between accuracy and computability.

The van der Waals Potential

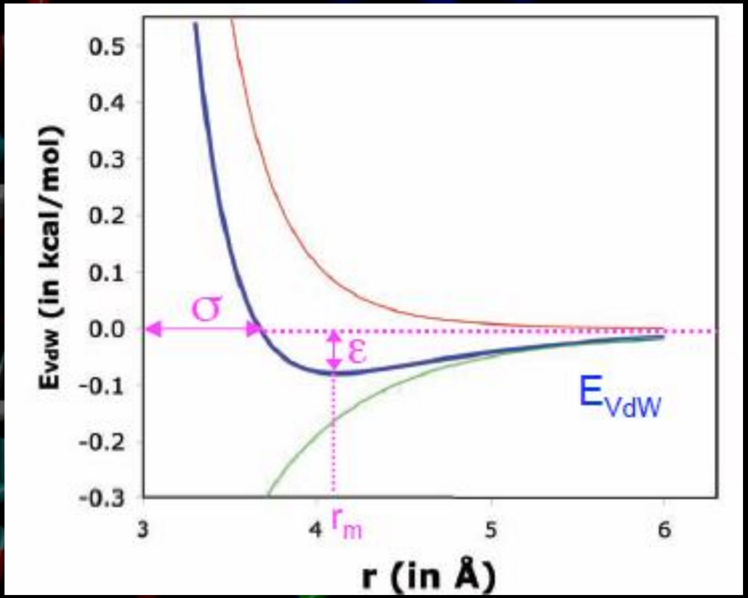
Lennard -Jones potential

Repulsive :
Pauli exclusion principle

$$\propto \frac{1}{r^{12}}$$

Attractive:
induced dipole / induced dipole

$$\propto -\frac{1}{r^{6}}$$



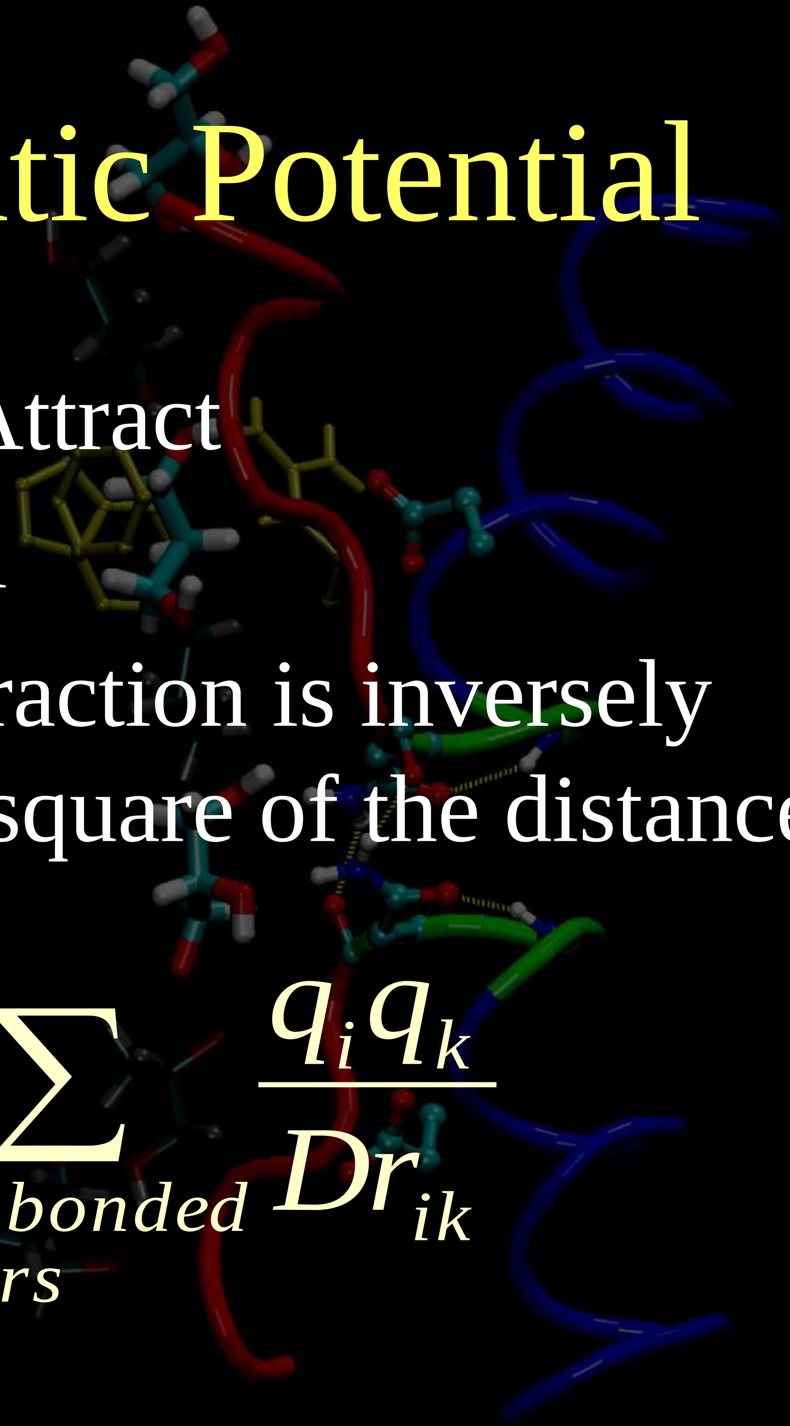
$$E_{VdW} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \varepsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right]$$

σ : collision parameter

ε : well depth

r_m : distance at min $\quad r_m = 2^{1/6}\sigma$

The Electrostatic Potential

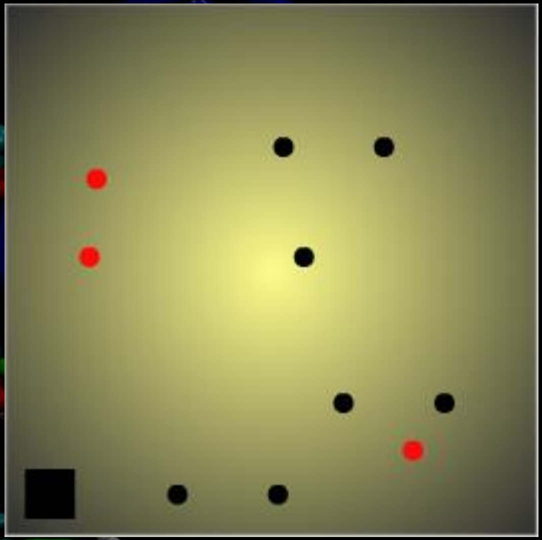


- Opposite Charges Attract
- Like Charges Repel
- The force of the attraction is inversely proportional to the square of the distance

$$E_{electrostatic} = \sum_{\substack{nonbonded\\pairs}} \frac{q_i q_k}{D r_{ik}}$$

The Non-Bonded Potential

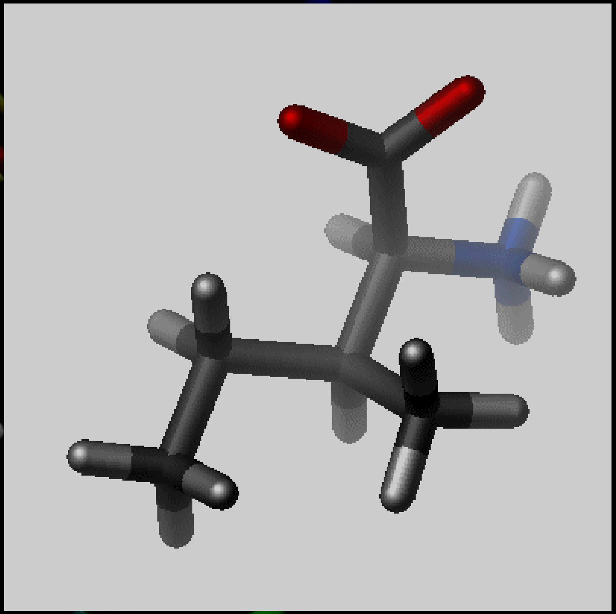
Combine the Lennard-Jones and Electrostatic Potentials



$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}$$

Bonded Atoms

There are three types of interaction between bonded atoms:



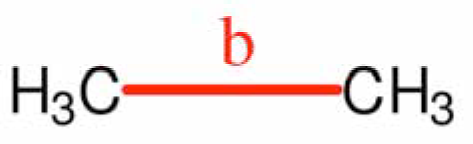
- Stretching along the bond
- Bending between bonds
- Rotating around bonds

$$E_{bonded} = E_{bond-stretch} + E_{angle-bend} + E_{rotate-along-bond}$$

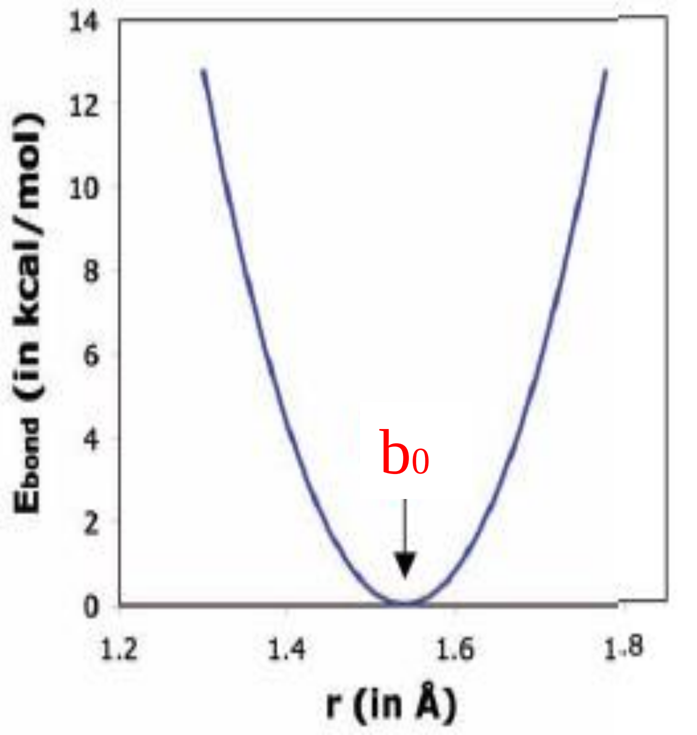
Bond Length Potentials

Both the spring constant and the ideal bond length are dependent on the atoms involved.

$$E_{bond-stretch} = \sum_{1,2\,pairs} K_b (b - b_0)^2$$



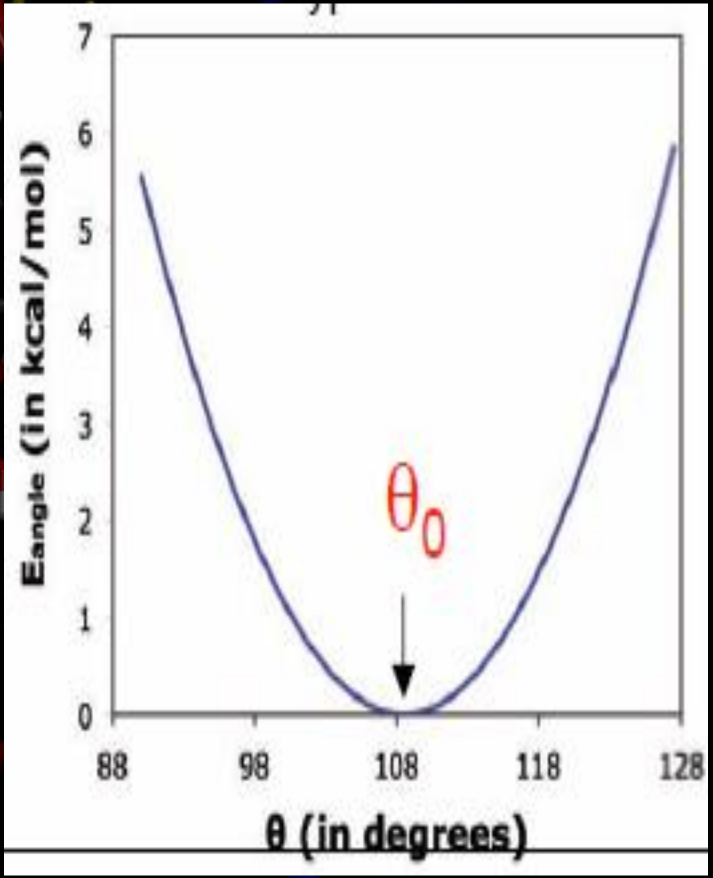
H_3C-CH_3

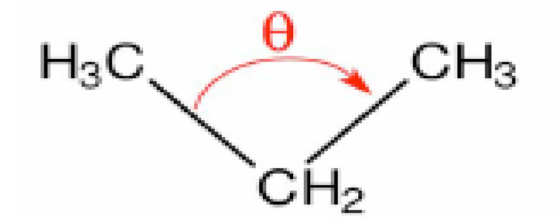


Bond Angle Potentials

The spring constant and the ideal angle are also dependent on the chemical type of the atoms.

$$E_{bond-bend} = \sum_{angles} K_\theta (\theta - \theta_0)^2$$

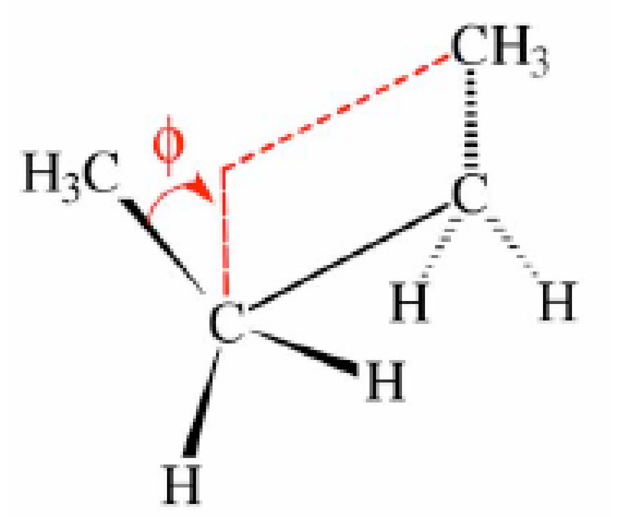


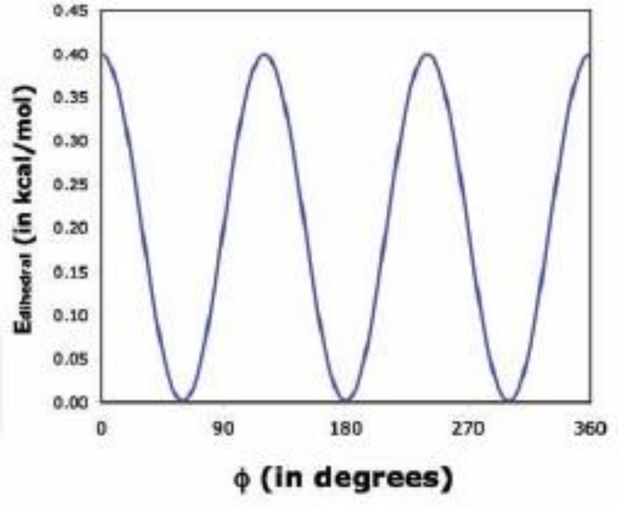


Torsional Potentials

- Described by a dihedral angle and coefficient of symmetry ($n=1,2,3$), around the middle bond.

