

# Survey of Computational Methods

January 2002

Ernest Chamot

- Personal Perspective
  
- Molecular Modeling Methods -
  - ◇ Molecular Mechanics
  - ◇ Quantum Mechanics
  - ◇ Density Functional Theory
  - ◇ G2 Theory
  
- Bridging to Larger Scale -
  - ◇ Cluster Models
  - ◇ Solvation Models
  - ◇ Periodic Boundary Conditions
  - ◇ QSPR
  - ◇ Coarse Grain
  - ◇ Mesoscale
  
- Summary



## Modeling Methods

### Molecular Mechanics

- based on classical chemical concepts of molecules as atoms connected with bonds: Force Field description of balls and springs model, Newtonian laws of motion.
- Harmonic oscillator
- Standard hybridization

### Quantum Mechanics

- based on physics principles describing molecules as nuclei and electrons: solve electronic Schroedinger's equation.
- **Born Oppenheimer Approximation** – fix nuclear positions
- **Basis Set** – true molecular orbital approximated by a combination of wave functions
- **Variational Principle** – expectation value for energy will always be greater than the real energy, so vary the MO's and coefficients to minimize energy
- **Hartree Fock Approximation** – each electron interacts with average of other electrons

### Density Functional Theory

- based on solid state physics theory describing electron distribution as an electron gas: find functional given an electron distribution
- Approximate exchange/correlation functional
- Local Density Approximation

## Molecular Mechanics

- **Capabilities**

- ◆ **Established, tested Force fields**

- ◇ **MM2 since 1977: Bonds  $\pm 0.03 \text{ \AA}$ ,  $\Delta H \pm 0.5 \text{ kcal}$**
    - ◇ **Main Group/organics**
    - ◇ **Augmented for all elements**
    - ◇ **Geometries for stable molecules**
    - ◇ **Conformational analysis**

- **Limitations**

- ◆ **Parameterization**

- ◇ **XRD & ND Data: “Only”  $\sim 10^7$  compounds known**
    - ◇ **82 stable elements require  $\sim 82! \sim 10^{122}$  data**
    - ◇ **Main Group elements: H, C, O, N**

- ◆ **Single, double, triple, aromatic bonds**

- ◇ **No bond breaking**
    - ◇ **No electronic transitions**
    - ◇ **No excited states**
    - ◇ **Only rotational transition states**
    - ◇ **Poor transition metal description**

- **Large Systems: Thousands of atoms**

- ◇  **$N^2$  Scaling**



## Semiempirical Quantum Mechanics

- **Capabilities**

- ◆ **Established, tested parameters**

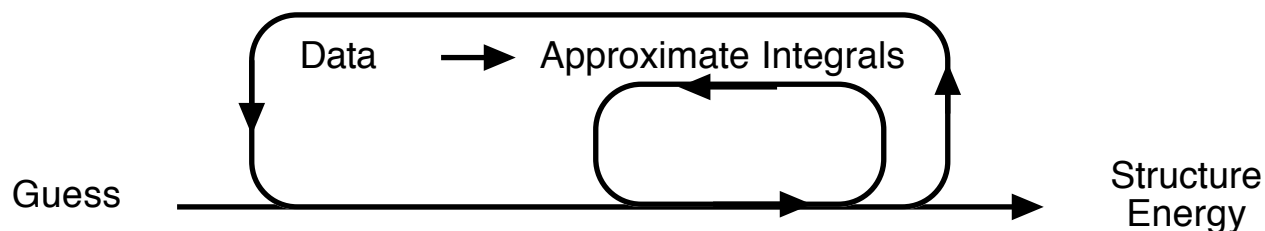
- ◇ **AM1 since 1977:** Bonds  $\pm 0.06 \text{ \AA}$ ,  $\Delta H \pm 8 \text{ kcal}$
- ◇ **Electronic transitions**
- ◇ **Multipole moments**
- ◇ **Excited States**
- ◇ **Transition states**
- ◇ **Some correlation & relativity included**

- **Limitations**

- ◇ **Valence electrons only**
- ◇ **Transition Elements**
- ◇ **Accuracy**
- ◇ **Minimal Basis Set (Poor Diffuse Interactions)**

- **Medium Size Systems: 40 ~ 150 heavy atoms (1000's)**

- ◇ **Put as much into the parameters as possible**
- ◇  **$N^2$ - $3$  Scaling**



## Ab Initio Hartree Fock

- **Capabilities**

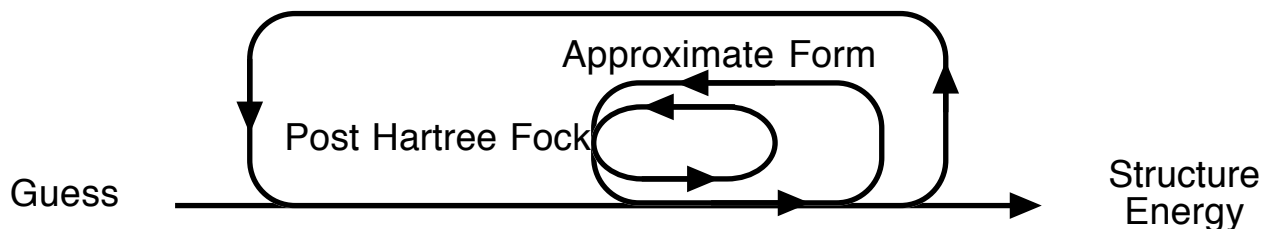
- ◆ **Established wavefunctions/basis sets**
  - ◇ **6-31G\***: Bonds  $\pm 0.04$  Å,  $\Delta H \pm 4$  kcal
- ◇ **All electron calculations**
- ◇ **Electronic transitions**
- ◇ **NMR shifts**
- ◆ **More accurate energies**
  - ◇ **Isodesmic reactions**
  - ◇ **More elaborate wavefunctions**
  - ◇ **Fix-ups**

- **Limitations**

- ◆ **Correlation**
  - ◇ **Activation energies**
  - ◇ **Nuclear shielding**
  - ◇ **Post Hartree Fock** – computationally demanding
- ◇ **Relativity** – Effective Core Potentials
- ◇ **Cumbersome programs**

- **Small Systems:  $\leq 10 \sim 20$  heavy atoms**

- ◇ **Put as much into the wavefunctions as possible**
- ◇  **$N^3-5$  Scaling**



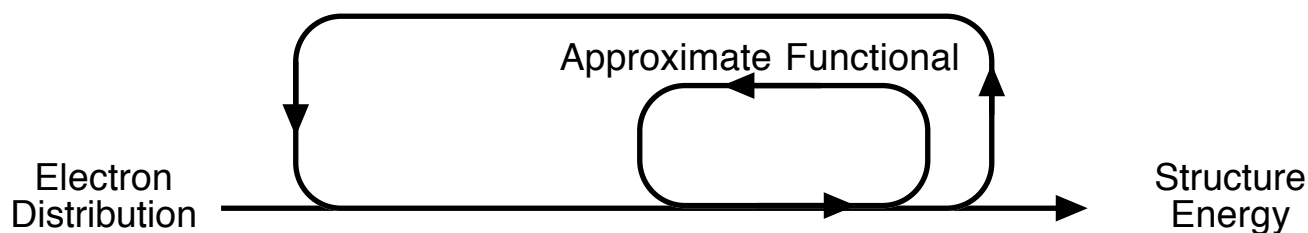
# Density Functional Theory

## • Capabilities

- ◇ Inherently includes static correlation & exchange
- ◆ **Established Basis Sets**
  - ◇ **DNP, DZVP:** Bonds  $\pm 0.04$  Å,  $\Delta H_{rxn} \pm 7$  kcal,  $\Delta H^\ddagger \pm 5$  kcal
- ◇ **Electronic transitions**
- ◇ **Transition states**
- ◇ **Organics, Inorganics**
- ◆ **Nonlocal Fix Ups**
  - ◇ Generalized Gradient Approximation:  $\Delta H_f \pm 4$  kcal,  $\Delta H_{BDE} \pm 5$  kcal
  - ◇ Hybrid Functionals

## • Limitations

- ◆ **Quasi-Particle Wavefunctions not Molecular Orbitals**
  - ◇ Spin
  - ◇ Excited States
- ◆ **Local Density Approximation Overpredicts Binding:**  
 $\Delta H_{BDE} +19$  kcal,  $\Delta H_f +100$  kcal
- ◇ **No Dynamic Correlation:** poor intermolecular interactions
- ◆ **Medium Sized Systems: 10 ~ 60 heavy atoms**
  - ◇ Put as much into the functionals as possible
  - ◇ “Big” $\times N^2$  Scaling



