Applied Statistical Mechanics
Lecture Note - 1

Introduction

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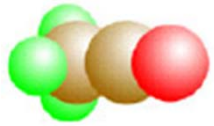
Contents of This Lecture



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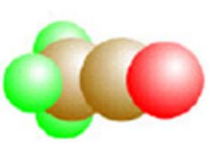
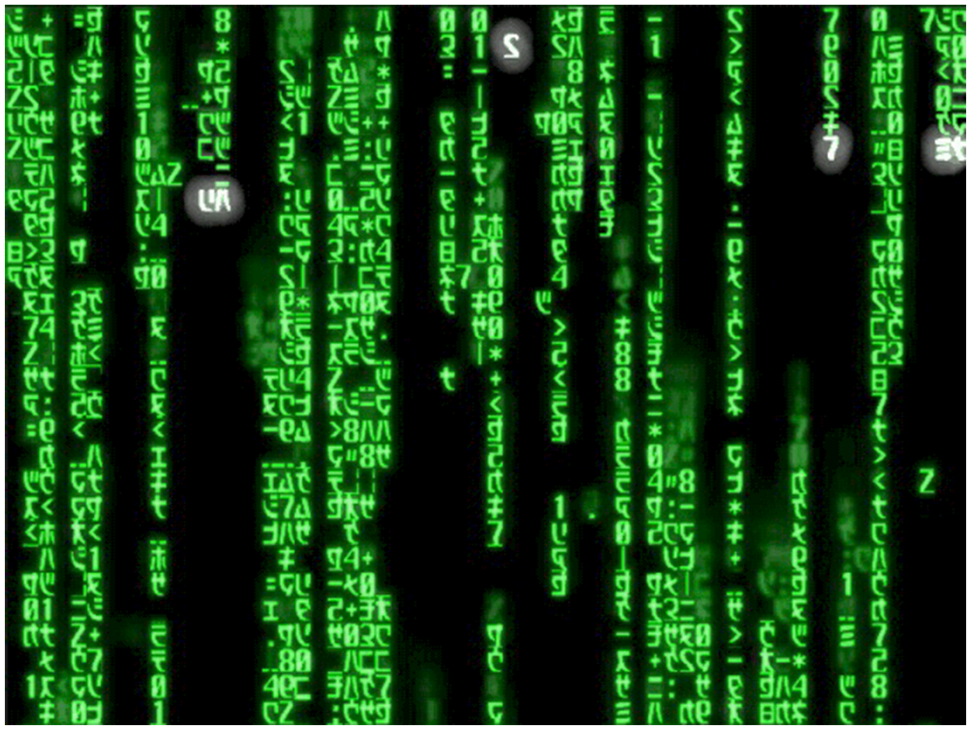
- Applied Statistical Mechanics and Related Subjects for “Molecular Modeling”

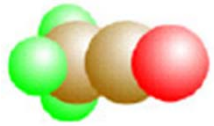
If you believe Matrix …



- There are no experimental data, only simulated data ….



Molecular Modeling…



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- Computational Quantum Chemistry
  - Numerical Solution to Schrodinger equation
    - Computationally intensive for small molecules
    - In principle, yield exact electronic structure and energy as limiting case of increasingly accurate method (HF, MP2, MP4, ….)
    - DFT (Density Function Theory) is approximate but fast
- Molecular Simulation
  - Monte Carlo Simulation
  - Molecular Dynamic Simulation
  - Both require intermolecular and intramolecular potentials (force field) as input

Molecular Simulations

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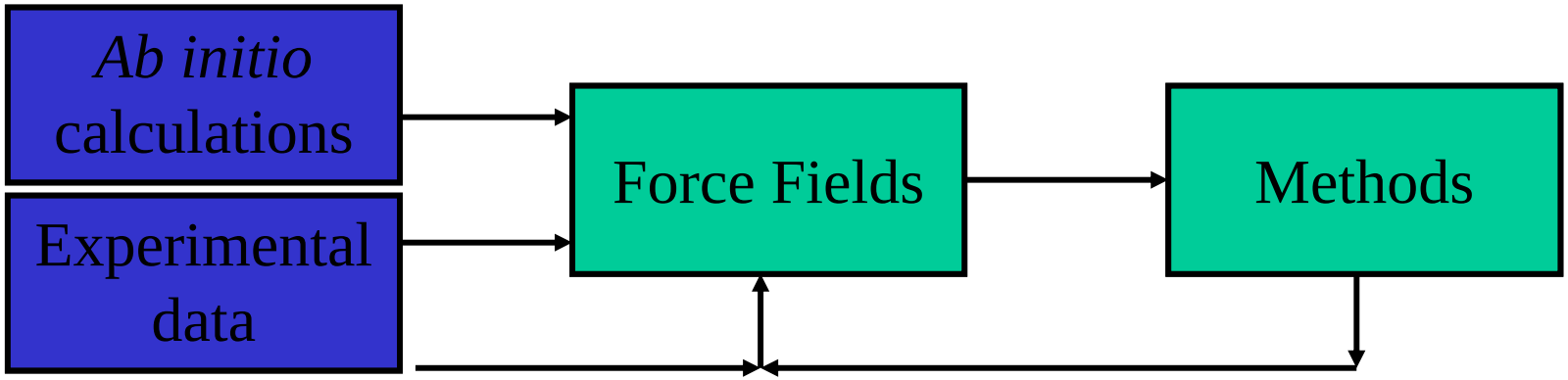