$$E_{rotate-along-bond} = \sum_{1,4\,pairs} K_{\phi}(1-\cos(n\phi))$$

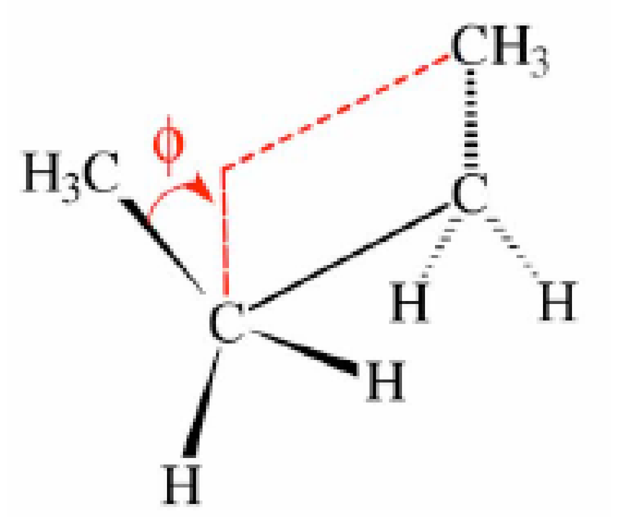


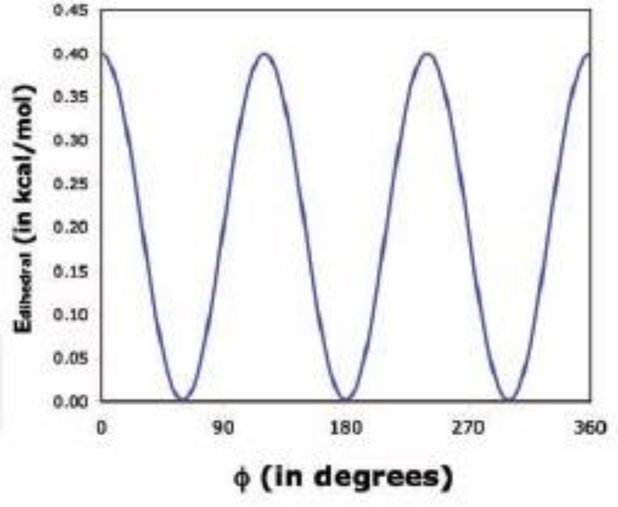


Torsional Potentials

Described by a dihedral angle and coefficient of symmetry (*n=1,2,3*), around the middle bond.

$$E_{rotate-along-bond} = \sum_{1,4\,pairs} K_{\phi}(1-\cos(n\phi))$$



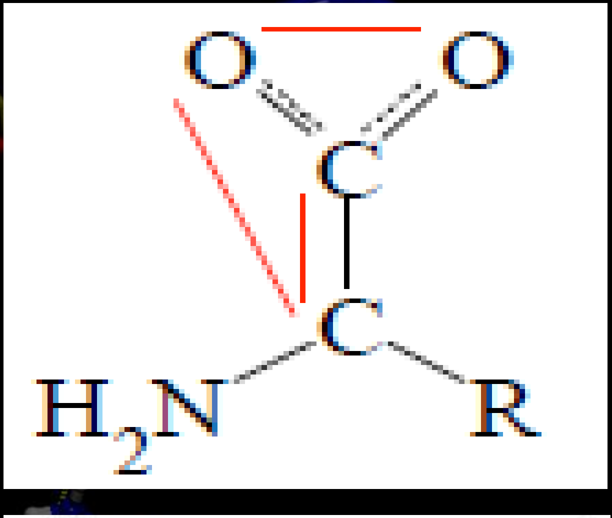


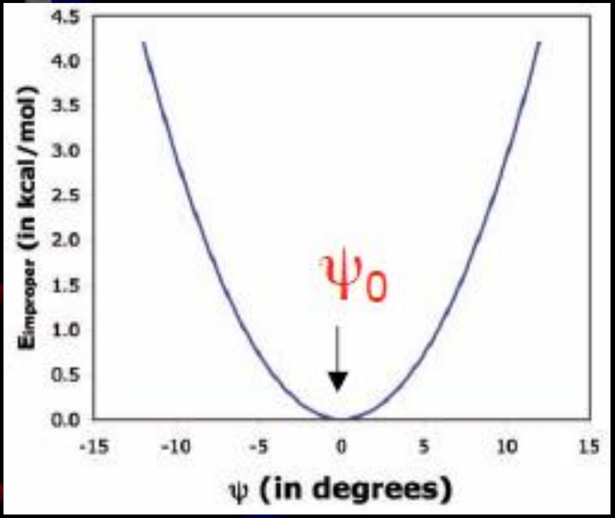
Torsional Potentials

Described by a

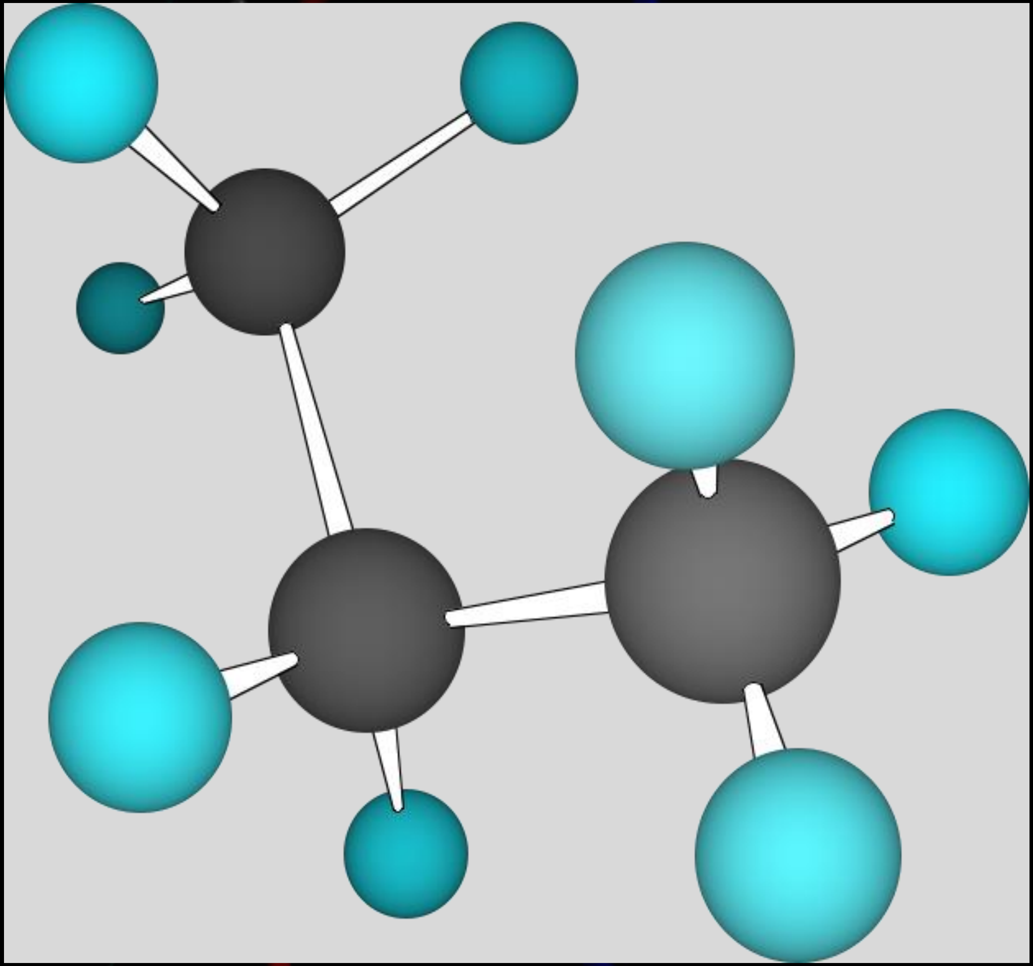
- Improper angles around the middle bond.

$$E_{\text{improper}} = K_{\phi}(\psi - \psi_0)^2$$





How many types of bonded and non-bonded ineractions?



46 Bonded

10 bonds

18 angle terms

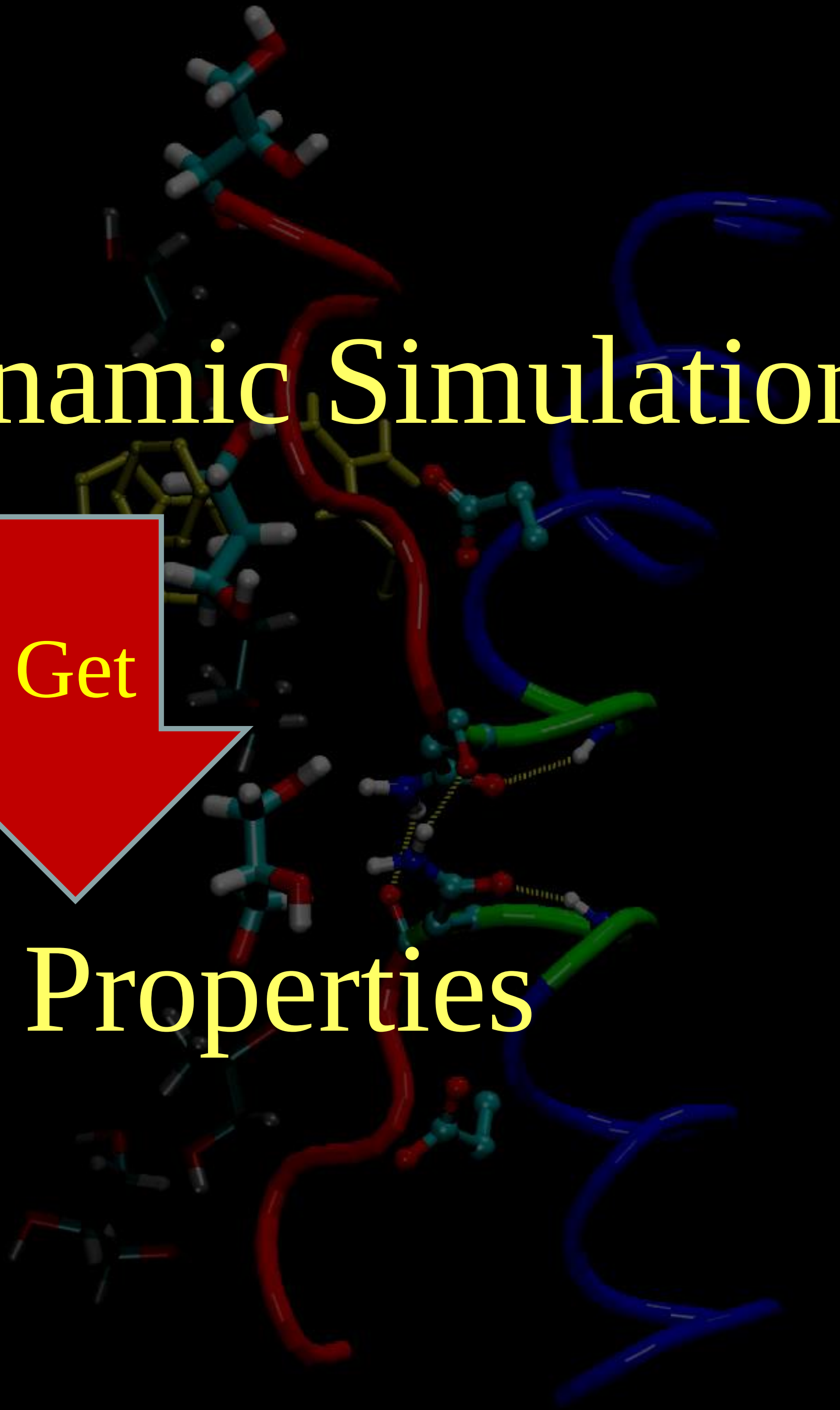
18 torsional terms

45 Non-bonded

H-H 28

C-H 16

C-C 1



Molecular Dynamic Simulation

Get

System Properties

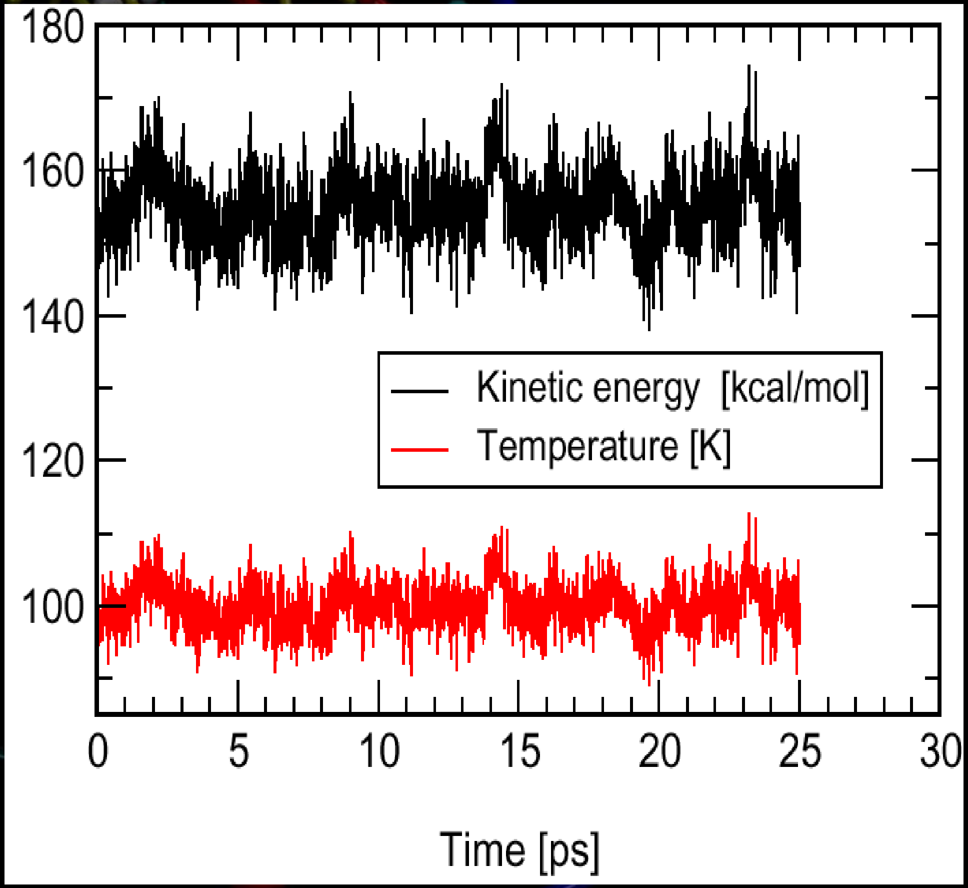
System Properties

- Thermodynamic Properties
  - Kinetic Energy:

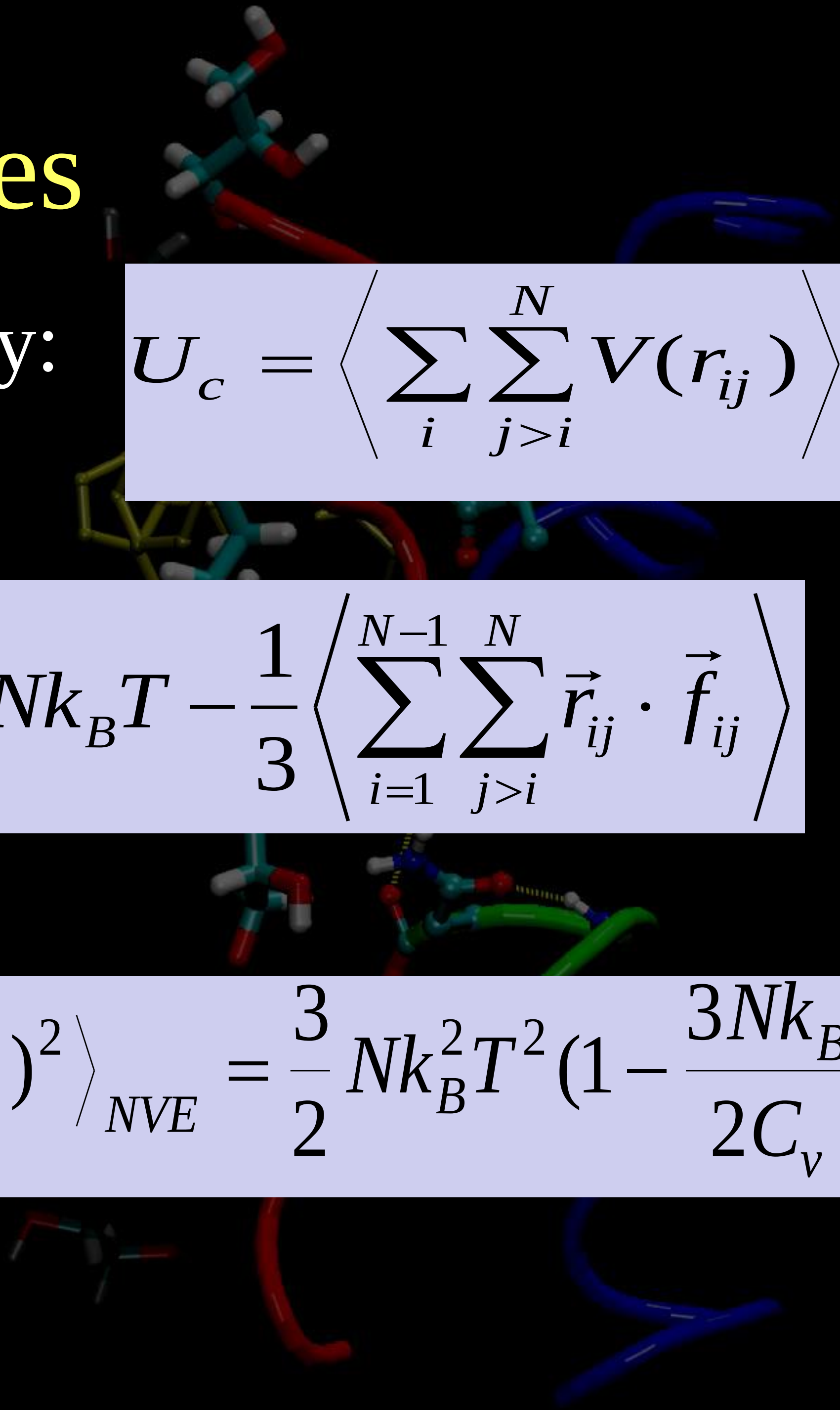
$$\langle K.E.\rangle = \left\langle \frac{1}{2}\sum_{i}^{N} m_i v_i^2 \right\rangle$$

  - Temperature

$$T = \frac{2}{3Nk_B}\langle K.E.\rangle$$



System Properties



- Configuration Energy:

$$U_c = \left\langle \sum_{i} \sum_{j>i}^{N} V(r_{ij}) \right\rangle$$

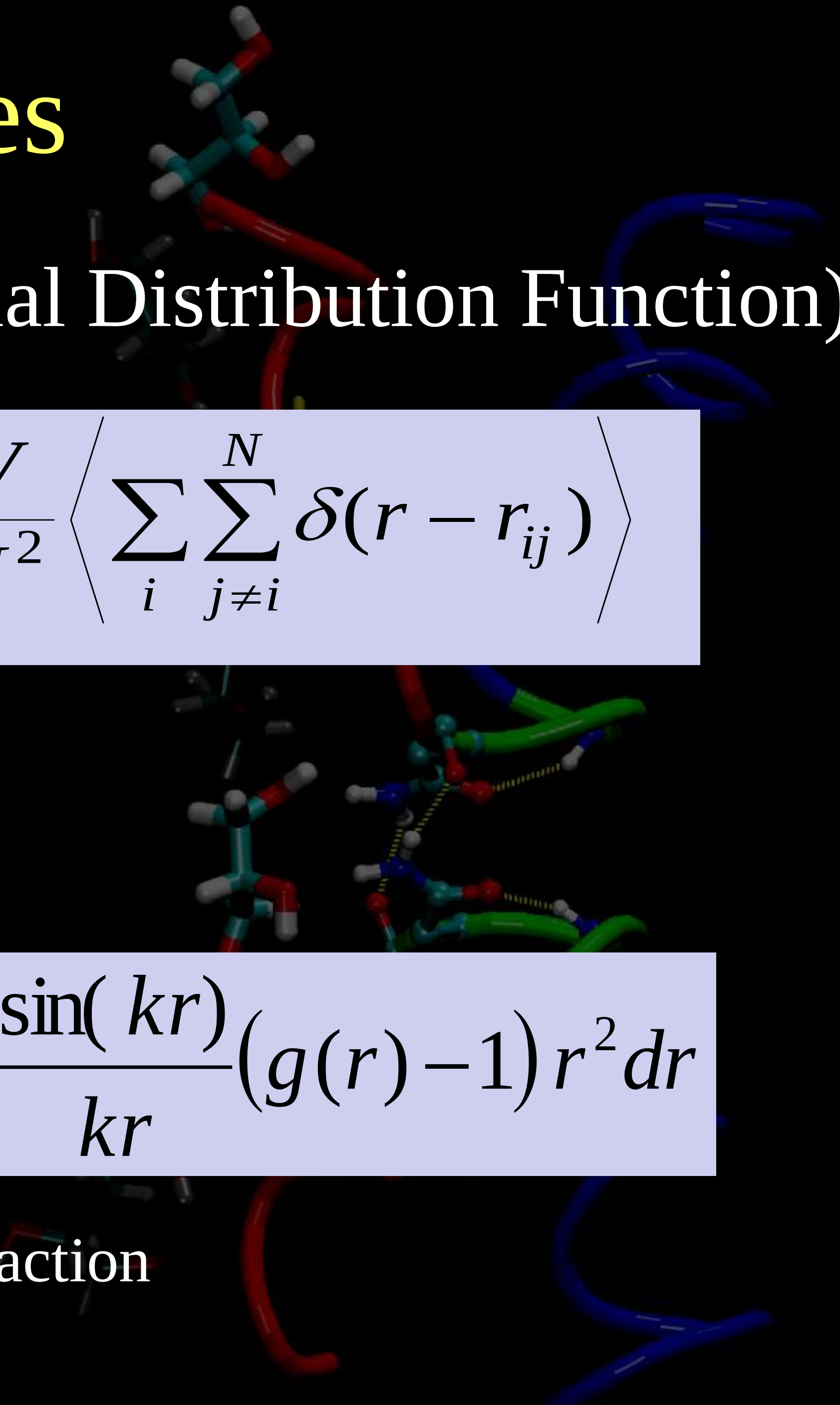
- Pressure:

$$PV = Nk_B T - \frac{1}{3}\left\langle \sum_{i=1}^{N-1} \sum_{j>i}^{N} \vec{r}_{ij} \cdot \vec{f}_{ij} \right\rangle$$

- Specific Heat:

$$\left\langle \delta(U_c)^2 \right\rangle_{NVE} = \frac{3}{2} N k_B^2 T^2 \left(1 - \frac{3Nk_B}{2C_v}\right)$$

System Properties



- Pair correlation (Radial Distribution Function):

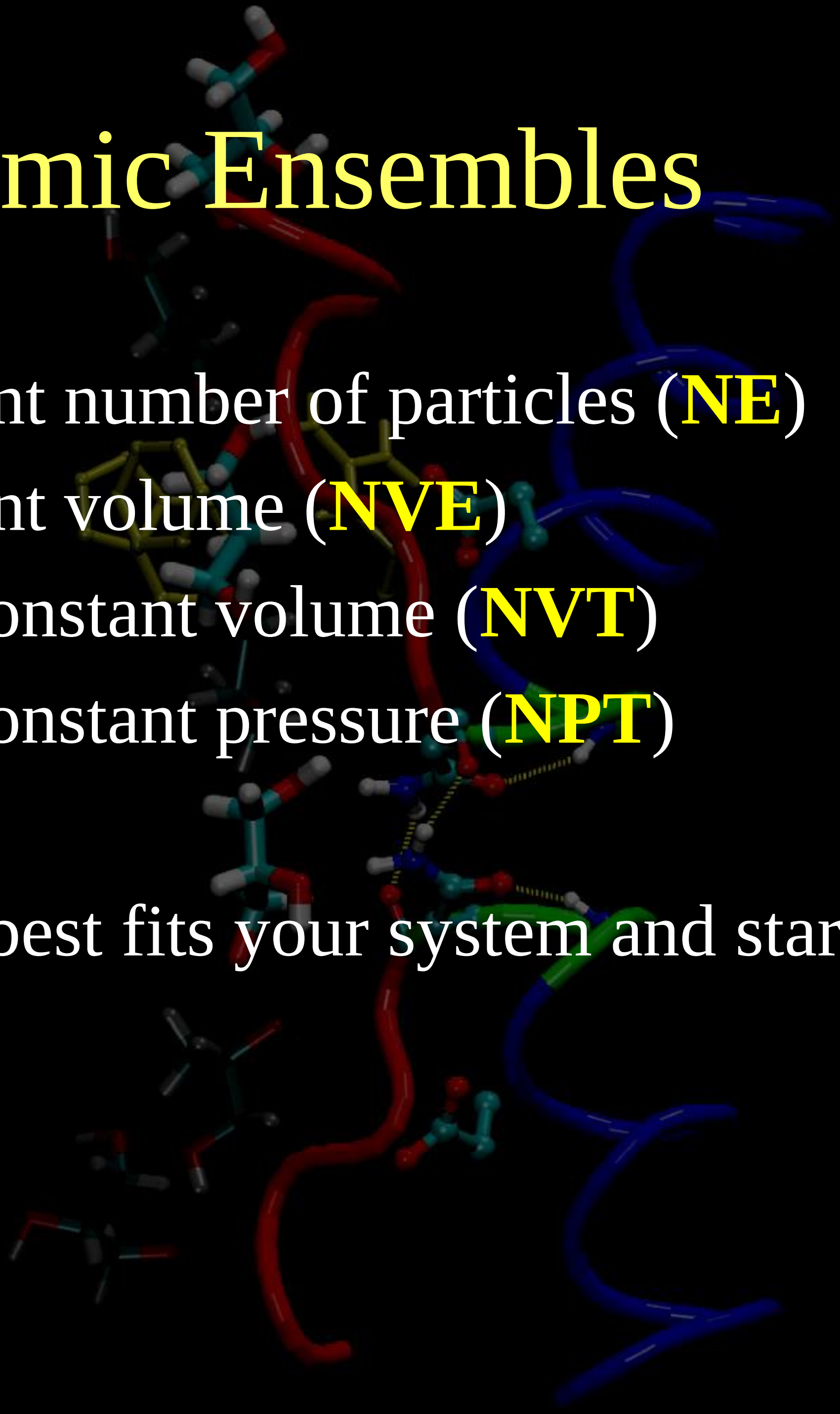
$$g(r) = \frac{\langle n(r) \rangle}{4\pi \rho r^2 \Delta r} = \frac{V}{N^2} \left\langle \sum_{i} \sum_{j \neq i}^{N} \delta(r - r_{ij}) \right\rangle$$

- Structure factor

$$S(k) = 1 + 4\pi\rho \int_0^\infty \frac{\sin(kr)}{kr} \left(g(r) - 1\right) r^2 dr$$