## Accuracy Ranges for Various Computational Chemistry Methods

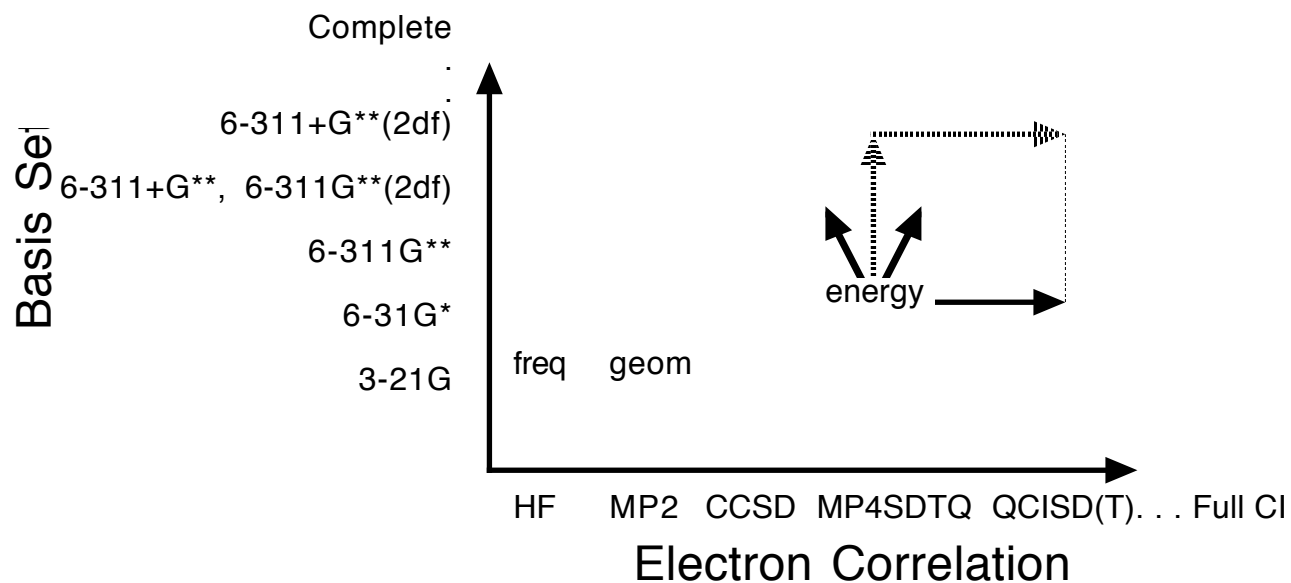
	Atoms parametrized:					Geometry ave. errors:			Energy ave. errors:		
	Main Group	Alkali Metals	Transition Metals	Group VIII	Rare Earths	Bonds, Å	Angles, °	Dihedrals	$\Delta H_f$ , kcal	$\Delta H_r$ , kcal	$\Delta H_{\ddagger}$ , kcal
<b>Molecular Mechanics Force Fields</b>											
MM2	15	2	7	3		0.03	0.1-2	8	0.4-1	0.1-0.6	0.7-3
Augmented MM2	15	7	25	9	3	0.1	6				0.4
MM3	7	9				0.01	0.7-2	8	0.4-0.7	0.3-0.5	0.6-1.3
Amber	10									0.5-0.9	1
Dreiding	15	2	7	1		0.03	3	8		0.7-1.7	1-2
CFF	10					0.01	1-2		2	0.2-1.2	0.8
<b>Semiempirical Hamiltonians</b>											
INDO/1(S)	9	6	14	6		0.04-0.12			140		
MINDO/3	10					0.02	6		2-12	8	1
MNDO	12	2	7			0.05-0.09	3-8	12-22	3-24	12-36	1-32
MNDO/d	9	2	11	3		0.04-0.12	2-3		4-9		
AM1	12		1			0.05-0.08	3-4	13	4-14	1-9	0.7-16
SAM1	11		2	1		0.04	3		4-14		
PM3	14	3	12			0.04-0.07	4-30	15	4-18	1-14	1-18
<b>Ab Initio Basis Sets</b>											
					Noble Gases						
STO-3G	15	8	20	6	4	0.02-0.3	1-13	4		0.9	1-9
3-21G	10	4	1		3	0.02-0.1	1-9	19	7	3-10	2-3
6-31G*	10	4	1		3	0.01-0.2	0.9-23	4	4	1-8	0.04-3
MP2/6-31G*	10	4	1		3	0.01	1-1.3	1	1-5		

**CHAMOT LABS, INC.**

Chemical Research and Consulting

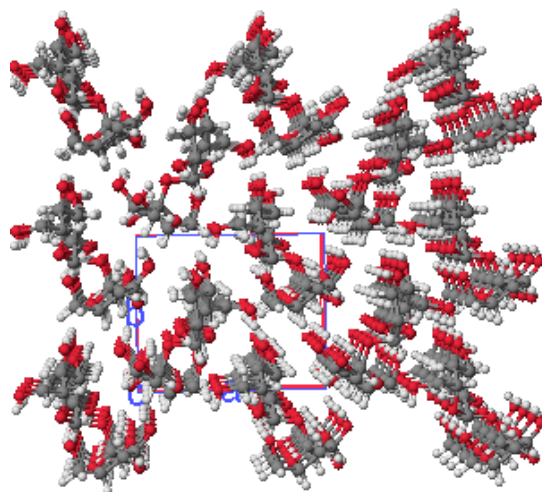
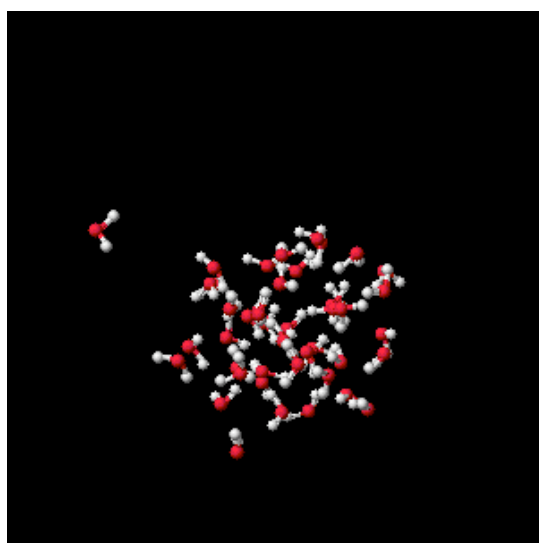
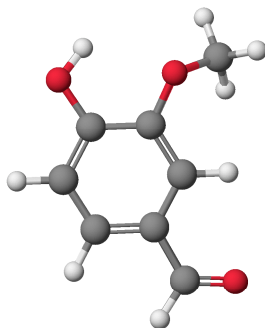
## G2 Theory

Empirical Correction Factor to Extrapolate to Full QM Calculation



*L. Curtiss, K. Raghavachari, G. Trucks, & J. Pople, J. Chem. Phys., **94**, 7221 (1991)*

## Bridging to Larger Scale



## Bridging to Larger Scale

### Cluster Models

- isolated molecule or cluster, which realistically represents important features of full system

### Solvation Models

- simulate effect of surrounding molecules in condensed phase

### Periodic Boundary Conditions

- simulates infinite, symmetric system by surrounding unit cell with copies of itself

### QSPR

- predict properties based on empirical correlations

### Coarse Grain Models

- simulate larger scale without instead of molecular scale

### Mesoscale

- new science to combine molecular level processes into macroscopic effects

## Cluster Models

### Model Compound

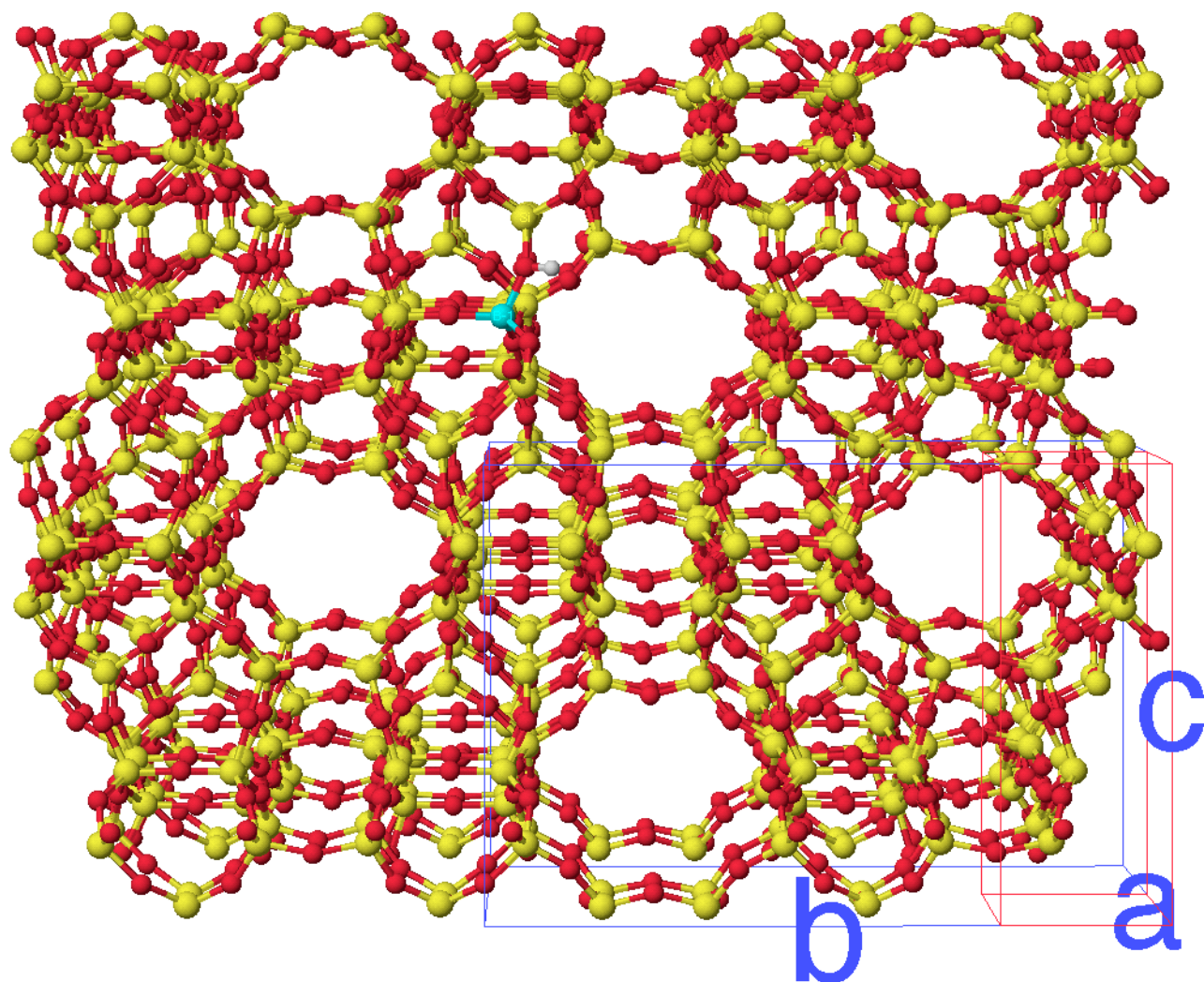
- isolated molecule or cluster which contains important features of full system