Theory vs. MM

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Quantum Mechanics

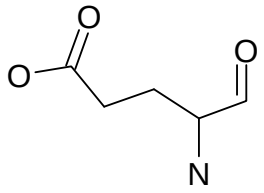
Classical Mechanics

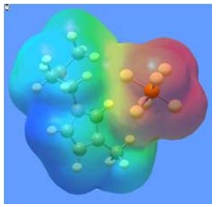
Statistical Mechanics

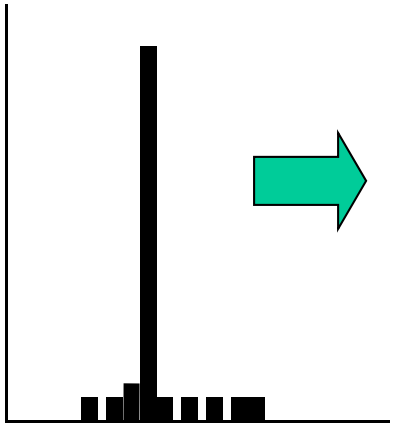
Approximate Theory

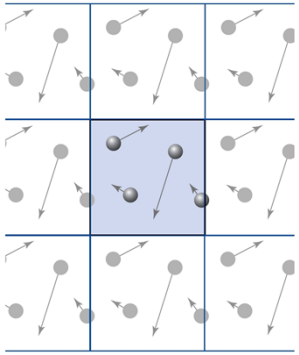
Molecular Simulation

Physical Properties





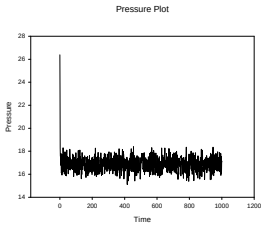




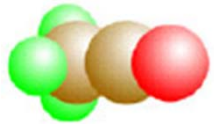
T,P

U,H,A,G,S

μ,Cp,…



Molecular Simulation / Experiment / Theory



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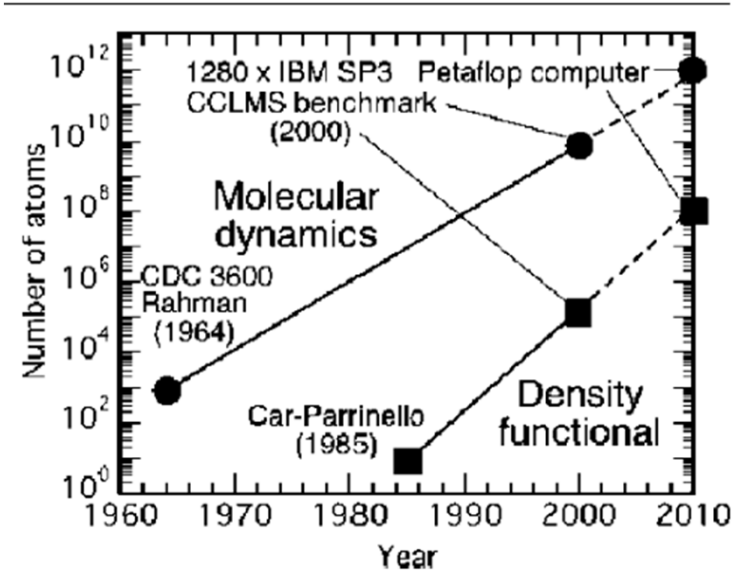
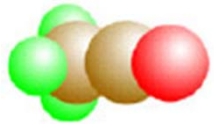
- Advances in Hardware and Software : Moore's Law
  - Computing speed doubles every 18 months
  - Order of magnitude every 5 years
  - Add 2-3 orders of magnitude using parallelization
- Experimental Cost
  - Labor intensive, high capital cost
- Theory
  - Labor intensive
  - Do graduate students and lab equipment improve by and order of magnitude every five years ?



Time Scale and Space Scale in Molecular Modeling



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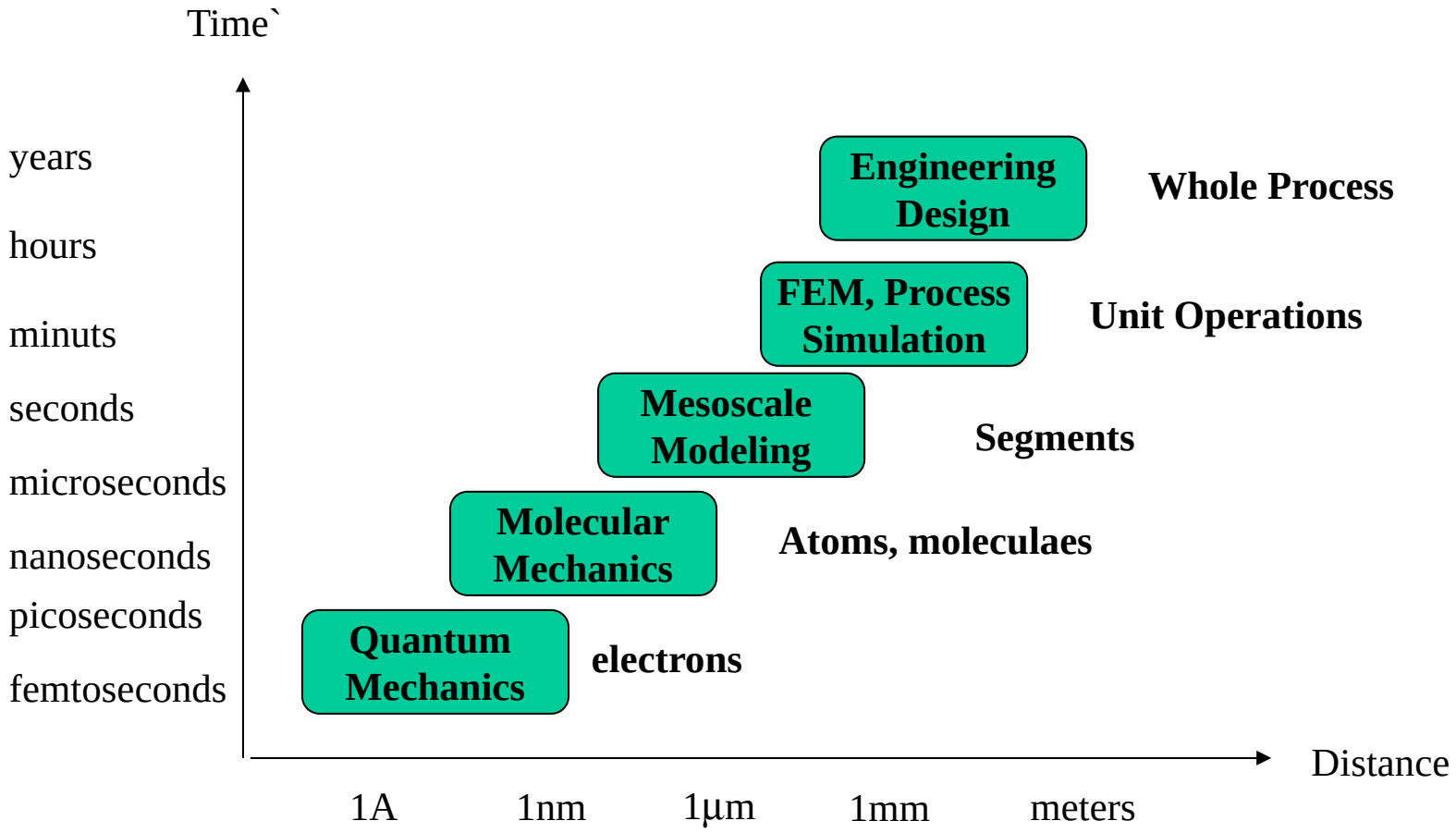
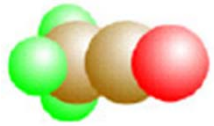