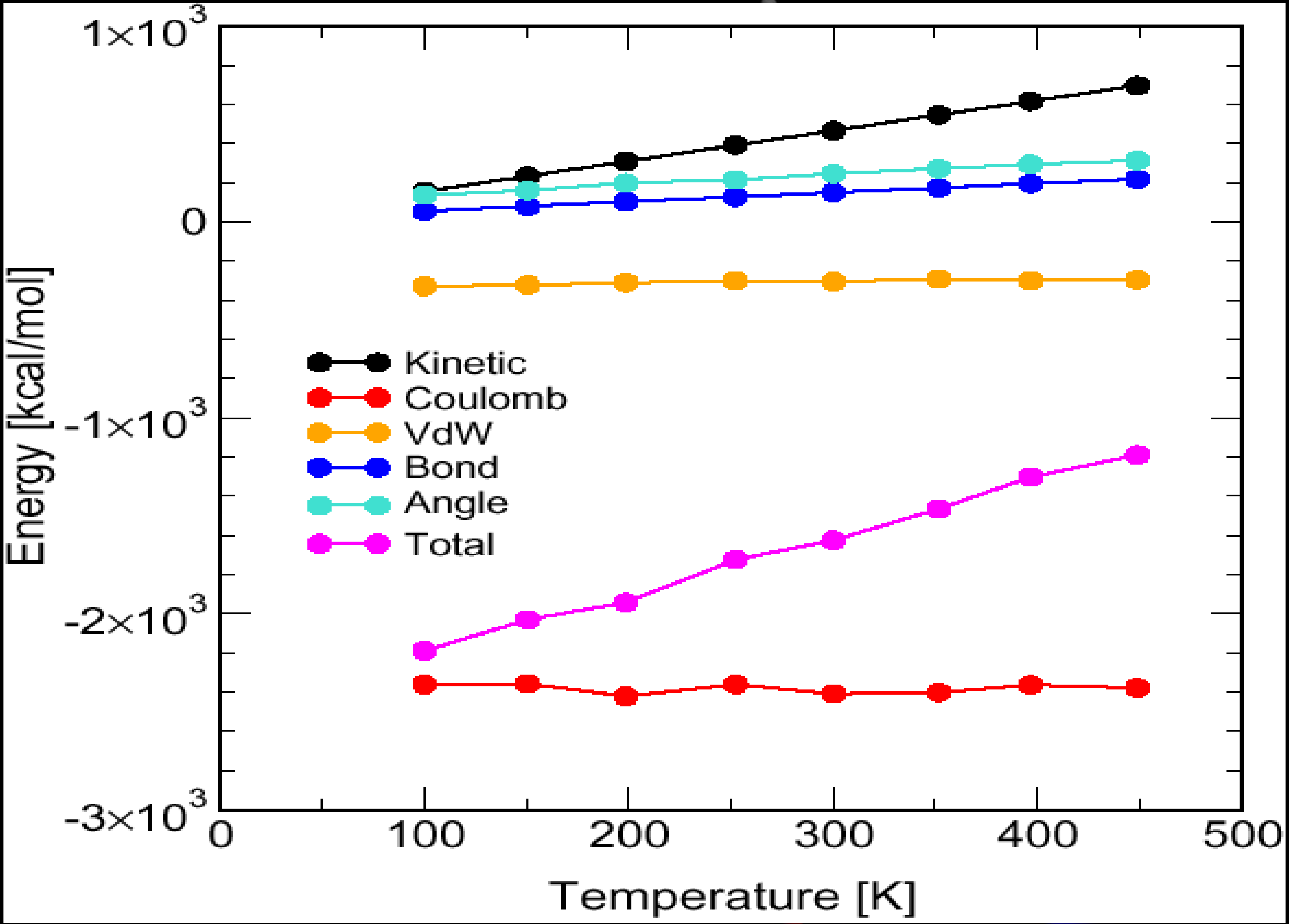
* S(k) available from x-ray diffraction

Molecular Dynamic Ensembles



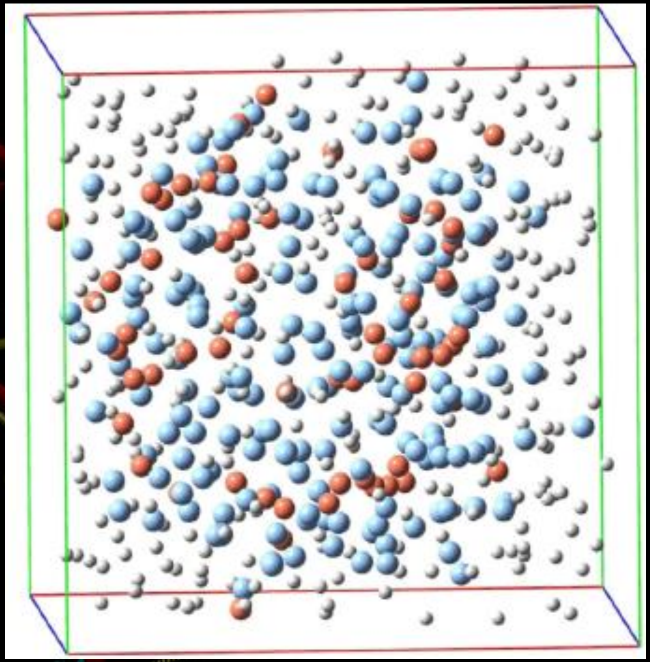
- Constant energy, constant number of particles (**NE**)
- Constant energy, constant volume (**NVE**)
- Constant temperature, constant volume (**NVT**)
- Constant temperature, constant pressure (**NPT**)

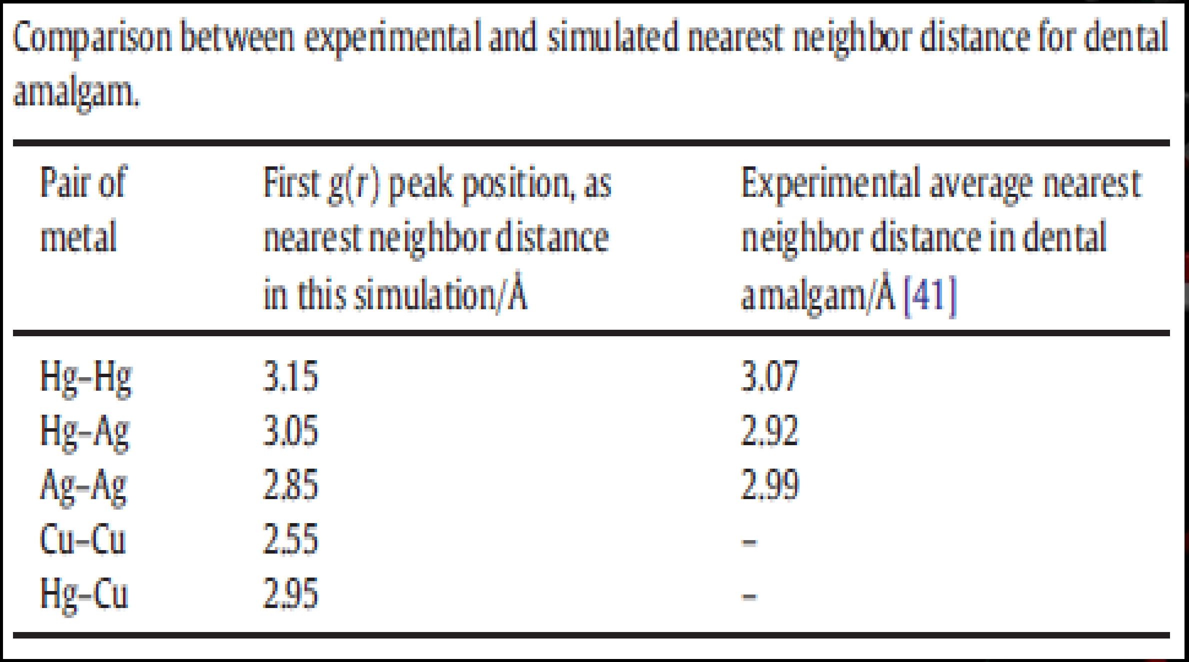
Choose the ensemble that best fits your system and start the simulations.


1×10³
0
-1×10³
-2×10³
-3×10³
0
100
200
300
400
500
Energy [kcal/mol]
Temperature [K]
Kinetic
Coulomb
VdW
Bond
Angle
Total

Silver amalgam filler

- silver amalgam is popularly used as a direct restorative filler material available due to its high strength, durability, and low cost as well as long-term satisfactory clinical performance





Comparison between experimental and simulated nearest neighbor distance for dental amalgam.

Pair of metal	First $g(r)$ peak position, as nearest neighbor distance in this simulation/Å	Experimental average nearest neighbor distance in dental amalgam/Å [41]
Hg-Hg	3.15	3.07
Hg-Ag	3.05	2.92
Ag-Ag	2.85	2.99
Cu-Cu	2.55	–
Hg-Cu	2.95	–

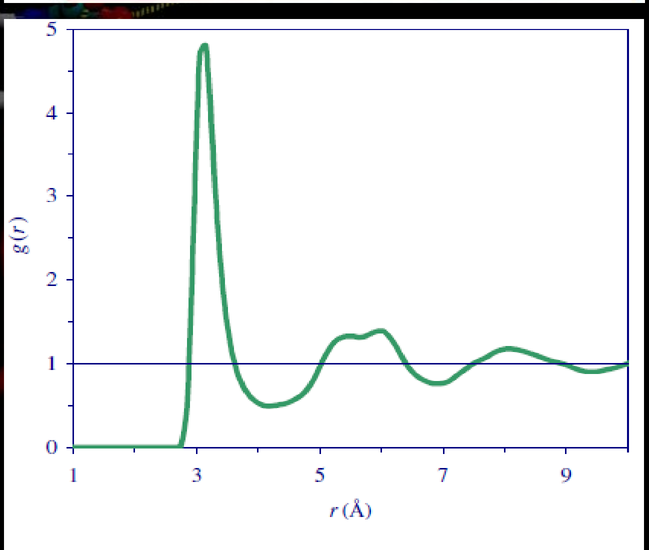
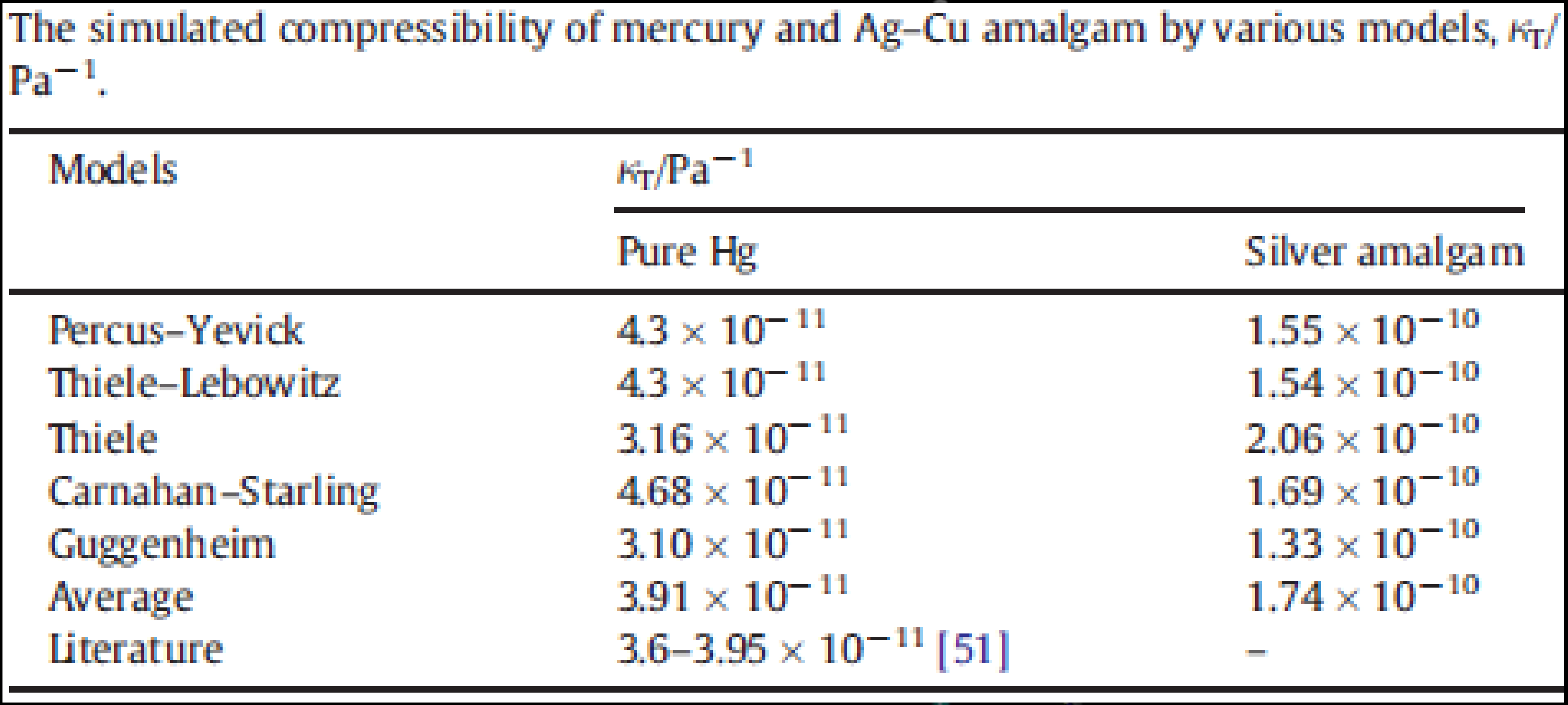


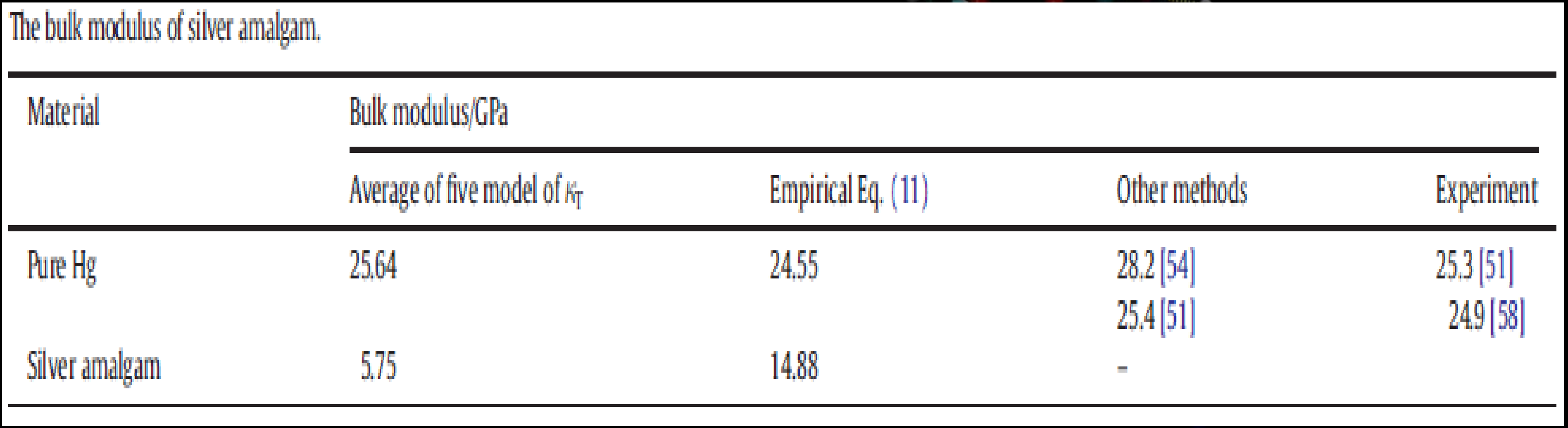
Fig. 5. Pair correlation function for Hg···Hg in the amalgam.

Journal of Molecular Liquids 211 (2015) 96–104



The simulated compressibility of mercury and Ag–Cu amalgam by various models, κ_T/Pa^{-1}.

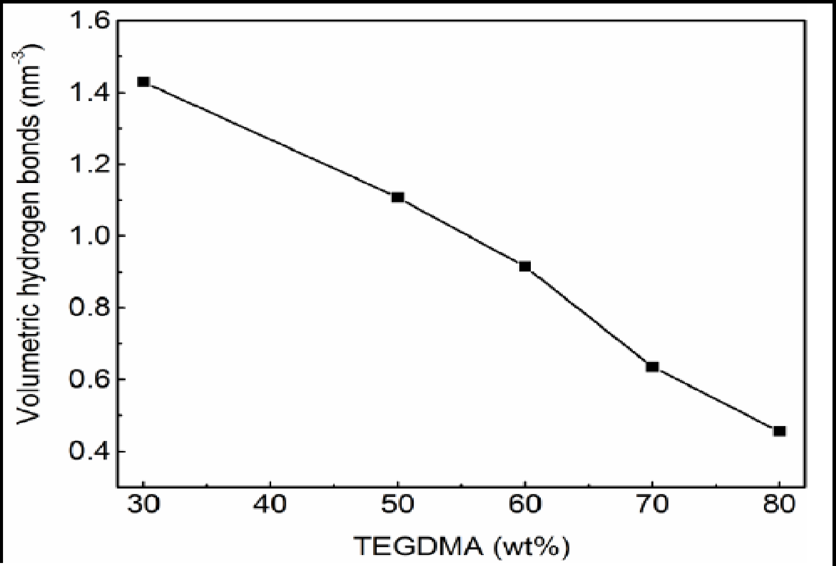
Models	κ_T/Pa^{-1}	
	Pure Hg	Silver amalgam
Percus–Yevick	4.3×10^{-11}	1.55×10^{-10}
Thiele–Lebowitz	4.3×10^{-11}	1.54×10^{-10}
Thiele	3.16×10^{-11}	2.06×10^{-10}
Carnahan–Starling	4.68×10^{-11}	1.69×10^{-10}
Guggenheim	3.10×10^{-11}	1.33×10^{-10}
Average	3.91×10^{-11}	1.74×10^{-10}
Literature	$3.6–3.95 \times 10^{-11}$ [51]	–

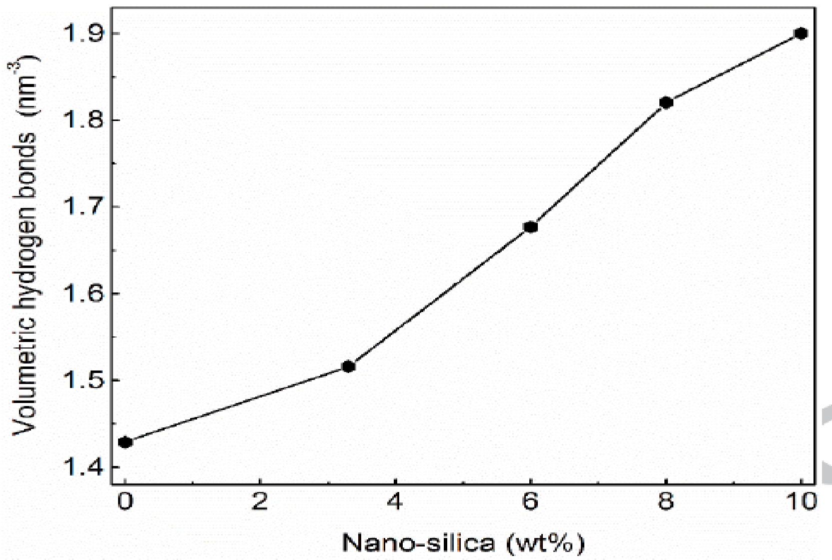


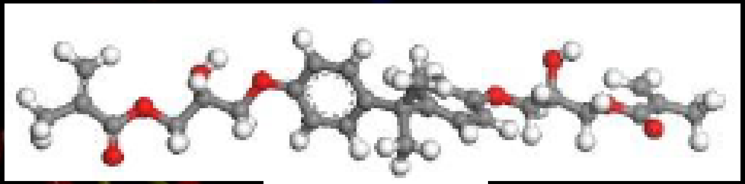
The bulk modulus of silver amalgam.