### Effect of Surrounding Environment

- Calibration/Correction
- Onion Model - Salahub
- Embedded Cluster - Teunissen, Sauer
- Integrated Molecular Orbital Molecular Mechanics - Morokuma
- Correlated Capped Small Systems

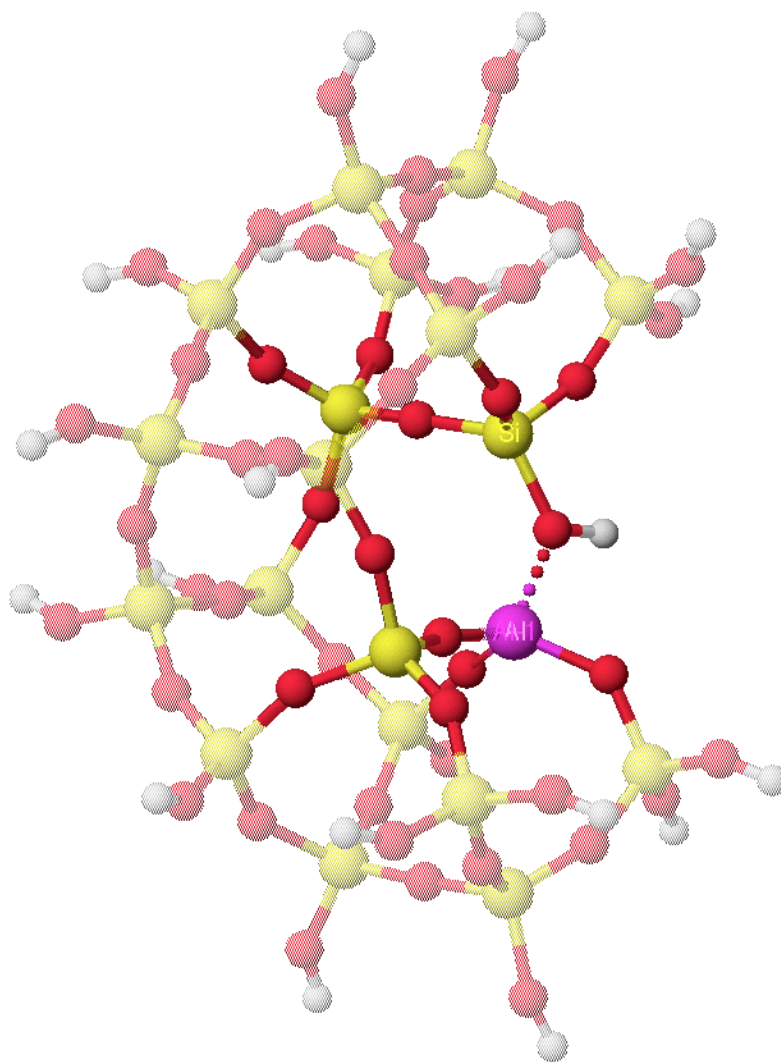
# Modeling a Metallosilicate Acid Site

MFI Zeolite



# Cluster Model of T2-O-T3 Aluminosilicate Acid Site

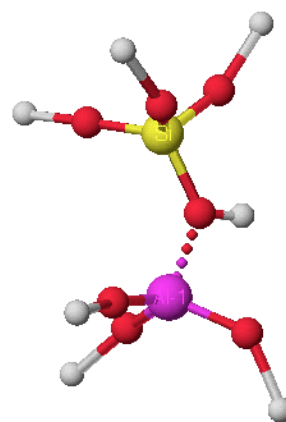
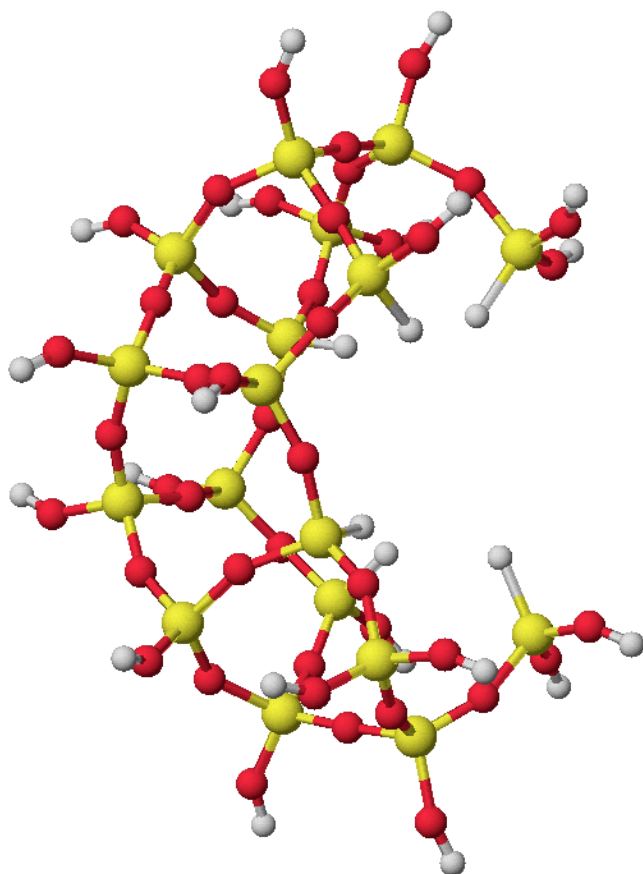
Relaxation with Realistic Geometric Constraints



*Ernest Chamot*  
*Relative Acidity of Borosilicate and Aluminosilicate Zeolites*  
*San Francisco ACS Meeting, 1992*  
*Division of Petroleum Chemistry Preprints, 37(2), 608-10 (1992)*

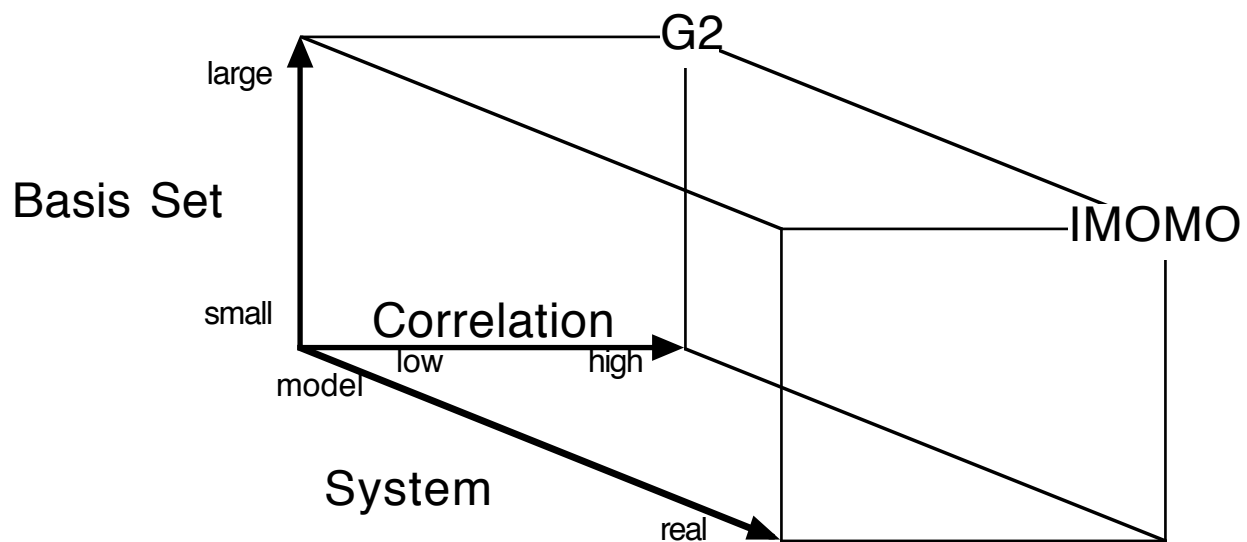
# Embedded Cluster

Linked Potentials or Atoms



# Integrated Molecular Orbital & Molecular Orbital (Mechanics)

Extrapolation to Full System



*S. Humbel, S. Sieber, K. Morokuma, J. Chem. Phys., 105, 1959 (1996)*

# Solvation

## Explicit Models

- include many solvent molecules to represent environment
- **Specific interactions**
- **Computationally demanding**

## Implicit Models

- represent solvent as a continuum

- **Computationally tractable**
- **Spherical-Cavity Models**

SCRF implementations - cavity radius, dielectric constant, refractive index

Solvent-dipole interactions

No solvent reorganization

- **Solvent-Accessible-Surface Models**

Cavity matched to shape of molecule

SM2 (C. Cramer & D. Truhlar, AM1 based Solvation Model 2) –

Interaction of Hamiltonian with dielectric

Parameterized for water (SM4 for alkanes, SM5 general)