Computational Chemistry



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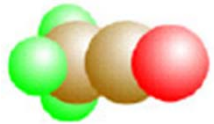
- Quantum Scale
  - Solve Schrodinger Equation
  - Electronic structures of atoms and molecules
  - Results are often used in the design of force field providing connection to next scale
- Atomistic or Molecular Scale
  - Molecular dynamics or Monte Carlo Simulation
  - Force fields are required
  - Thermophysical properties and transport properties using statistical mechanics
- Mesoscale
  - Systems composed of too many atoms
  - Polymers , block copolymers, …

Bridge between molecular modeling and process simulation



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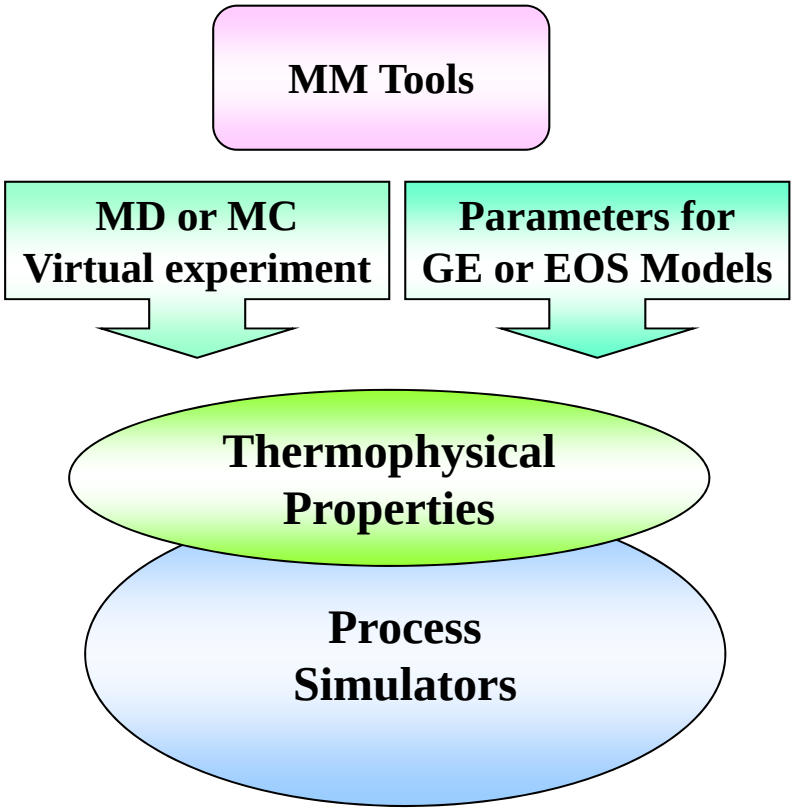
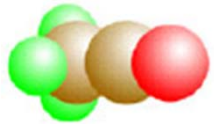
- More than 75 % of code in process simulator is physical property estimations, calculation and prediction
- Physical property availability plays important role in process simulator
- Role of Molecular Modeling tools
  - Generation of thermophysical properties data by means of virtual experiments
  - Generation of parameters to be used in semi-empirical model built in process simulators`



Molecular Modeling and Process Simulation : Next Generation Process Simulator



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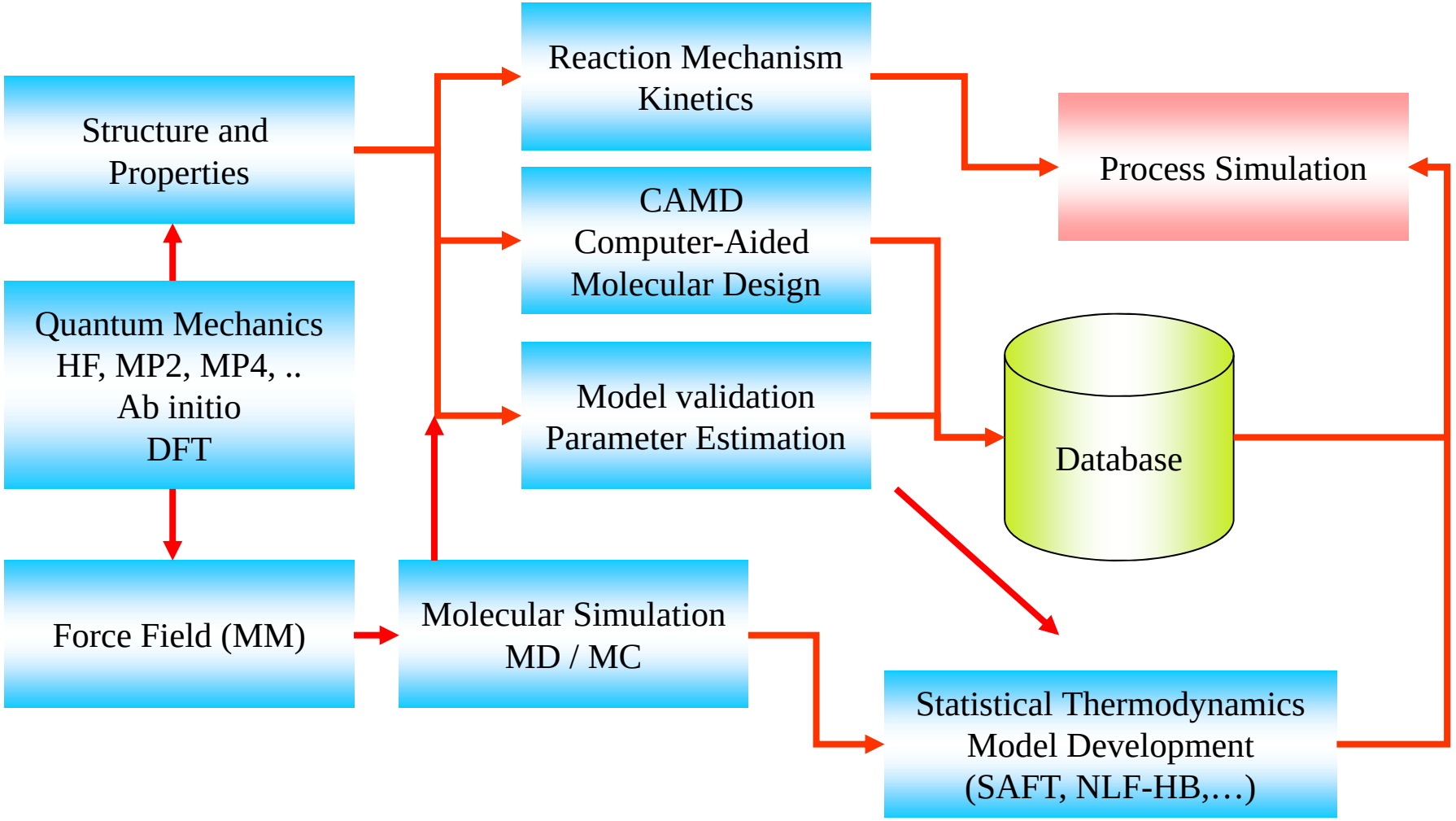
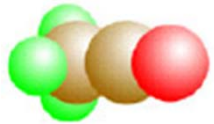