Material	Bulk modulus/GPa			
	Average of five model of κ_T	Empirical Eq. (11)	Other methods	Experiment
Pure Hg	25.64	24.55	28.2 [54] 25.4 [51]	25.3 [51] 24.9 [58]
Silver amalgam	5.75	14.88	-	

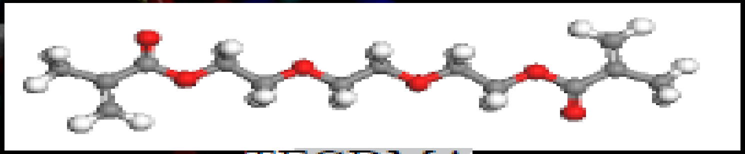
Silica Nanoparticle Reinforced Bis-GMA/TEGDMA Resin Composite



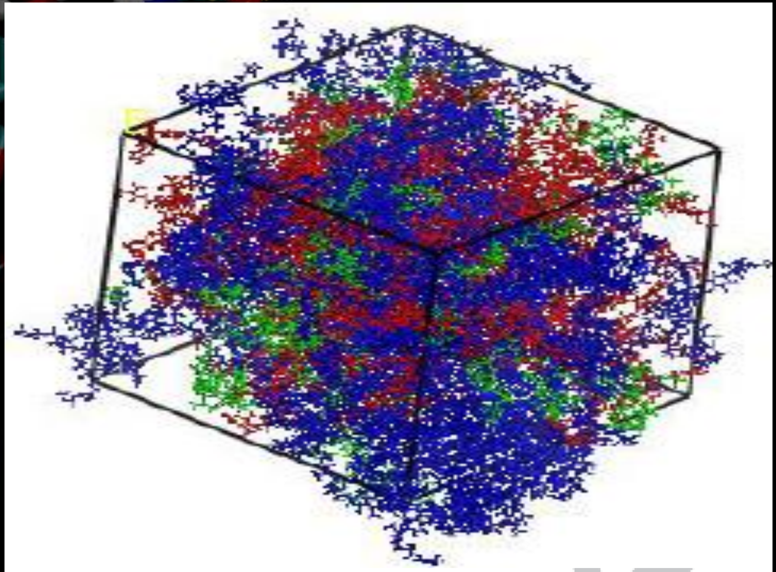




Bis-GMA



TEGDMA



Bis-GMA/TEGDMA 70/30 (w/w) resin blend

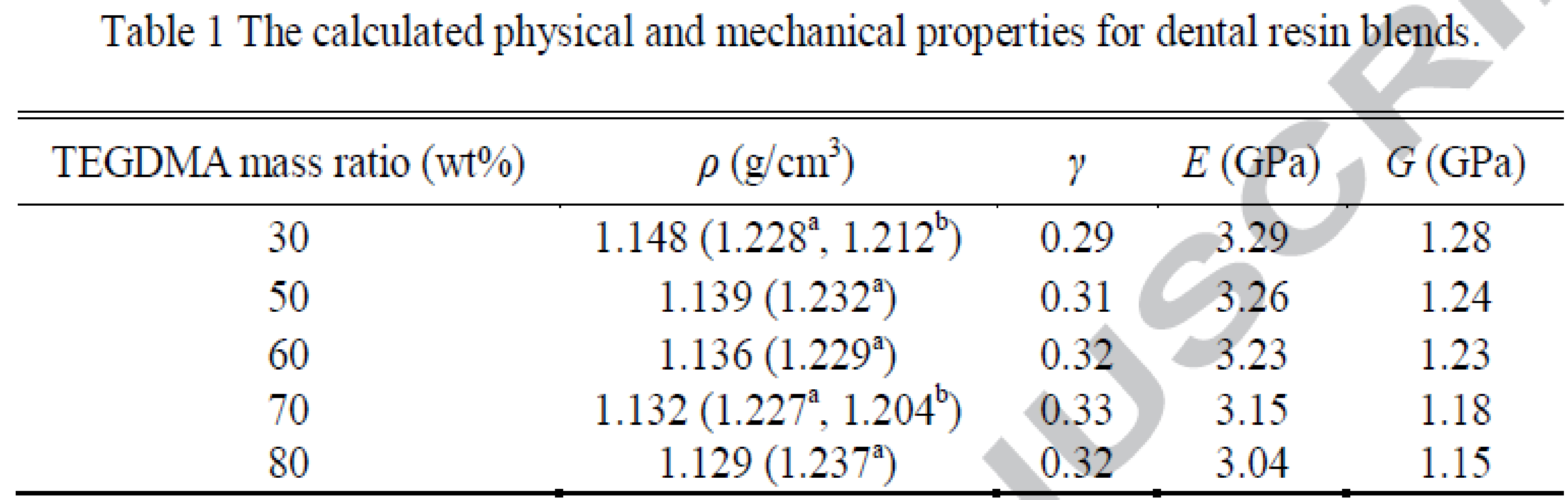


Table 1 The calculated physical and mechanical properties for dental resin blends.

TEGDMA mass ratio (wt%)	ρ (g/cm^3)	γ	E (GPa)	G (GPa)
30	1.148 (1.228^a, 1.212^b)	0.29	3.29	1.28
50	1.139 (1.232^a)	0.31	3.26	1.24
60	1.136 (1.229^a)	0.32	3.23	1.23
70	1.132 (1.227^a, 1.204^b)	0.33	3.15	1.18
80	1.129 (1.237^a)	0.32	3.04	1.15

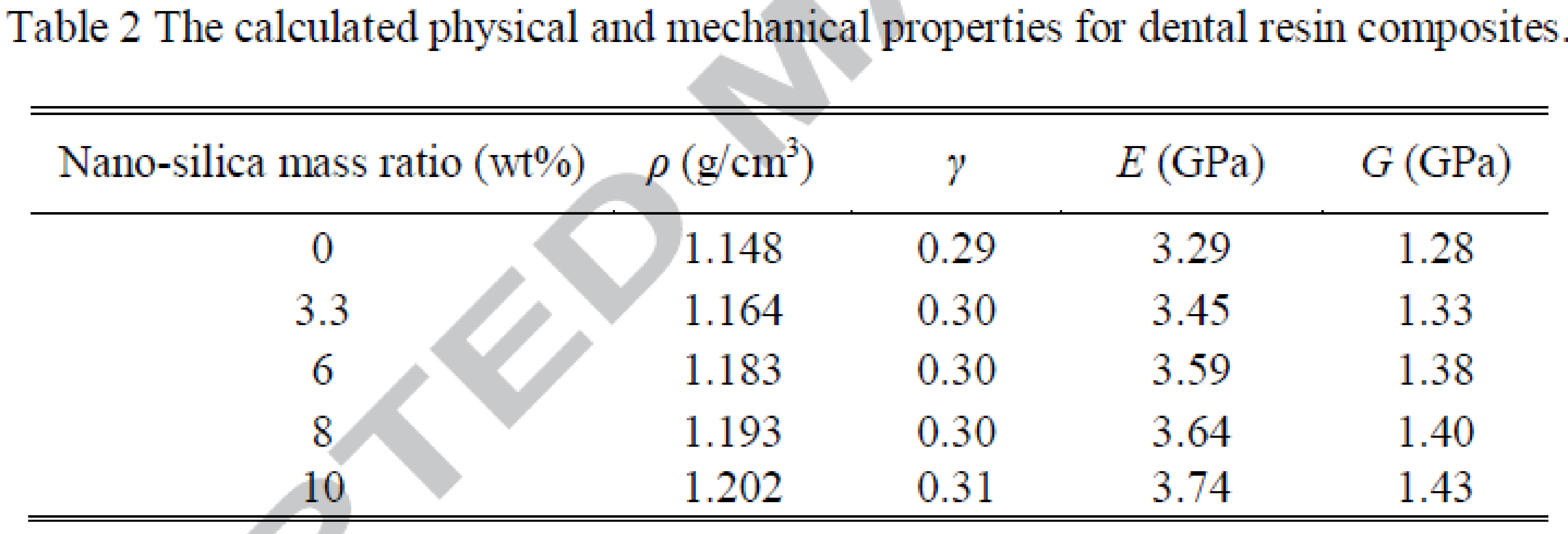


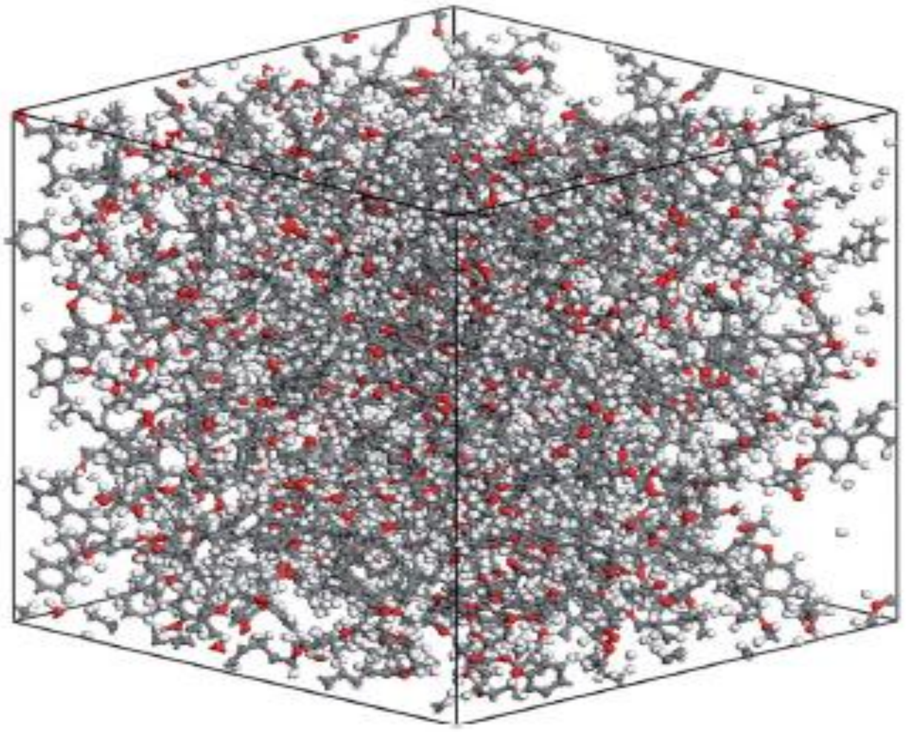
Table 2 The calculated physical and mechanical properties for dental resin composites.

Nano-silica mass ratio (wt%)	ρ (g/cm^3)	γ	E (GPa)	G (GPa)
0	1.148	0.29	3.29	1.28
3.3	1.164	0.30	3.45	1.33
6	1.183	0.30	3.59	1.38
8	1.193	0.30	3.64	1.40
10	1.202	0.31	3.74	1.43

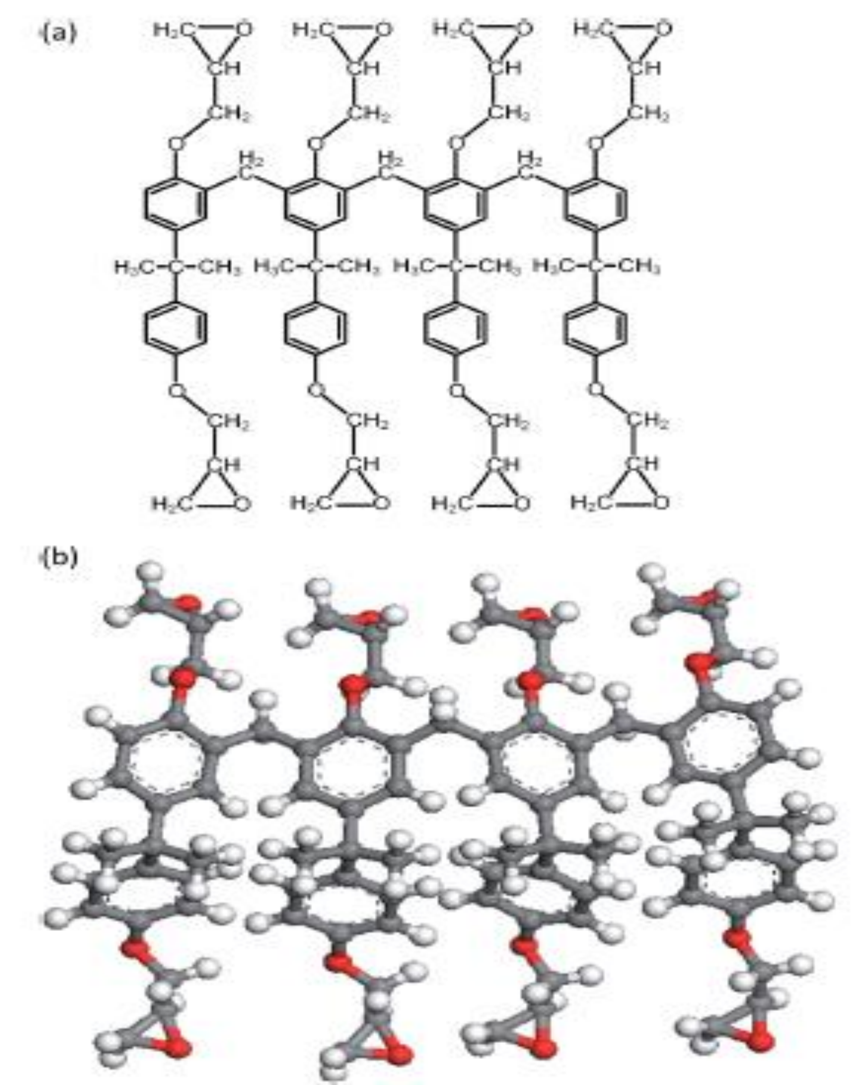
DOI: https://doi.org/10.1016/j.compstruct.2018.02.001

Crosslinking and Physical Properties of Epoxy-based Materials

SU-8 has become a favorable epoxy-based photoresist for the fabrication of high-aspect ratio and three-dimensional micro-electro-mechanical systems (MEMS).