Specific multipole interactions

COSMO (A. Klamt, COnductor-like Screening MOdel) –

Interaction with surface charge distribution

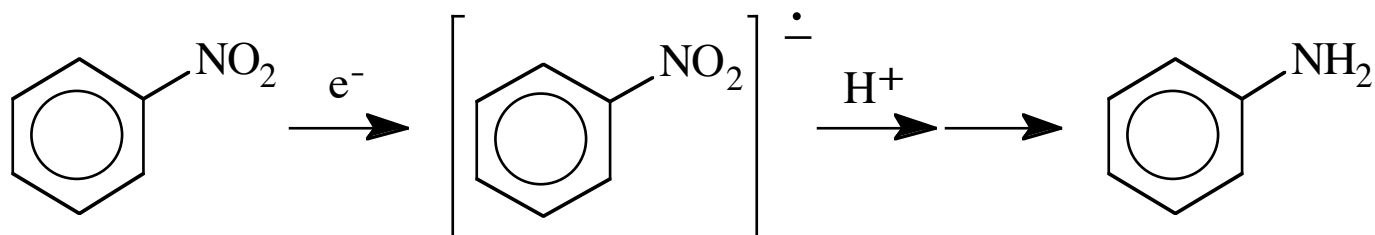
Solvent reorganization via dielectric screening

T. Clark

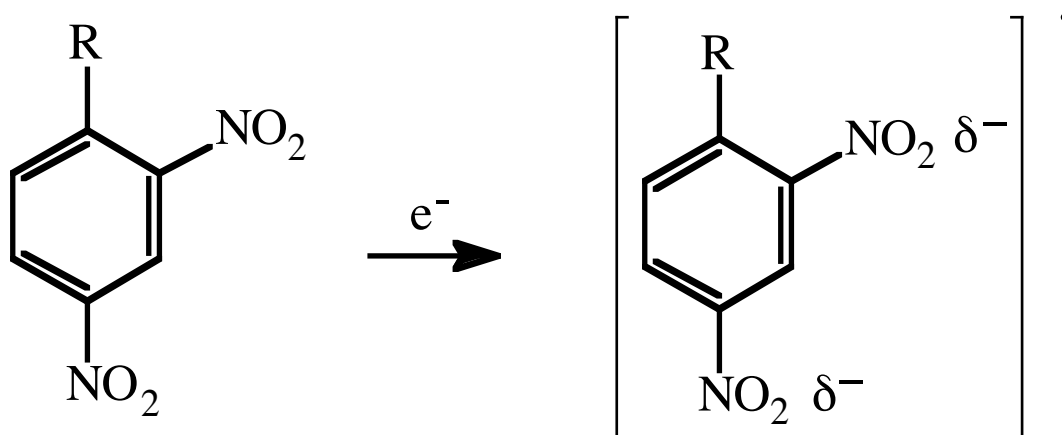
W. C. Still

## Specific Solvation Interactions

Biodegradation of aromatic nitro compounds via reduction to amine in anoxic, aqueous environment:



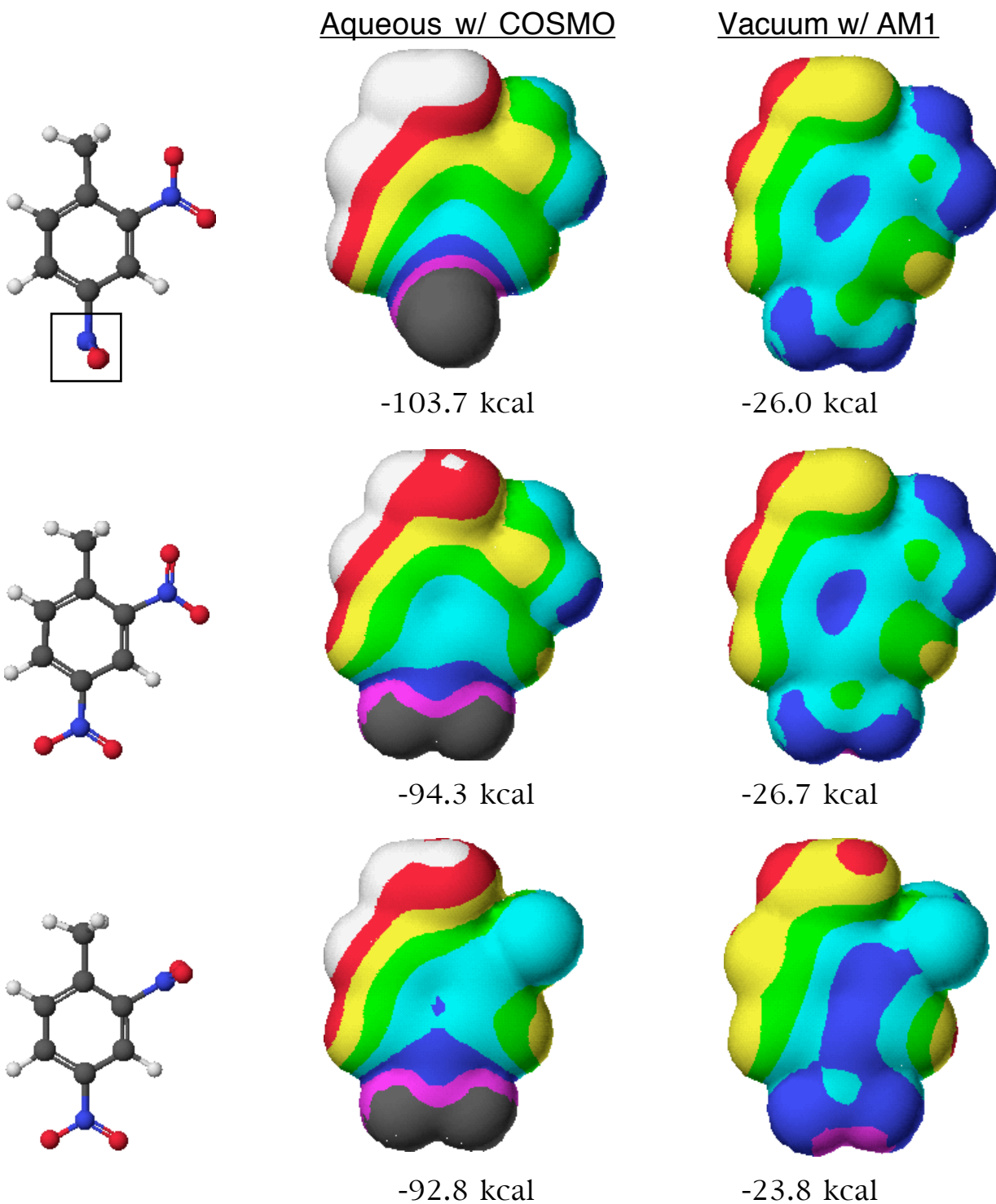
Selectivity arises via protonation of most negative site:



*S. Barrows & C. Cramer, ECTOC-1, #46 (1995)*

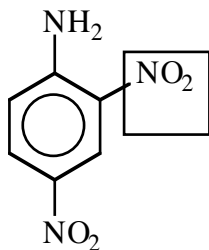
*E. Chamot, 51st Midland Section ACS Meeting, #A7 (1995)*

## Dinitrotoluene Radical Anion Modeled w/ AM1

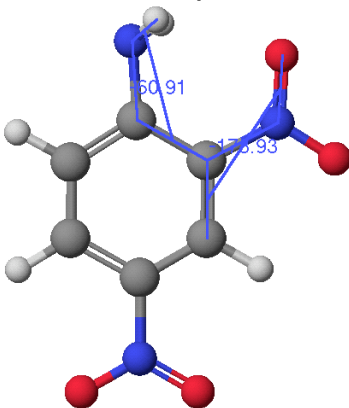


# Reduction Selectivity at Most Negatively Charged Site on Surface of Radical Anion

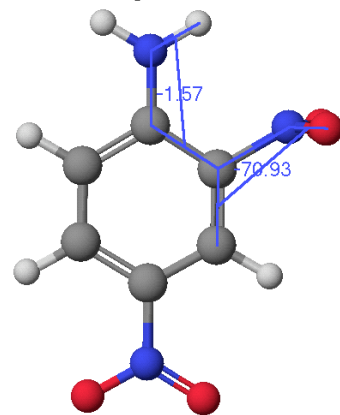
## Dinitroaniline



## Gas Phase (in vacuo)

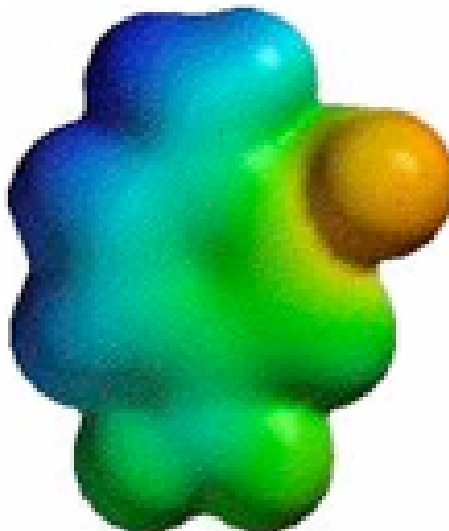


## Aqueous

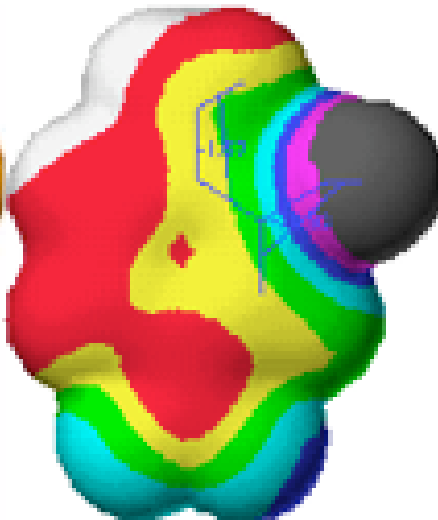


## Dinitroaniline(aq) Surface

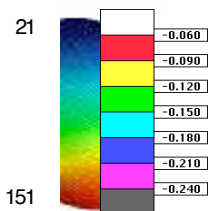
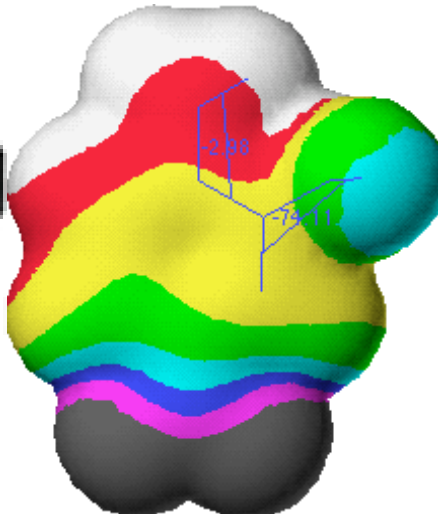
### AM1-SM2