Industrial Cases …
Westmore et al. (ITRC Report)



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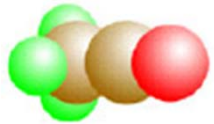
Application	
High volume chemicals and p	
Sorbents for gas sepa	oducts
Polymer, glass a	55 l
Electronic an	m
Catalyst	
Dye and pigme	
Fuel and automo	izol
Bio-active material (pharm	erial (pharmaceutical)
Film and imaging	Fuji-photo, Xerox
Crop-protection che als	Dupont, Sumimoto chemicals
Software and Ha ware	MSI , Accelrys, Gaussian, COSMOlogic

A lot of European and Japanese companies are also interested in molecular modeling and its application !
Also including conventional prediction methods !

Examples of Molecular Modeling



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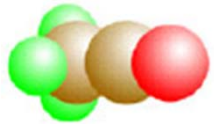
- Simple properties estimation
  - Heat of reaction, heat of formation
  - Properties for complex molecules
  - Properties at nono spacing
- Model parameters estimation
  - Critical constants
  - Parameters for a specific model
- Theory development/validation
  - Self association model for SAFT EOS
- Structure prediction
  - Protein folding problem
- Computer-Aided Molecular Design (CAMD)
  - Group contribution based design
  - QM/MM application
- Phase equilibrium calculation

Simple Properties Estimation using QM / MM



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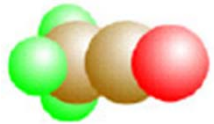
- Heat of reaction / Heat of formation
  - G2 Method (Pople et al. J.Physics, 1989)
    - A high level ab-initio method (from quantum mechanics)
  - Case 1

    $NH{=}CHNH_2 + CH_3{-}N{=}CH{-}CH_3 \rightarrow CH_3{-}N{=}CH{-}NH_2 + NH{=}CH{-}CH_3$
    - Heat of reaction using Benson Method : 0 kJ/mol
    - Heat of reaction using G2 Method : 1.8 kJ/mol

    Prone to hydrolysis and decomposition
  - Case 2
    - Heat of formation for THP (1,4,5,6-tetrahydropropyrimidine)
      - DIPPR Project 871 : 13.2 + 0.5 kcal /mol
      - G2 Method : 18.9 + 0.1 kcal /mol
        - » 40 hours on CRAY C-90 computer and 10 GB storage space
    - **G2 Method is believed to be more accurate !**

Properties of Complex Molecules



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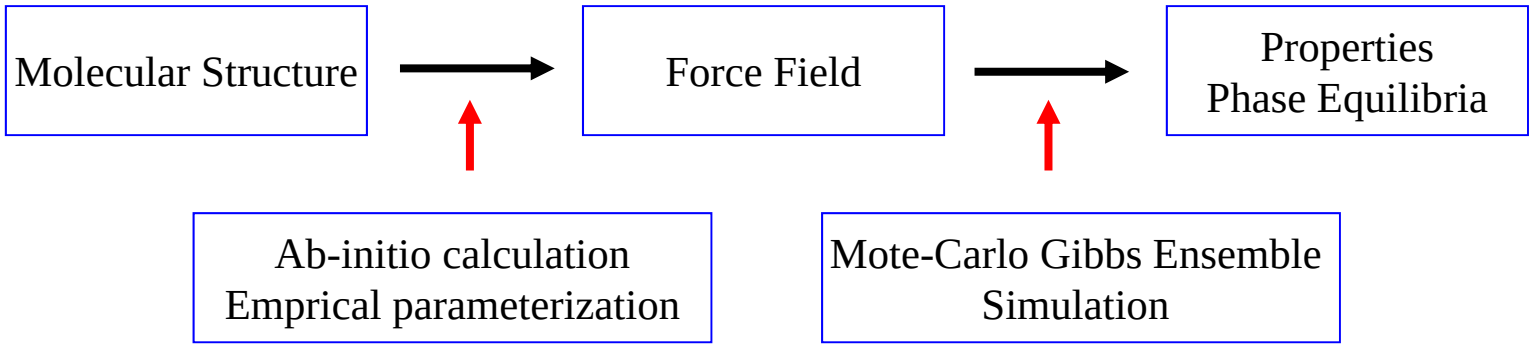
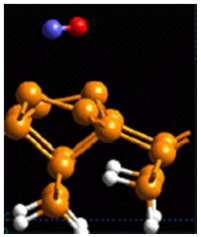
- Properties Prediction for alternative refrigerant (HCFCs)
- Fermeglia et al. FPE, 2003
  - Accurate force field (FF) calculation is most important factor
  - FF is important due to complex nature of molecular associations in H-F bonds



Software : Cerius v. 4.2 from Accelys Inc.
Hardware : Silicon Graphics Origin 2000