Cross-linked structure of SU-8 photoresist.



DOI: 10.1039/c4ra04298k

RSC Adv., 2014, 4, 33074

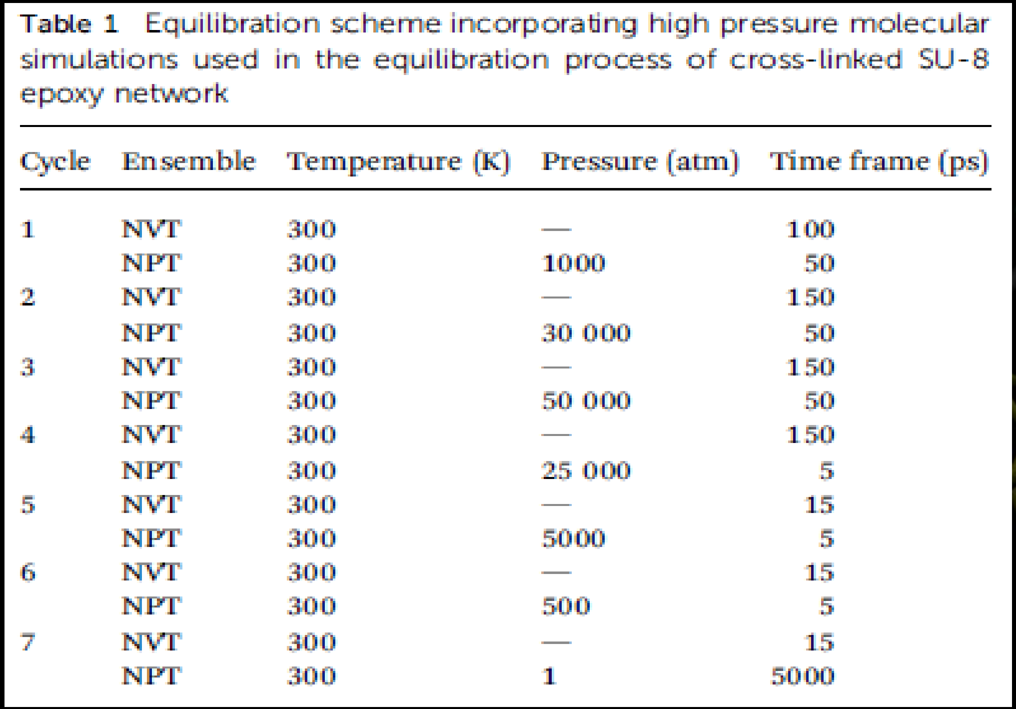
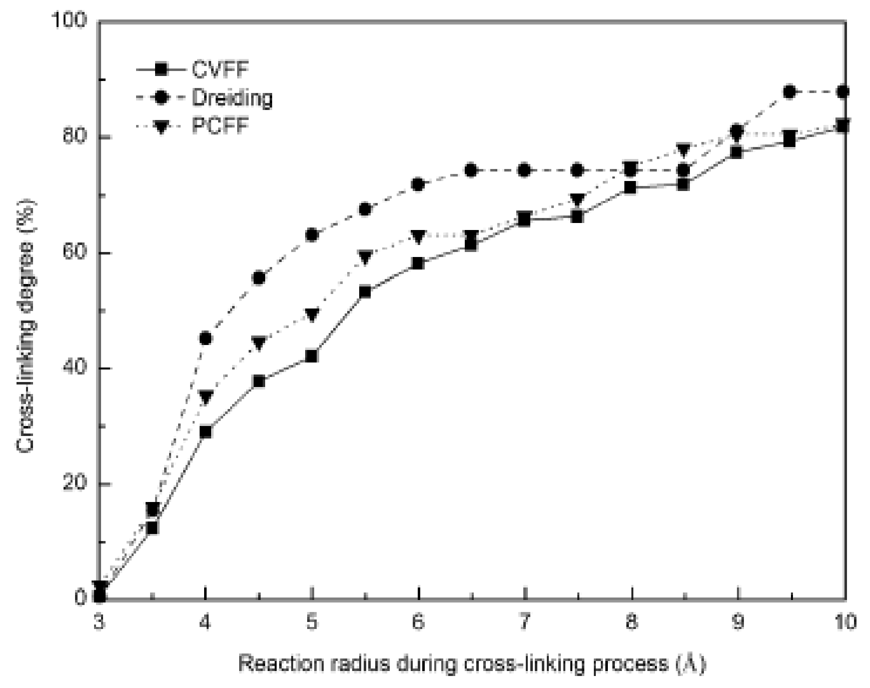


Table 1 Equilibration scheme incorporating high pressure molecular simulations used in the equilibration process of cross-linked SU-8 epoxy network

Cycle	Ensemble	Temperature (K)	Pressure (atm)	Time frame (ps)
1	NVT	300	—	100
	NPT	300	1000	50
2	NVT	300	—	150
	NPT	300	30 000	50
3	NVT	300	—	150
	NPT	300	50 000	50
4	NVT	300	—	150
	NPT	300	25 000	5
5	NVT	300	—	15
	NPT	300	5000	5
6	NVT	300	—	15
	NPT	300	500	5
7	NVT	300	—	15
	NPT	300	1	5000



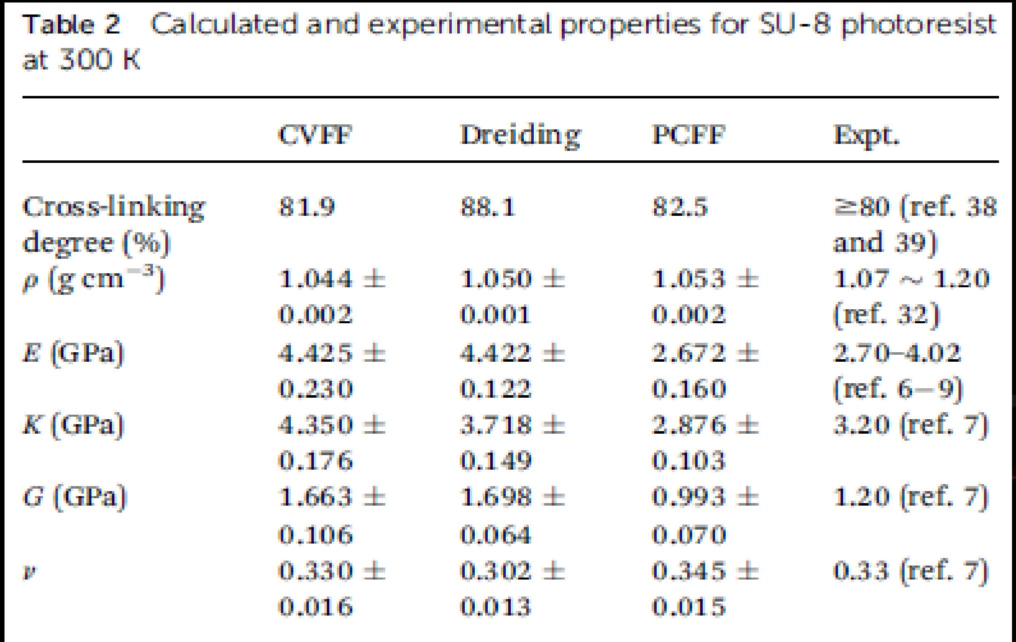
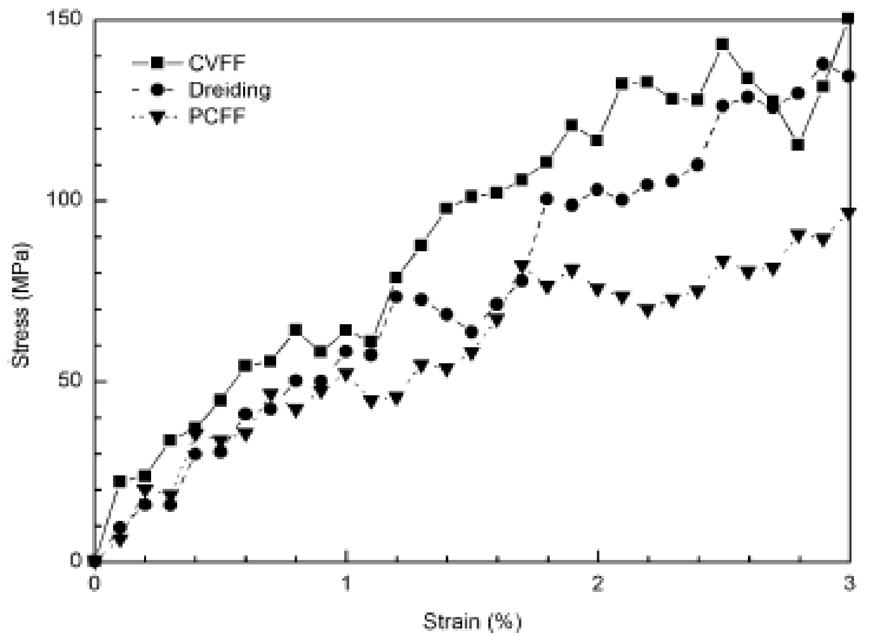


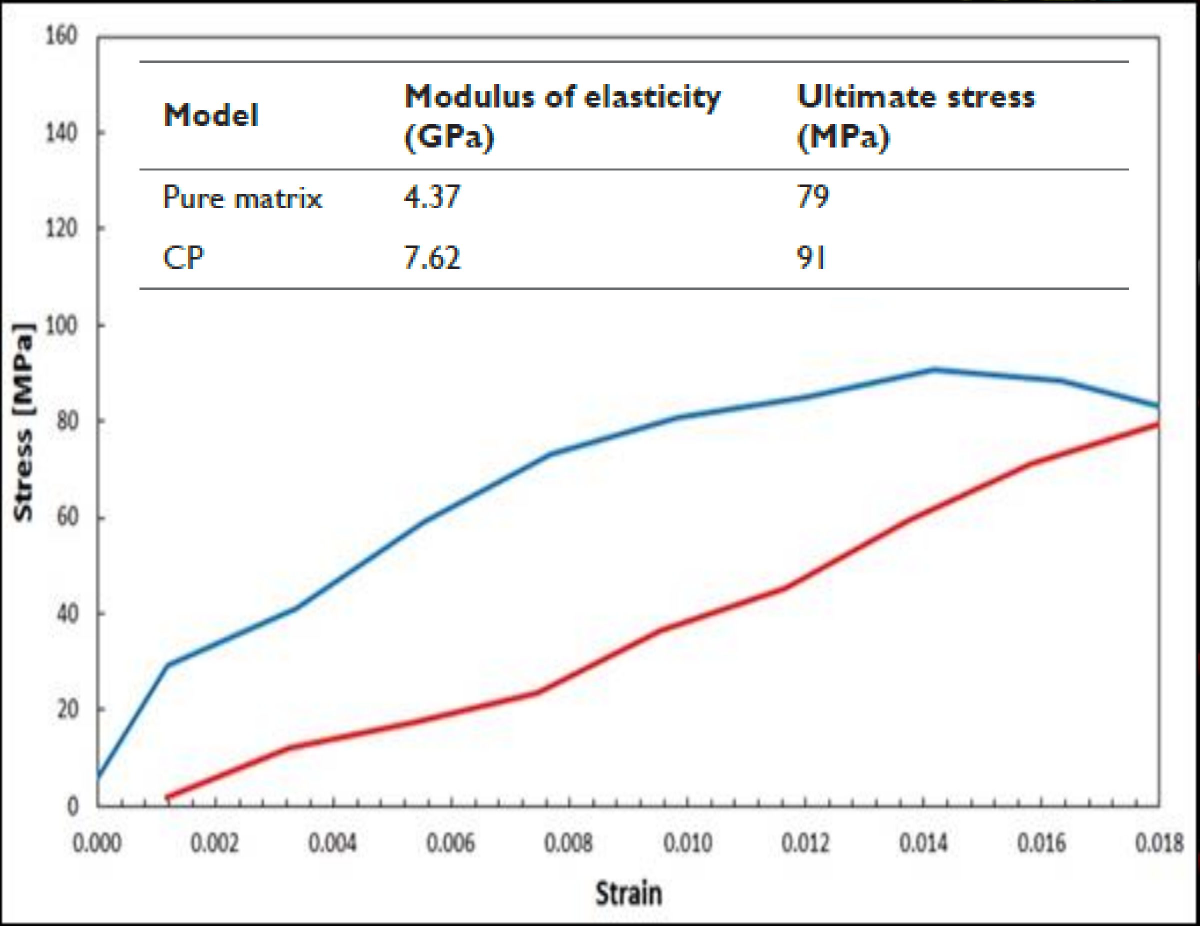
Table 2 Calculated and experimental properties for SU-8 photoresist at 300 K

	CVFF	Dreiding	PCFF	Expt.
Cross-linking degree (%)	81.9	88.1	82.5	≥80 (ref. 38 and 39)
ρ (g cm^{-3})	1.044 ± 0.002	1.050 ± 0.001	1.053 ± 0.002	1.07 ~ 1.20 (ref. 32)
E (GPa)	4.425 ± 0.230	4.422 ± 0.122	2.672 ± 0.160	2.70–4.02 (ref. 6–9)
K (GPa)	4.350 ± 0.176	3.718 ± 0.149	2.876 ± 0.103	3.20 (ref. 7)
G (GPa)	1.663 ± 0.106	1.698 ± 0.064	0.993 ± 0.070	1.20 (ref. 7)
ν	0.330 ± 0.016	0.302 ± 0.013	0.345 ± 0.015	0.33 (ref. 7)

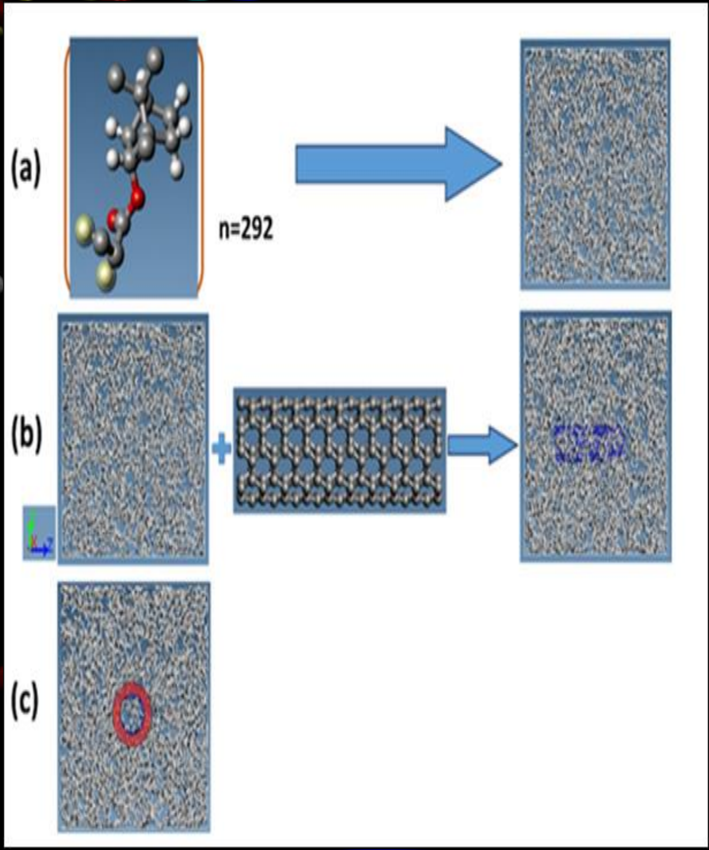


Carbon Nanotube Reinforced Nanocomposites

Nanocomposites are constructed by embedding single wall CNT (5,5) into acrylate based polymer under the periodic boundary condition with different interface interaction.