### AM1-COSMO



### INDO1-SCRF



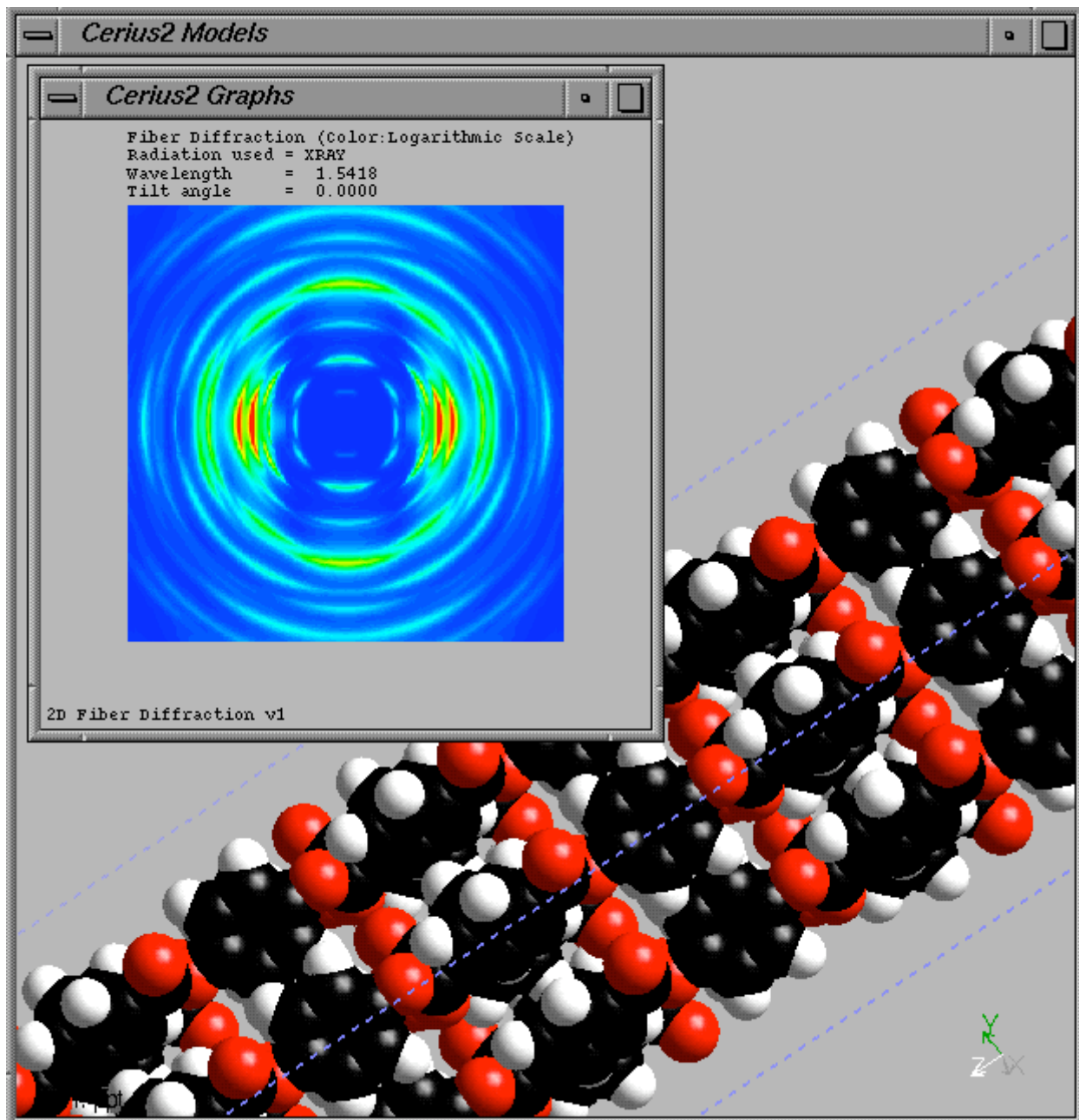
## **Bulk Systems: Unit Cell Repeated Infinitely with Periodic Boundary Conditions**

- simulates infinite, symmetric system by surrounding unit cell with copies of itself

### **Crystal Cell**

- X-Ray crystal structure and symmetry space group
- Predict/Interpret XRD
- Properties:
  - fiber or single crystal X-ray diffraction pattern
  - density
  - vibrational dispersion
  - entropy
  - heat capacity
  - elastic constants

# Determination of the Crystal Structure of a Polymer Fiber Poly p-Phenylene Terephthalate

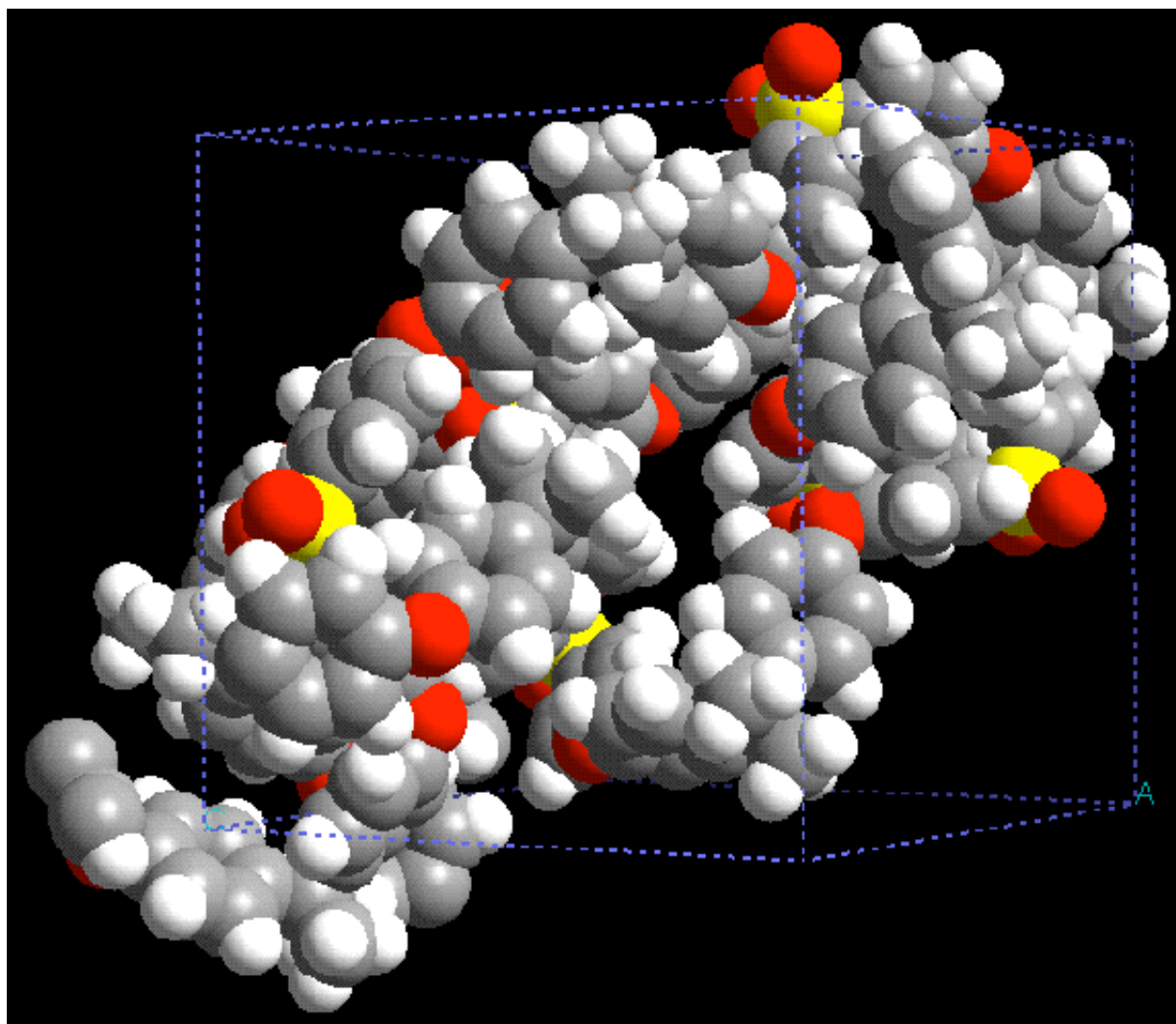


*D. Blundell, ICI*

## Amorphous Cell with Periodic Boundary Conditions

- Glassy, amorphous polymer, or melt
- Filling the cell (representative sample)
  - Monte Carlo
  - Molecular Dynamics
  - Statistical Mechanics
  - RIS
  - PRISM
- Atomistic Simulation
- Properties
  - IR
  - X-ray or neutron scattering curves
  - cohesive energy density
  - diffusivity
  - elasticity coefficients
  - stress-strain curve
  - correlation function
  - solubility parameter
  - C13 NMR
  - miscibility and phase diagrams