Properties of Complex Molecules

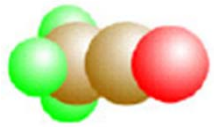


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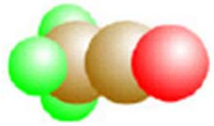
Table 1 – *Predicted vapor pressure P°, saturated liquid volume V_L and volumetric properties ρ for selected Chloro Fluoro Hydrocarbons*

$$AAD = Absolute\ Average\ Deviation = 100 \cdot \frac{1}{N} \sum_i \left| \frac{M^{exp} - M^{calc}}{M^{exp}} \right|$$

CFHs	PVT	VLE				
	P range (10^2 kPa)	T range (K)	AAD ρ (%)	P^0 range (10^2 kPa)	AAD P^0 (%)	AAD V_L (%)
R13	5 – 20	150 – 240	1.79	0.03 – 15.93	3.36	2.35
R14	6 – 20	110 – 200	1.93	0.07 – 15.50	1.71	2.27
R21	3 – 10	220 – 310	1.69	0.03 – 23.96	3.08	3.05
R22	5 – 20	250 – 340	1.59	1.77 – 19.82	4.62	1.16
R23	2 – 10	200 – 290	1.65	0.03 – 20.02	5.98	1.78
R32	12 – 98	253 – 333	3.74	3.47 – 8.64	4.33	2.66
R113	1 – 8	270 – 360	3.09	0.10 – 15.03	3.12	5.24
R114	1 – 8	300 – 390	1.16	0.11 – 8.67	4.43	2.91
R115	1 – 8	210 – 300	2.11	0.20 – 10.88	2.17	2.97
R123	1.013	203 – 393	0.622	0.12 – 21.022	3.30	4.29
R134a	8 – 20	285 – 374	1.79	2.16 – 4.27	5.34	0.722
R142b	1.03 – 3.45	266 – 350	1.90	1.14 – 6.20	2.10	1.01
R143a	5.74 – 8.26	274 – 364	2.66	0.25 – 17.5	2.37	3.76
R152a	1.03 – 3.10	266 – 350	1.01	1.09 – 14.3	1.42	1.61

Model Parameter Estimation - Critical Constants



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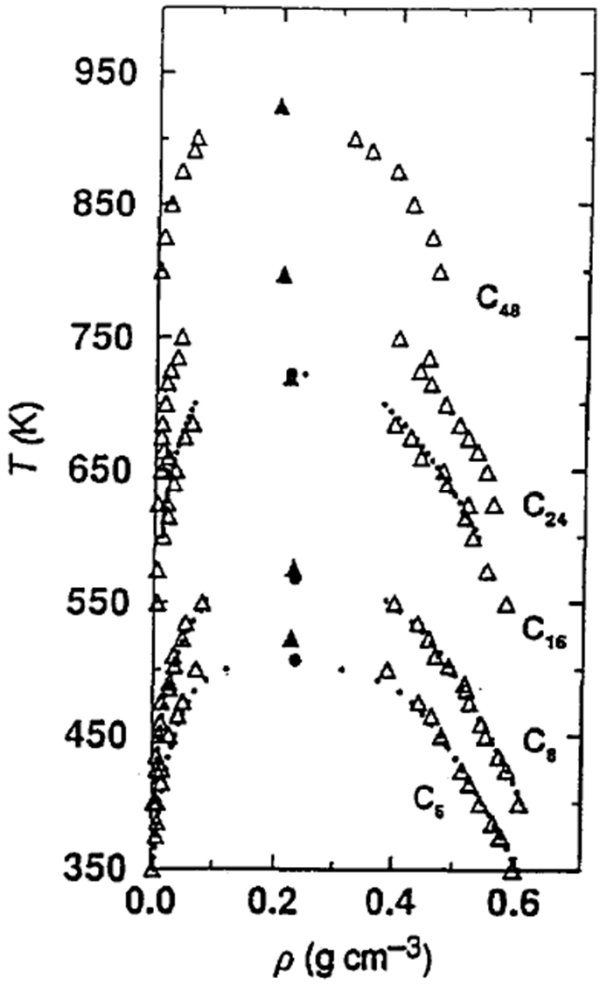
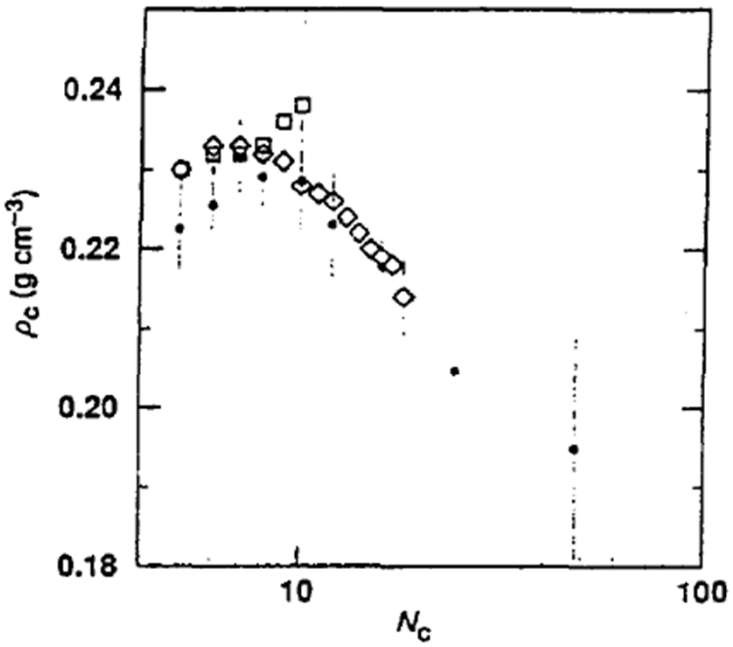
- Critical constants are normally used for parameters of cubic EOS.
- Panagiotopoulos (1987) proposed a new method for the simulation of vapor-liquid equilibrium (**Gibbs Ensemble Method**)
- Using Gibbs Ensemble Method, Smit and coworkers (Siepman et al., 1993) calculated coexistence diagram for normal paraffins to Nc = 48.