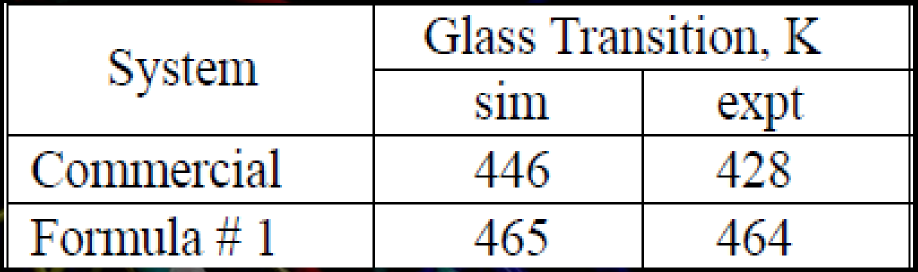
Model	Modulus of elasticity (GPa)	Ultimate stress (MPa)
Pure matrix	4.37	79
CP	7.62	91



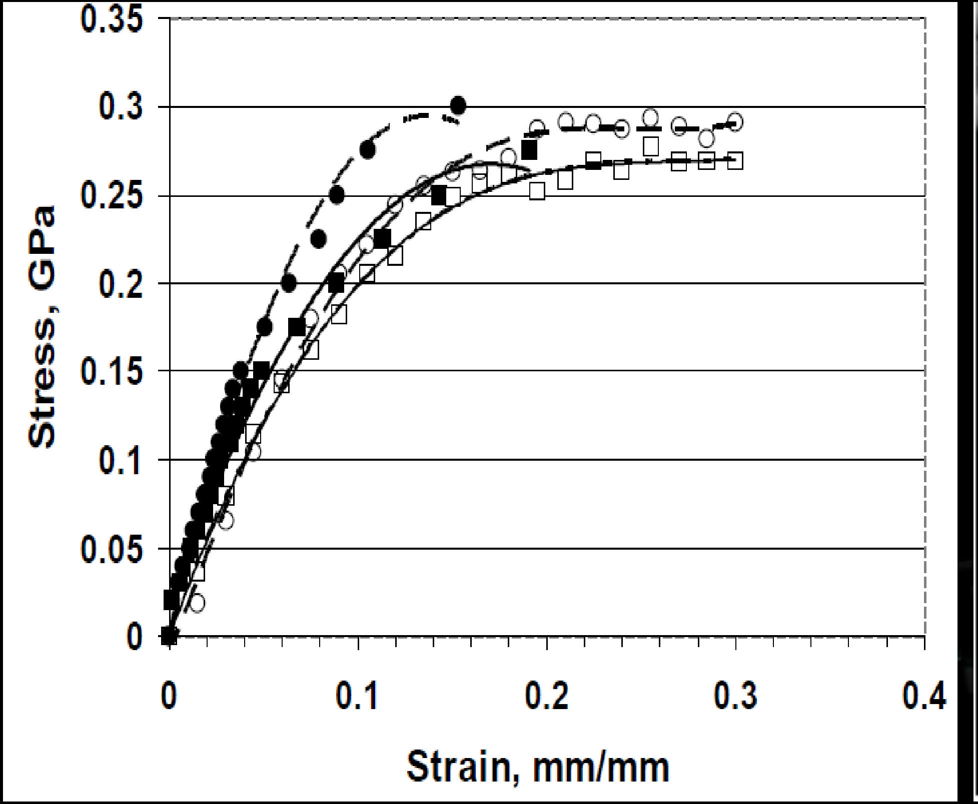
MOJ Poly Sci. 2018;2(1):6–10.

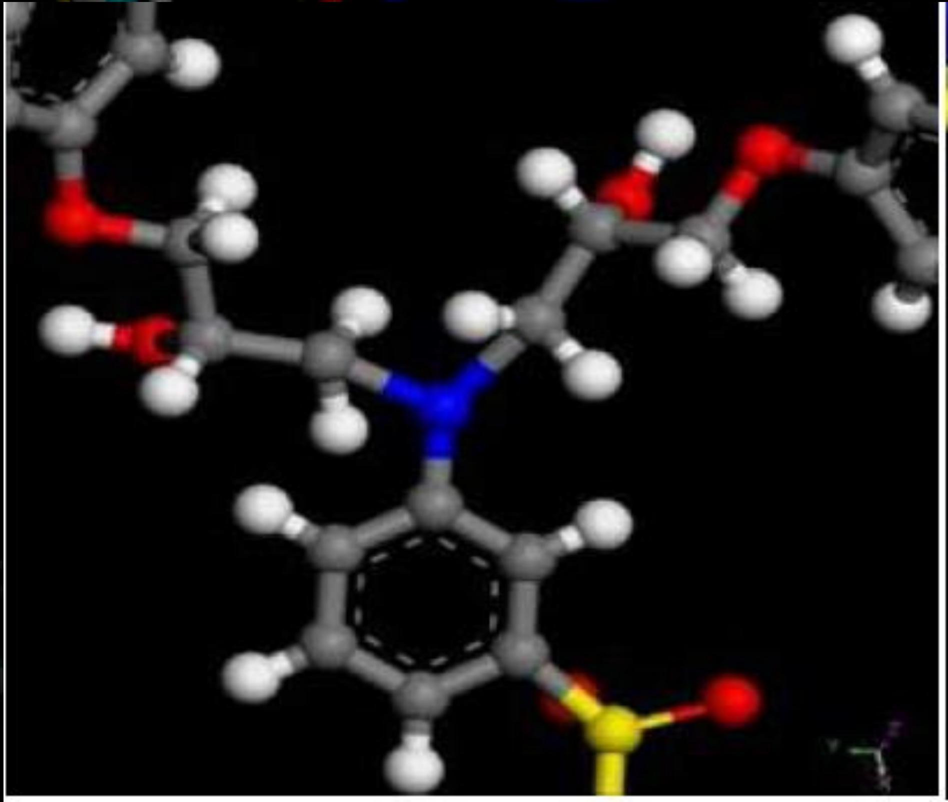
IMPROVED COMPOSITE MATRIX MATERIALS

A method to simulate fully dense and equilibrated high glass transition temperature and high cross-link density epoxy resins.



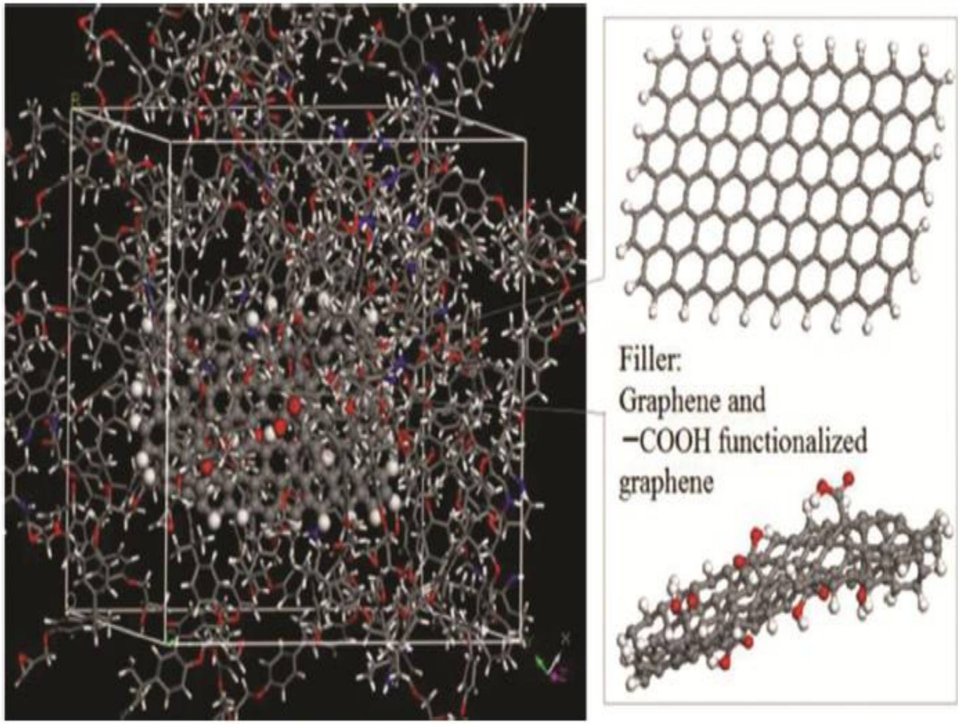
System	Glass Transition, K	
	sim	expt
Commercial	446	428
Formula # 1	465	464



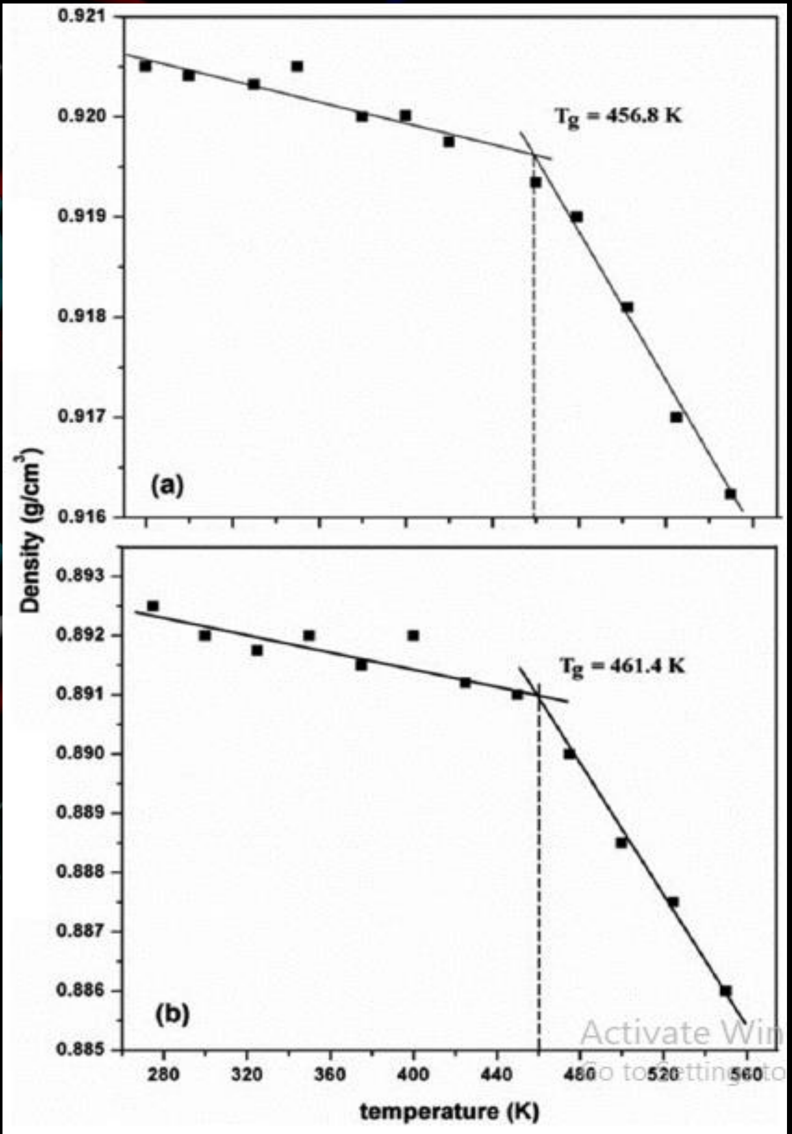


Glass Transition Temperature of Polymer Composites

Glass transition temperature is one of the remarkable prospect to investigate visco-elastic properties of polymers composites.

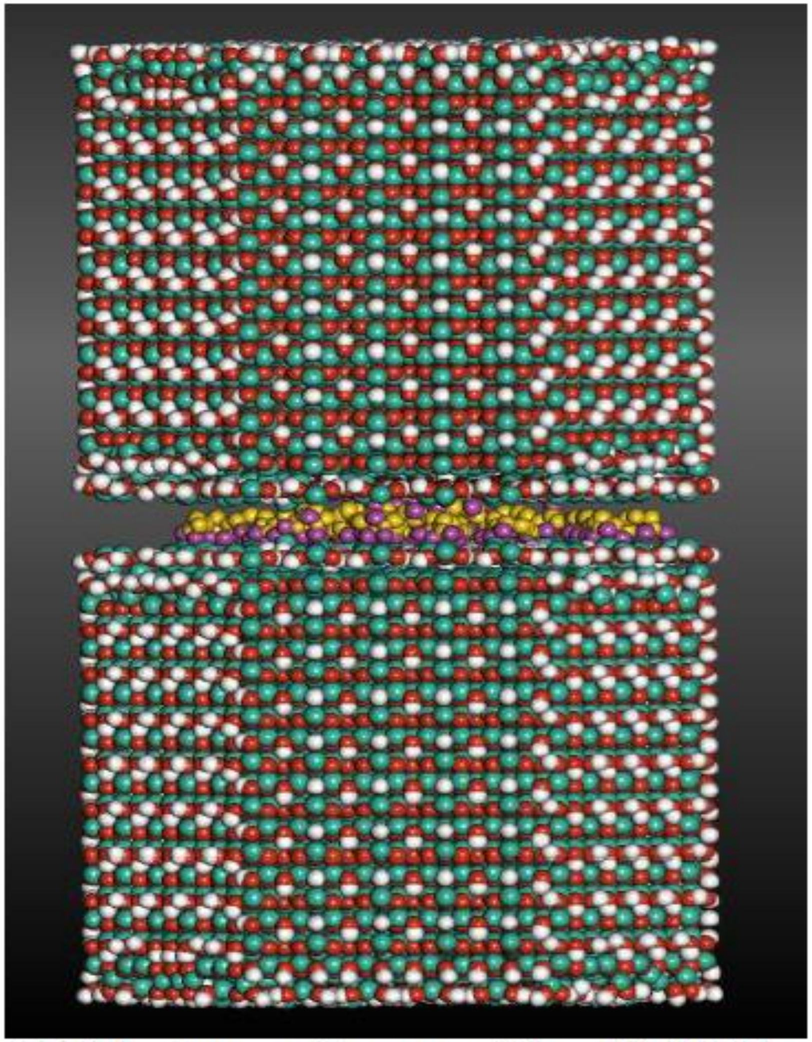


Nanocomposite unit cell consists of cross-linked LY556 epoxy resin as matrix and graphene or modified graphene as filler.