## Mechanical and Thermal Properties of Amorphous Polysulfone



*C. F. Fan & S. L. Hsu, 1992*

## QSPR (QSAR)

### Quantitative Structure Property Relationship

– develop correlation with empirical data

- Any properties with data available
- Relies on quality of data
- May or may not be fundamentally correct

### Molecular Level Descriptors

- Group contributions
- Theoretical descriptors

## Polymer Properties from QSPR Methods

- Methods

  - Van Krevelan

    - Strictly Group Contribution

    - Accurate when Interpolating

  - Bicerano - Dow

    - Theoretical Descriptors

    - Less Accurate

    - Extrapolative

- Properties

  - Glass Transition Temperature,  $T_g$

  - Cohesive Energy,  $E_{coh}$

  - Solubility Parameter,  $\Delta$

  - Inherent Viscosity

  - MVol

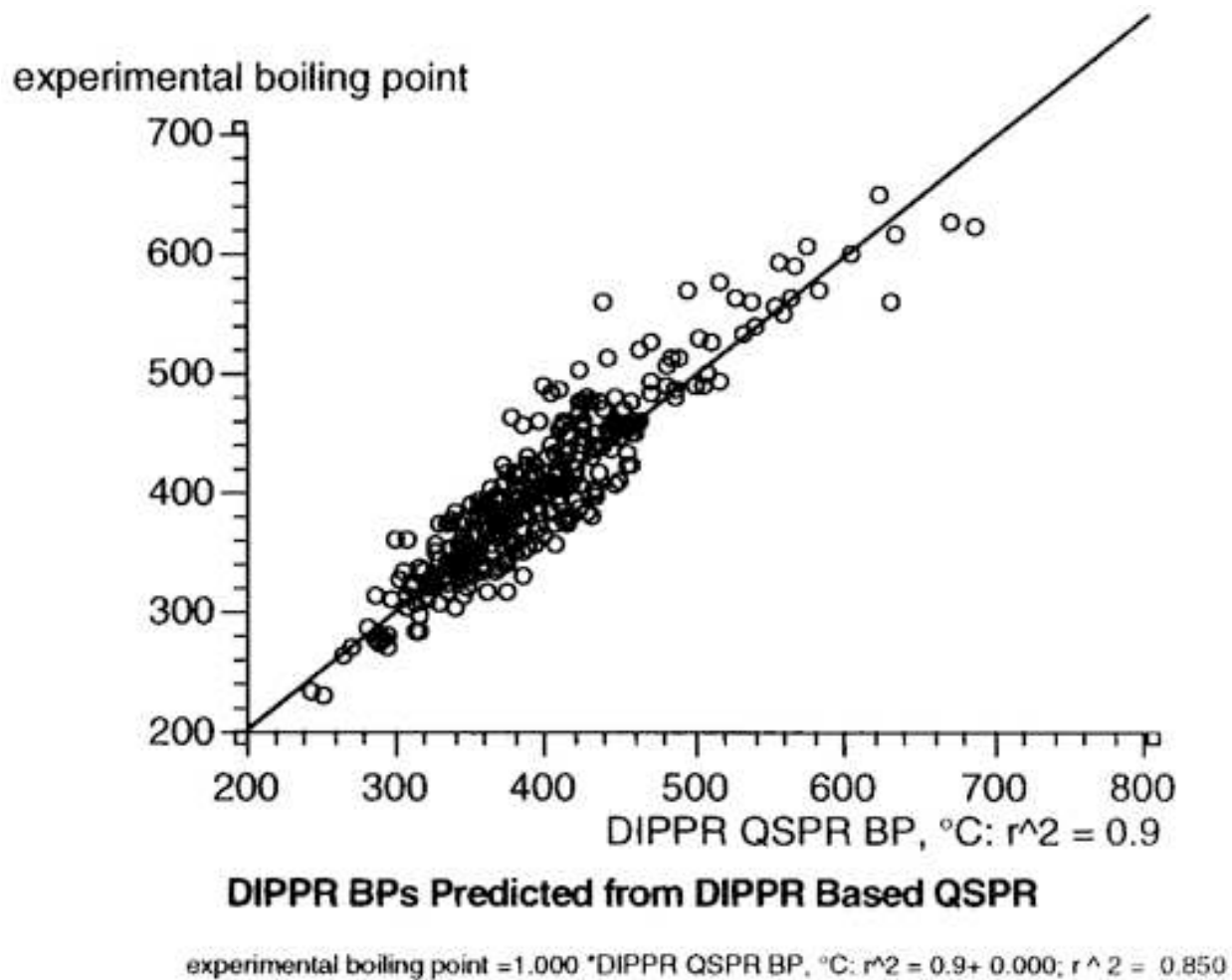
## Theoretical Descriptors

- Atom Count
- PM3  $\Delta H$  of Formation(g)
- Dipole Moment
- Connectivity Index, Chi0
- Chi1
- Chi2
- Molecular Weight
- Dielectric Energy
- PM3  $\Delta H_f$ (aq) w/ COSMO
- Solvent Accessible Surface

### Area

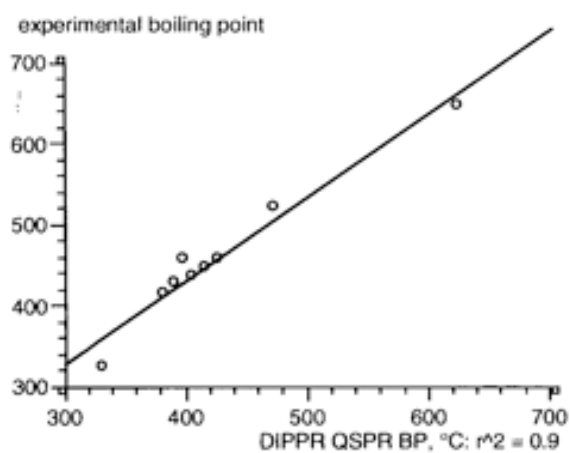
- Polarizability
- Solvation Energy,  $\Delta H_f$ (aq-g)
- $\log(\text{Chi1})$
- $\log(\text{Polarizability})$
- Polarizability/Chi1
- Chi1/Polarizability
- $\Delta H_f$ (aq)/Atom Count