Model Parameter Estimation - Critical Constants

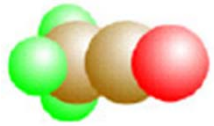


Critical densities of the normal alkanes (ρ_c) as a function of carbon number (N_c). The experimental data of Anselme et al are represented by diamonds, the data of Steele by squares and the results from the simulations by filled circles.

- □ Data of Steele (1993)
- ◇ Data of Ansleme (1990)
- ● Simulation (Siepman, 1993)

Data of Anselme shows maximum at Nc= 8 while data of Steele does not. Simulation calculations have settled the disagreement

Parameters for a specific model



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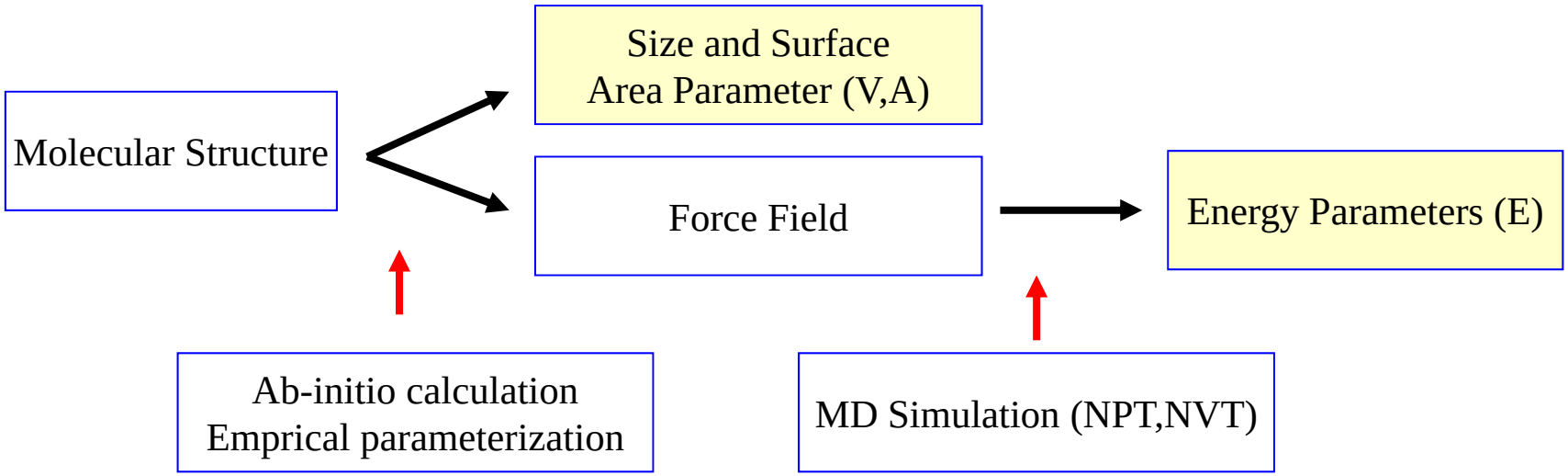
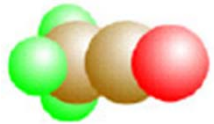
- Fermeglia et al. (1999, FPE)
  - Parameters for PHSCT (Perturbed Hard Sphere Chain Theory) EOS of several CHFs were estimated molecular modeling approaches.

Software : Cerius v. 4.2 from Accelys Inc.
Hardware : Silicon Graphics Origin 2000



Theory Development and Validation



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- Alder and Wainright(1957, 1959)
  - MD Simulation of Hard Sphere
  - Foundation of Carnahan-Starling EOS and SAFT EOS ,…
- Chapman and Coworkers

  (1999, FPE)
  - Validation of inter + intra-molecular hydrogen bonding model comparing with MC calculation

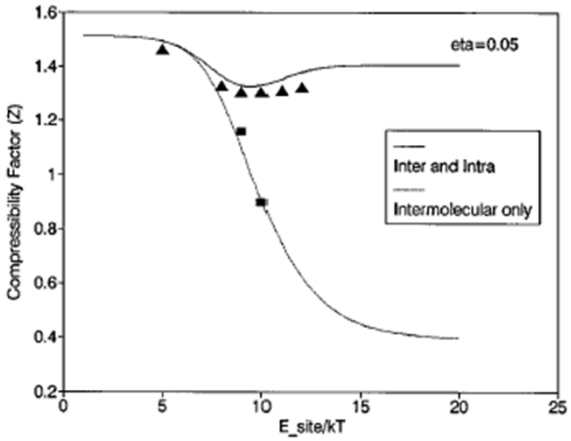

FIG. 6. Compressibility factor vs ϵ_{site}/kT at η=0.05. Symbols represent simulation results, solid triangles (inter- and intramolecular association), solid squares (no intramolecular association). Curves represent predictions from theory.

Product Design

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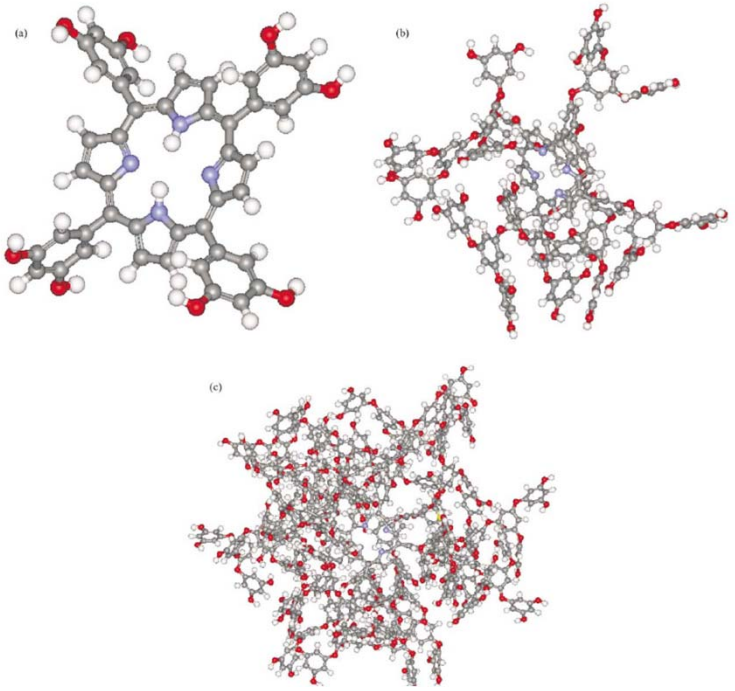
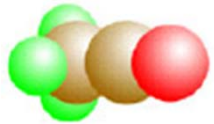
- Drug and Product Design have been long studied in the field of pharmaceutical industries and chemical industries.