Nanoparticle - Polymer - Nanoparticle Systems Under Tensile Load

- Composites of inorganic nanoparticles and polymers currently receive great attention because of its unique mechanical properties.
- In dental fillings, for example, composites of ZnO nanoparticles and polymers are applied to provide enamel-like properties.
- The mechanical properties of teeth generally (and of enamel in particular) encompass two mayor aspects: hardness and resilience.
- An ideal filling should reflect both properties to optimally replace parts of the tooth surface



2. Model system comprising nanoparticles which (001) faces are 'glued' by 3 polyacrylate molecules.

International Journal of Materials, Mechanics and Manufacturing, Vol. 1, No. 3, August 2013

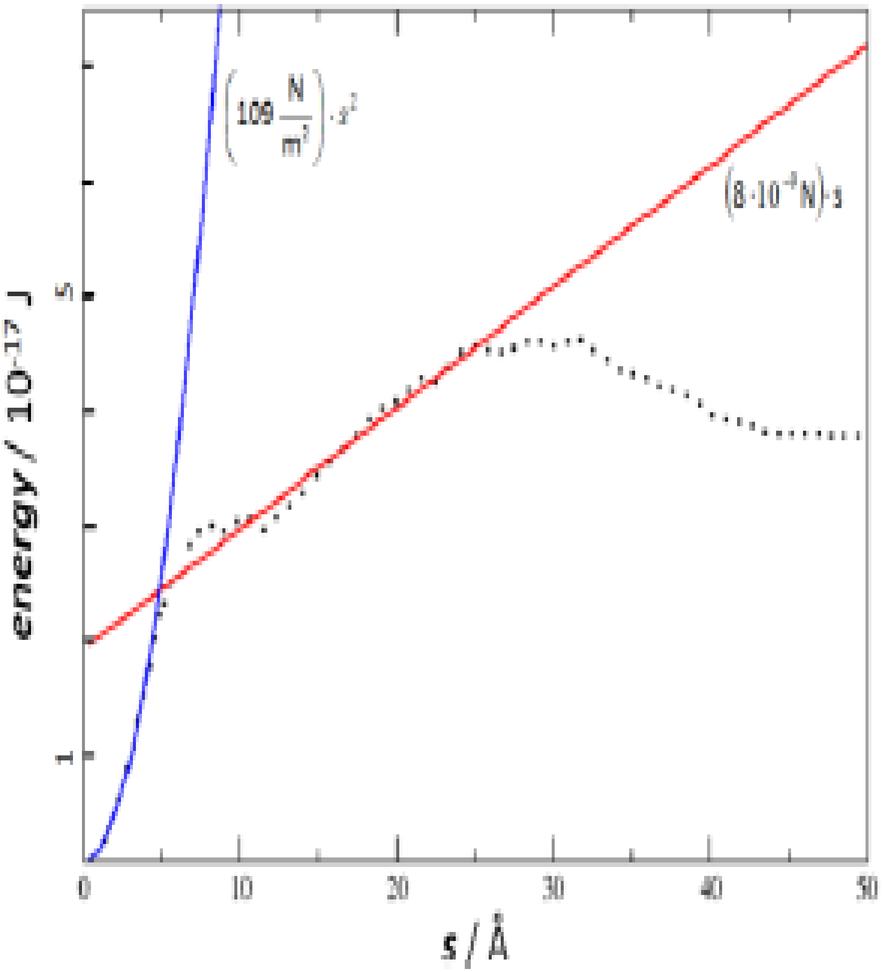
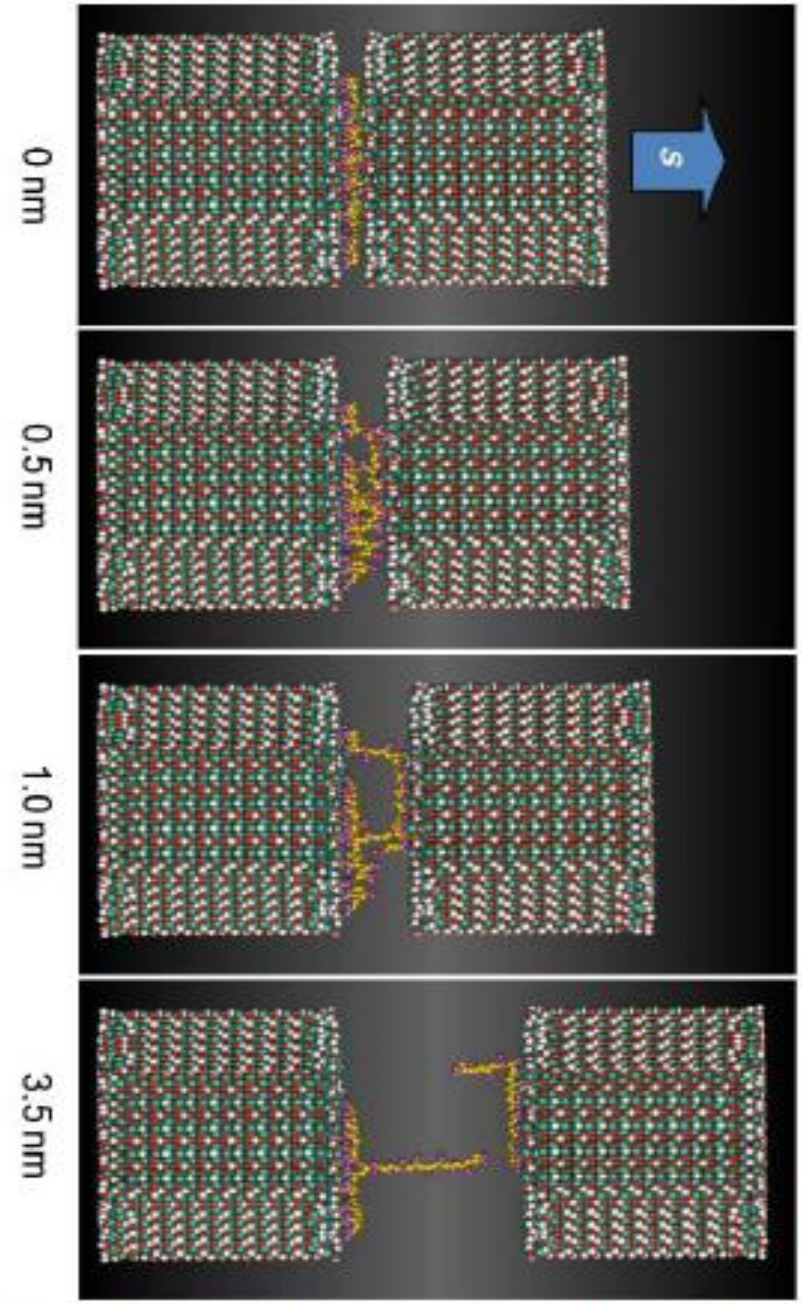


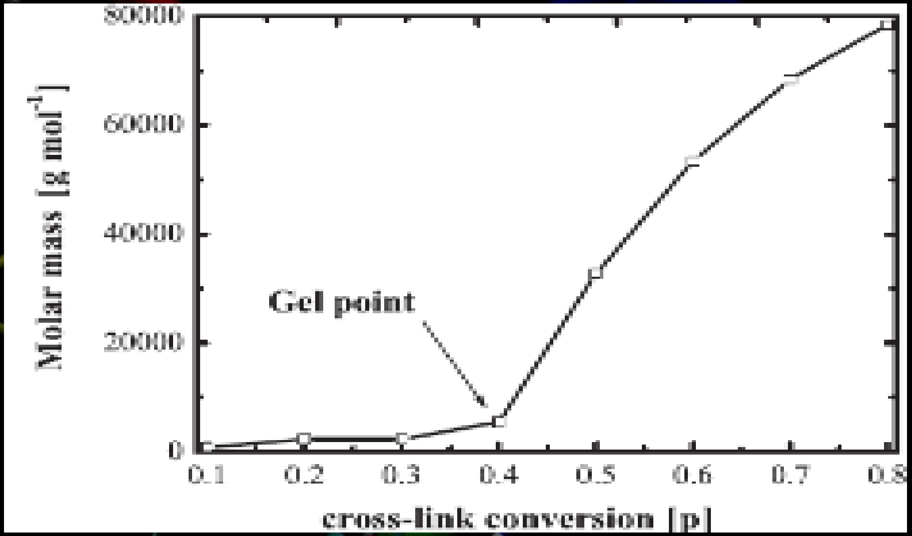
Fig. 3. Potential energy as a function of system elongation from the equilibrium structure. The blue and red curves correspond to quadratic and linear fits to the elastic and creep regime, respectively.

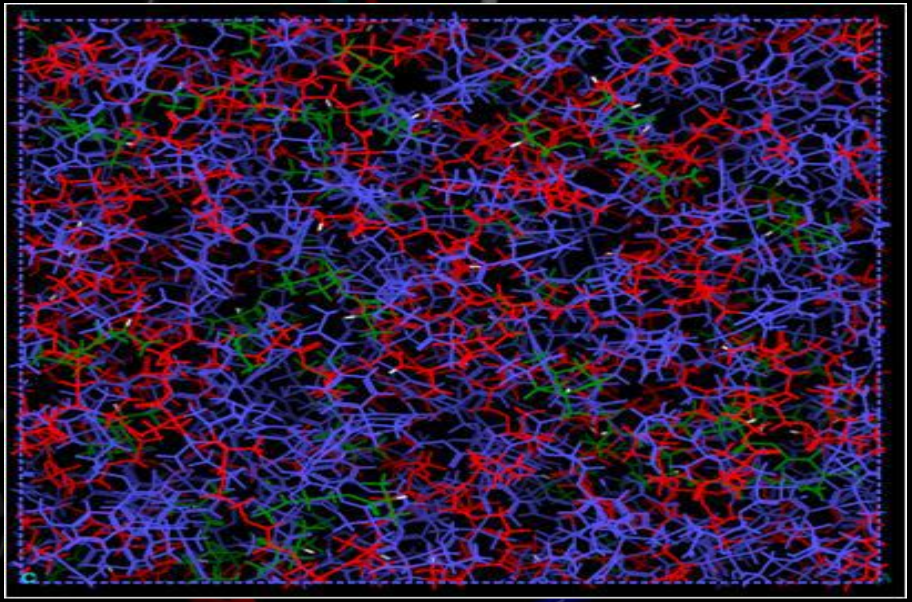


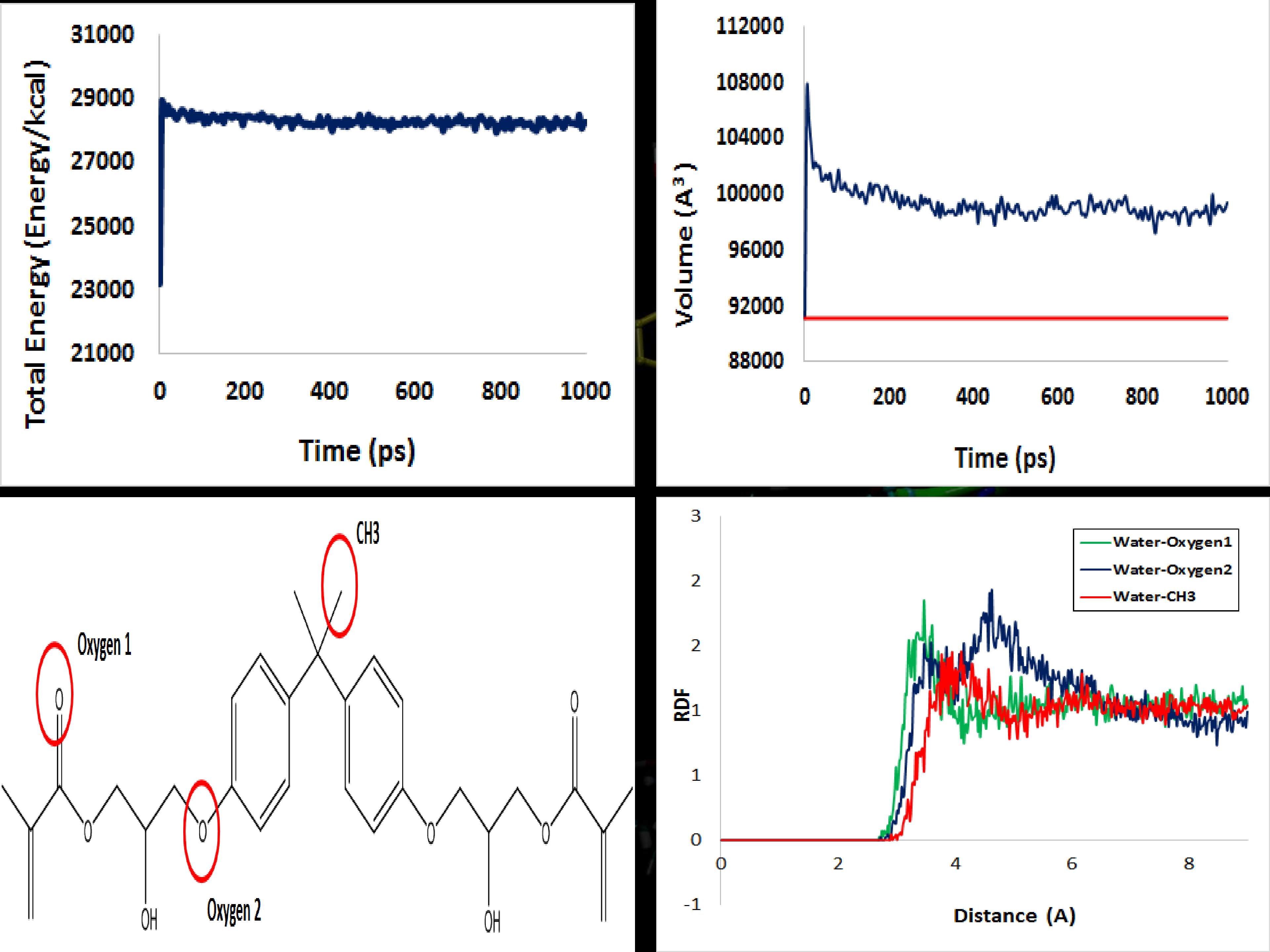
Nanorod-polyacrylate-nanorod model under tensile load.

Degradation of dental resin through water diffusion

- Dental resin is used in the dentistry field as restorative material that fills out cavity of teeth.
- Dental resin is mainly composed of two polymers called Bis-GMA and TEGMA.
- Most of the water molecules that penetrate inside the resin is saliva. These molecules go through all the way down into the gap between the dentin and resin.
- As water molecules accumulate between these gaps, resins start to fall apart slowly and eventually separates completely from the dentin.






Total Energy (Energy/kcal)
31000
29000
27000
25000
23000
21000
0
200
400
600
800
1000
Time (ps)
Volume (A³)
112000
108000
104000
100000
96000
92000
88000
0
200
400
600
800
1000
Time (ps)
CH3
Oxygen 1
O
O
O
O
O
O
OH
OH
Oxygen 2
RDF
3
2
2
1
1
0
-1
0
2
4
6
8
Distance (A)
Water-Oxygen1
Water-Oxygen2
Water-CH3

Thank You