## Correlation with DIPPR DB

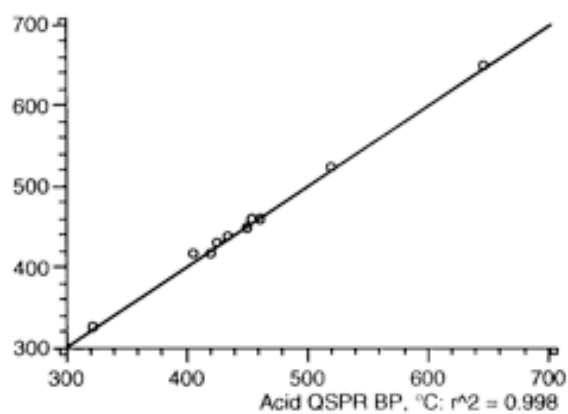


*Ernest Chamot, 1996*

## General vs. Specialized QSPR



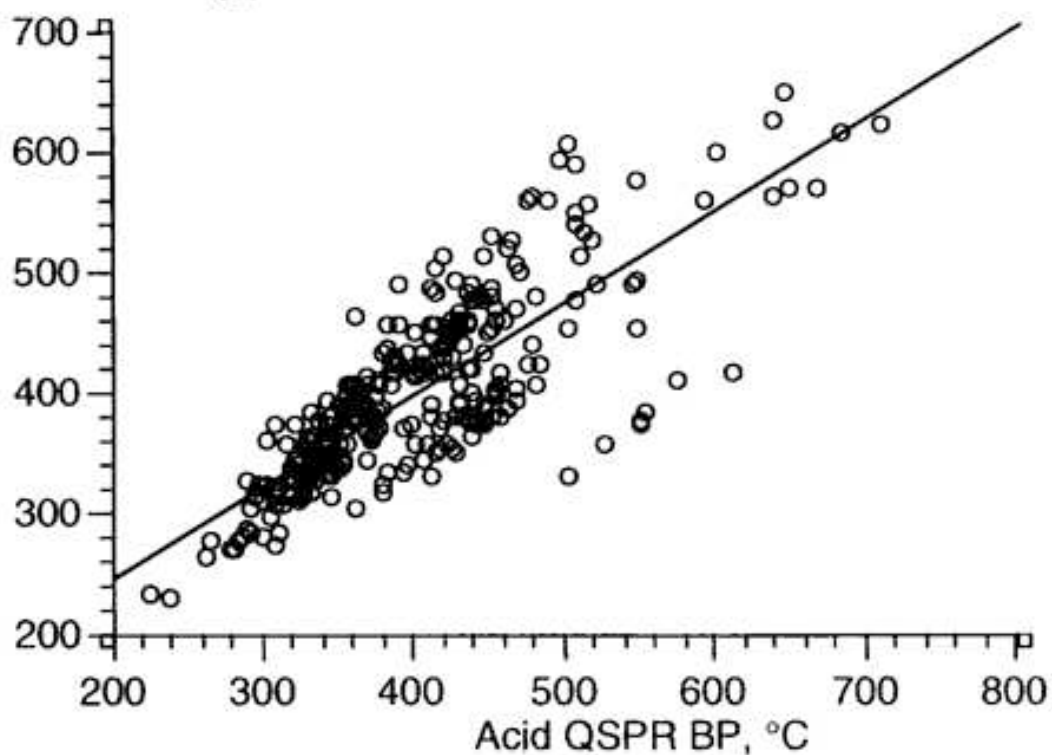
Acid BPs from DIPPR Based QSPR



Acid BPs from Acids Based QSPR

## Give Up General Accuracy

experimental boiling point



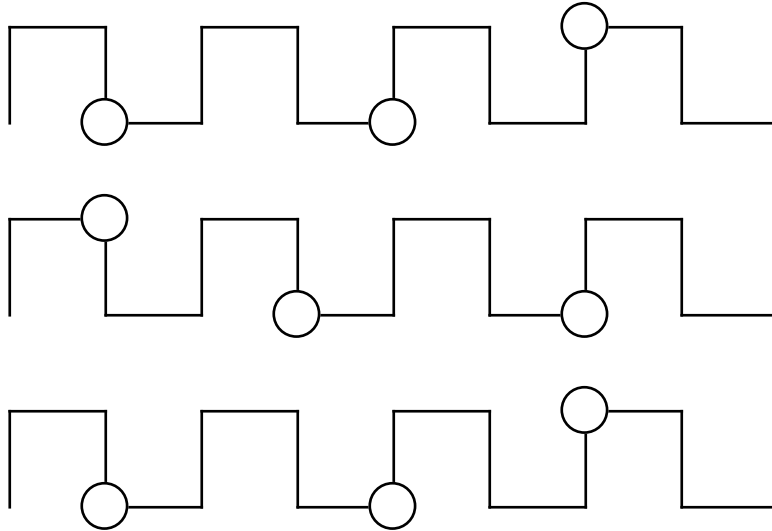
**DIPPR BPs Predicted from Acids Based QSPR**

experimental boiling point =  $0.768 \cdot \text{Acid QSPR BP, } ^\circ\text{C} + 89.819$ ;  $r^2 = 0.639$

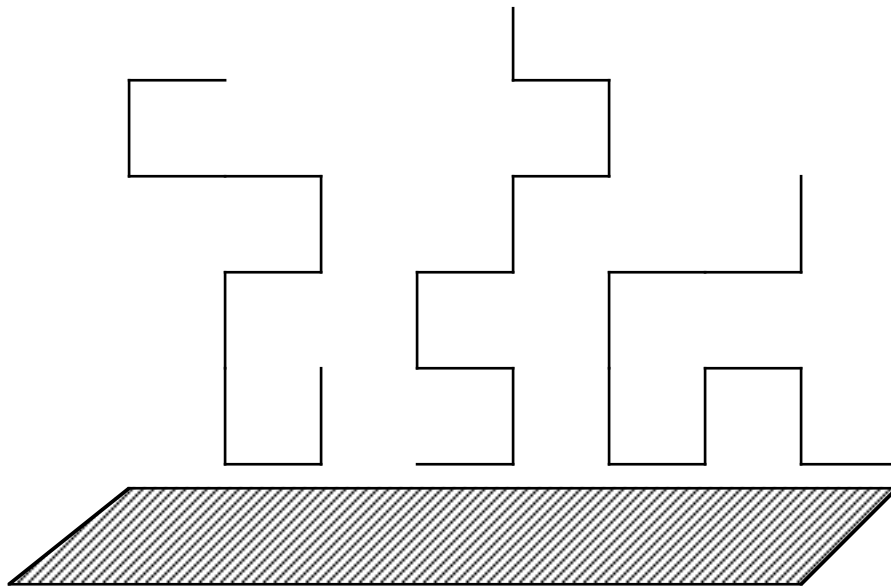
## Coarse Grain Methods

– model at bulk scale instead of molecular scale

### Polymer Gellation as Statistical Process



### Surface Adhesion as Graph Theoretical Model



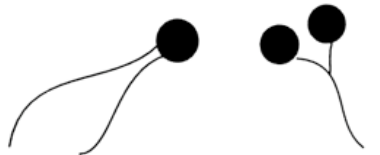
## Mesoscale

- engineering problem to combine individual molecular species and molecular level processes into overall macroscopic observable

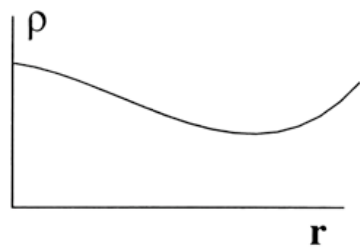
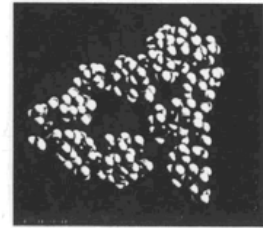
- Brute Force
- Histogram Reweighting Monte Carlo Method
- Mapping to Sparsely Occupied Lattice - Mattice et. al.
- Extended Soft Particle
- Cooperative Kinematics
- Mean Field Density Functional - Fraaije et. al.
- Dissipative Particle Dynamics - Groot et. al.
- Others

## Micro-Meso-Macro Scales

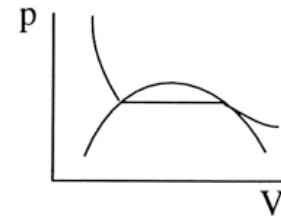
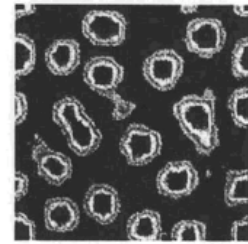
0.1 nm  
10 nm  
1 mm



**Microscopic**



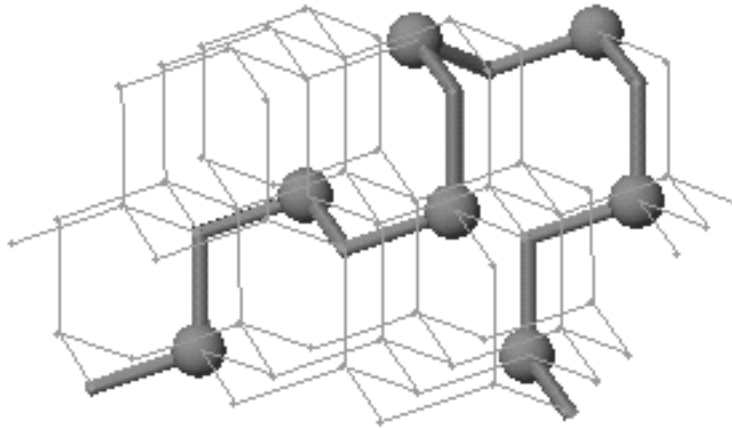
**Mesoscopic**



**Macroscopic**

## Coarse Graining RIS Models on a Lattice

- map atomistic representation to a high coordination lattice (diamond), and coarse grain to every other lattice site based on RIS weights: 2nd lattice

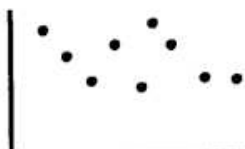


*W. L. Mattice*  
*Polyethylene Film Dynamics*

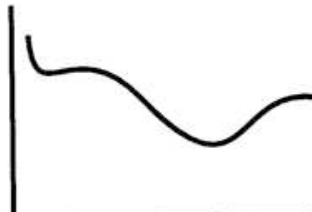
## Mean Field Density Functional Model

- Structures but no molecules
- Structures expressed as fields
- *Functionals* instead of *functions*

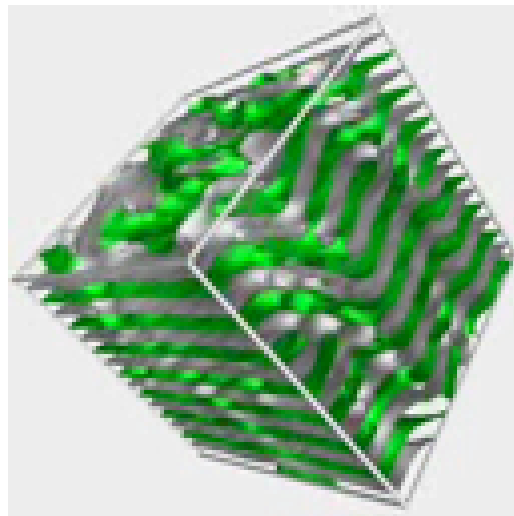
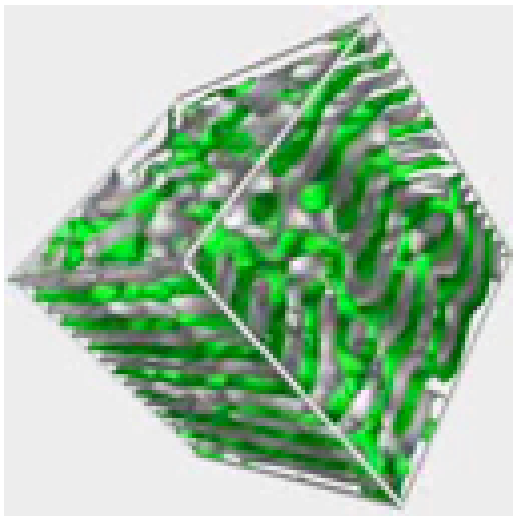
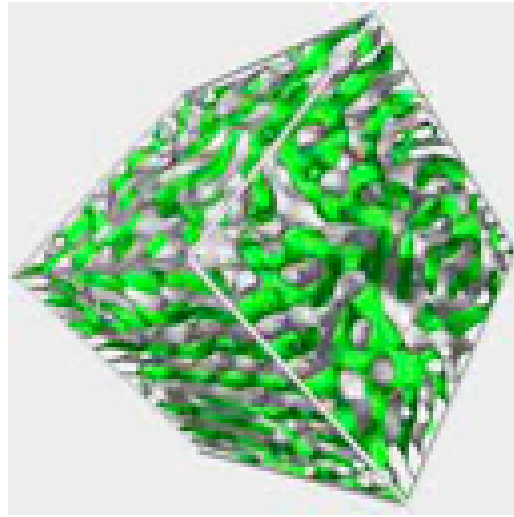
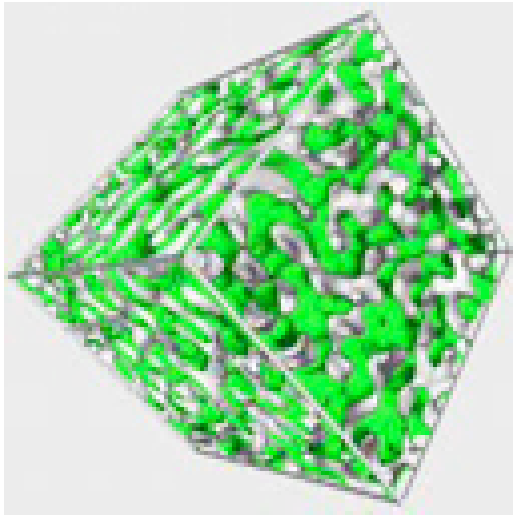
A *function* depends on  $N$  points in space