- Dendrimer as an alternative for human blood ingredient (Fermaglia et al. 2002, Bioorganic and Medicianl Chemistry)



Product Design



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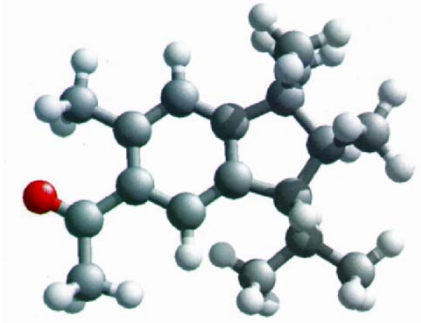
- Ionic solutions
  - Promising candidate for clean solvent
  - Almost infinite number of candidate ionic solution exist due to the variations in cation-anion pair combinations
  - Property measurement / process design is not a primary issue in this subject.
  - The structure-property relationship is the essential problem for the design of a ionic solution as a specific solvent



An almost infinite range of ionic liquids can be made by varying the ions used.

Property-Structure Relationship using COSMO-therm *(K. Marsh, MTMS '03 , 2003)*

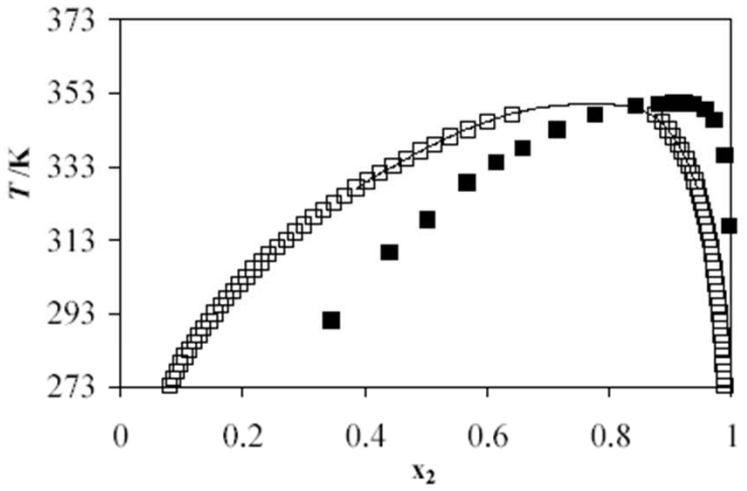


Figure 2a. Comparison of LLE phase diagram for the systems [C6mim][PF6] (1) + butan-1-ol (2) at 1 bar with values calculated from COSMOtherm: ■, experimental; □, COSMOtherm; —, eq 1 fit to COSMOtherm.

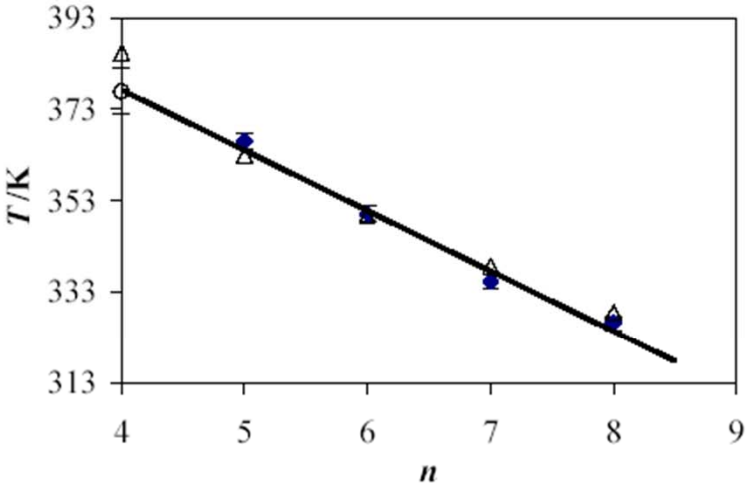
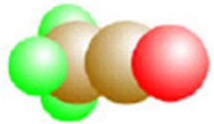


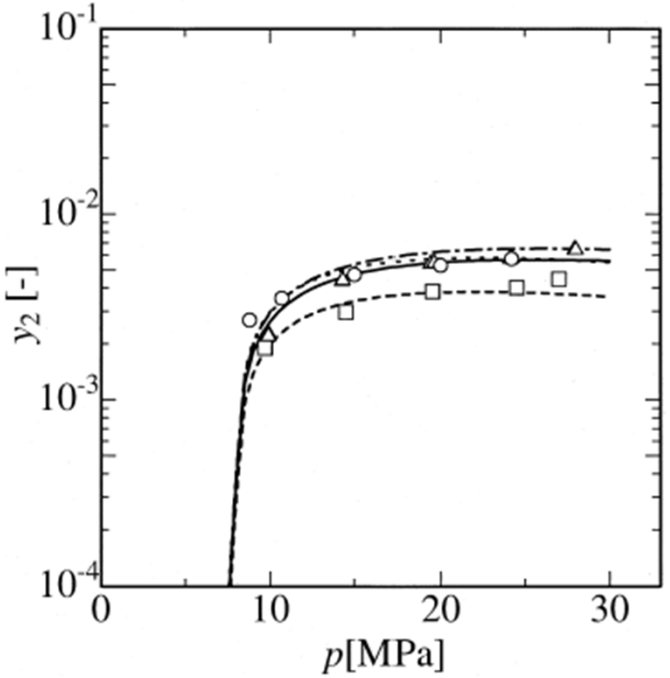
Figure 2b. Relationship between the UCST and the number of carbon in Rn: ◆, experiment; ○, 1-butyl estimated from experimental data; Δ, COSMO*therm.*

Obtaining Parameters for Conventional Models using MC Simulation

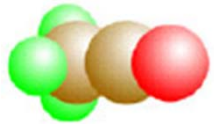


고려대학교

- Arai and coworkers
  - Iwai et al., 1999 , FPE
  - Monte Carlo Simulation using LJ potential and empirical potential parameters
  - Group interaction parameters for isomeric aromatic groups were obtained for PSRK model (UNIFAC parameters)