$$f = f(\mathbf{r}_1, \dots, \mathbf{r}_N)$$


A *functional* depends on  $\infty$  points in space

$$\mathcal{F}[u]$$
$$\mathcal{G}[u](\mathbf{r})$$


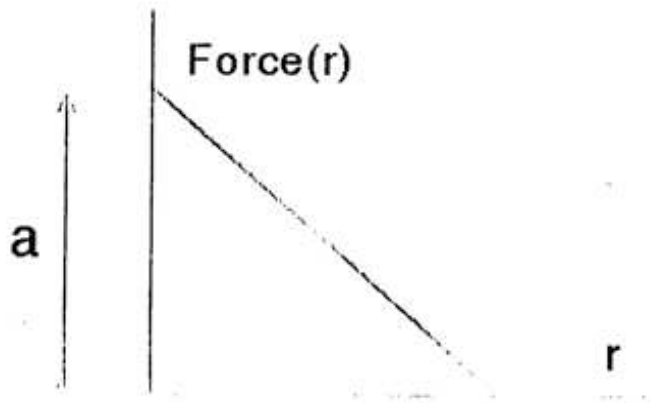
## Block Copolymer Phase Separation Under Shear



*J. G. E. M. Fraaije, et. al. - University of Gronigen  
O. A. Evers & C. Hoffmann - BASF  
Mean-field Density Functional  
J. Chem. Phys., **106**, 4260-69 (1997)*

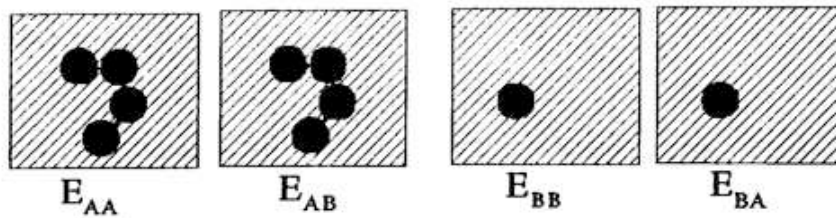
## Dissipative Particle Dynamics

- Use soft repulsive interaction force
- Add pairwise *random* force
- Add pairwise *friction* force
- Integrate Newton's equations of motion



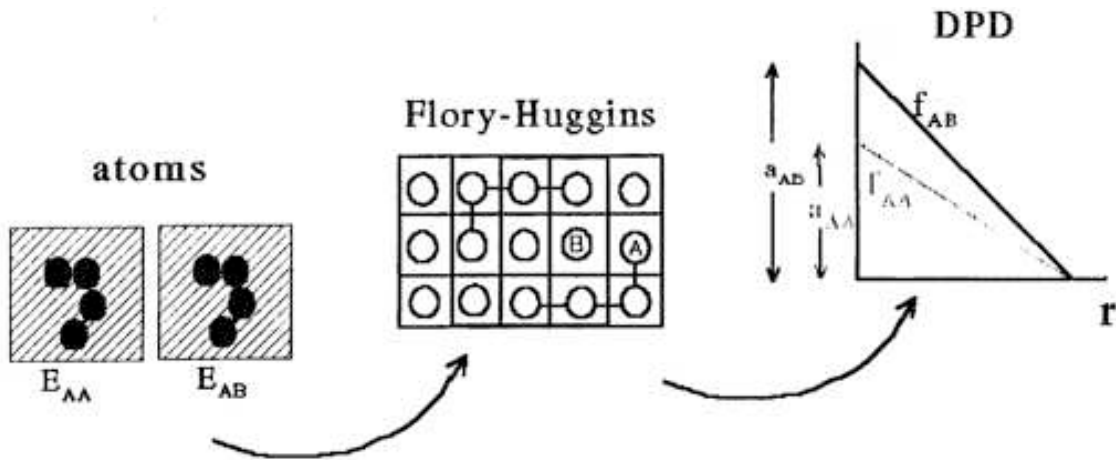
## Flory-Huggins $\chi$ -parameter

- Connection to atomistic simulation



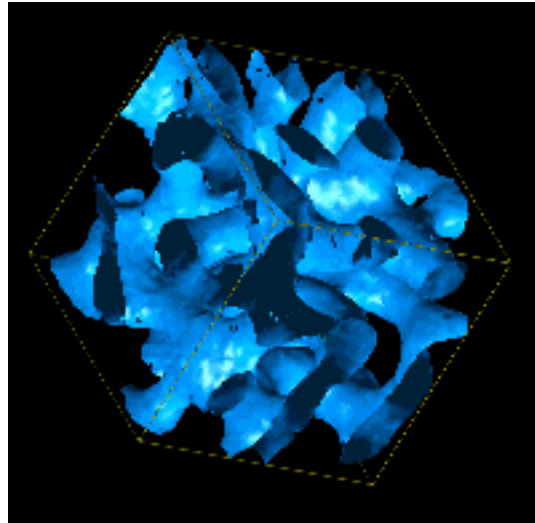
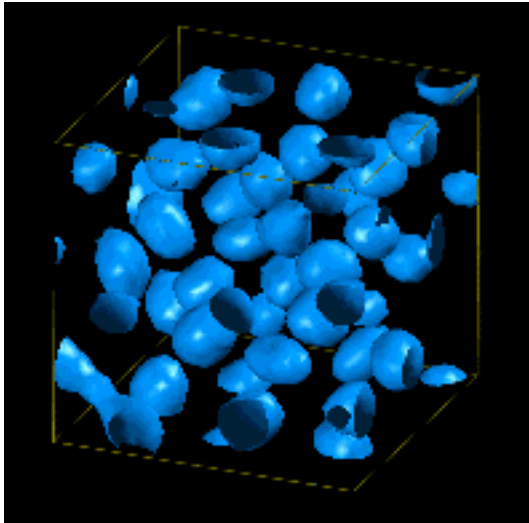
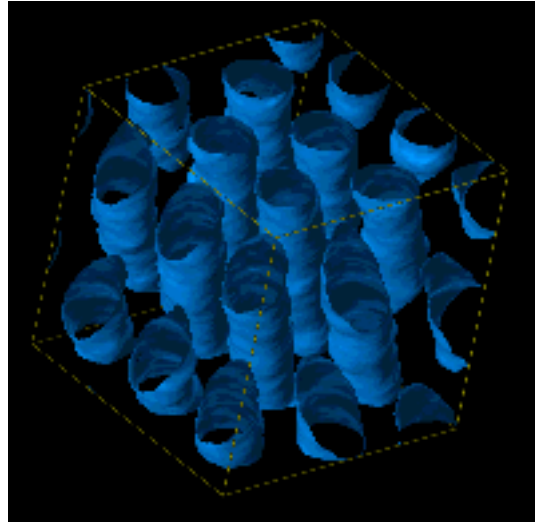
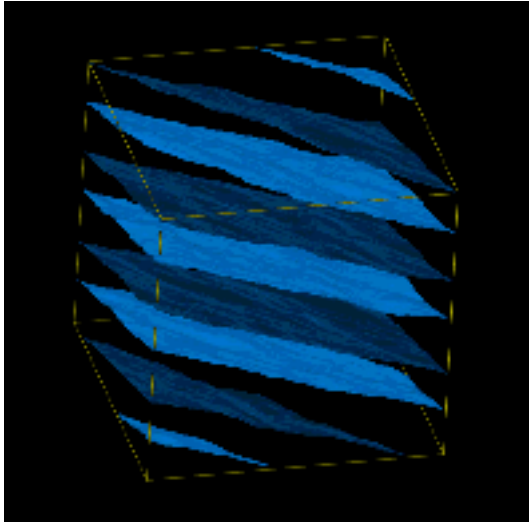
$$\chi = \frac{1}{2k_B T} \left( \frac{E_{AB} - E_{AA}}{N_A} + \frac{E_{BA} - E_{BB}}{N_B} \right)$$

## Mapping atoms on DPD



$$\frac{1}{2k_B T} \left( \frac{E_{AB} - E_{AA}}{N_A} + \frac{E_{BA} - E_{BB}}{N_B} \right) = \chi = (0.306 \pm 0.003) \times \frac{(a_{AB} - a_{AA})}{k_B T}$$

## Copolymer Phase Separation: Morphology vs. Block Size



*R. Groot & T. Madden - Unilever Research  
Dissipative Particle Dynamics  
submitted to J. Chem. Phys.*

## Summary

- **Computational Methods to Complement Traditional**
- **Molecular Modeling for Molecular Level Processes**
  - Molecular Mechanics
  - Quantum Mechanics
  - Density Functional Theory
- **Bridge to Larger Scale**
  - Condensed Phases
  - Bulk Properties