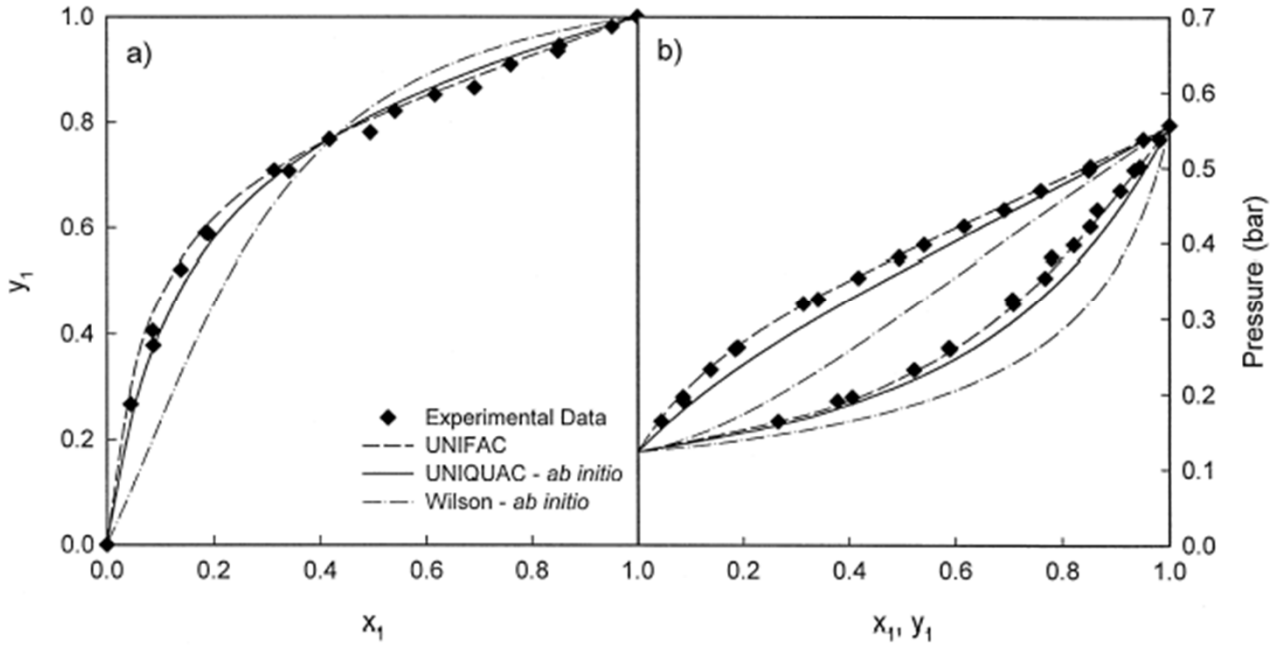
Obtaining Parameters for Conventional Model using QM



고려대학교

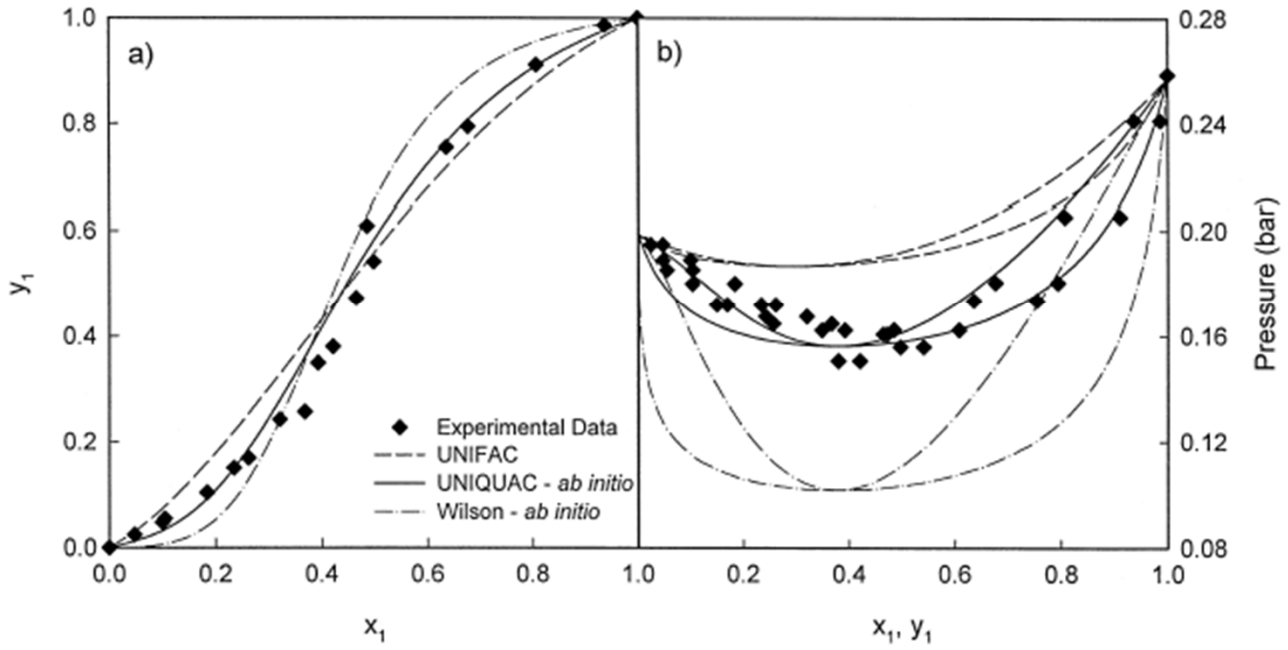
- Sum and Sandler (1999, FPE)
  - Interaction energy parameter for WILSON and UNIQUAC models
  - HF (Hartree Fock) method is used to determine interaction energy between molecular pair in cluster.
  - Gaussian 94 program
  - Wilson Equation
  - UNIQUAC equation

Obtaining Parameters for Conventional Model using QM



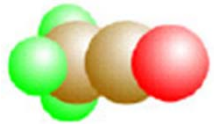
Methanol + Water system at 323.15 K

Obtaining Parameters for Conventional Model using QM



Formic acid + + Water system at 323.15 K

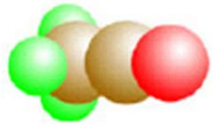
COSMO-RS



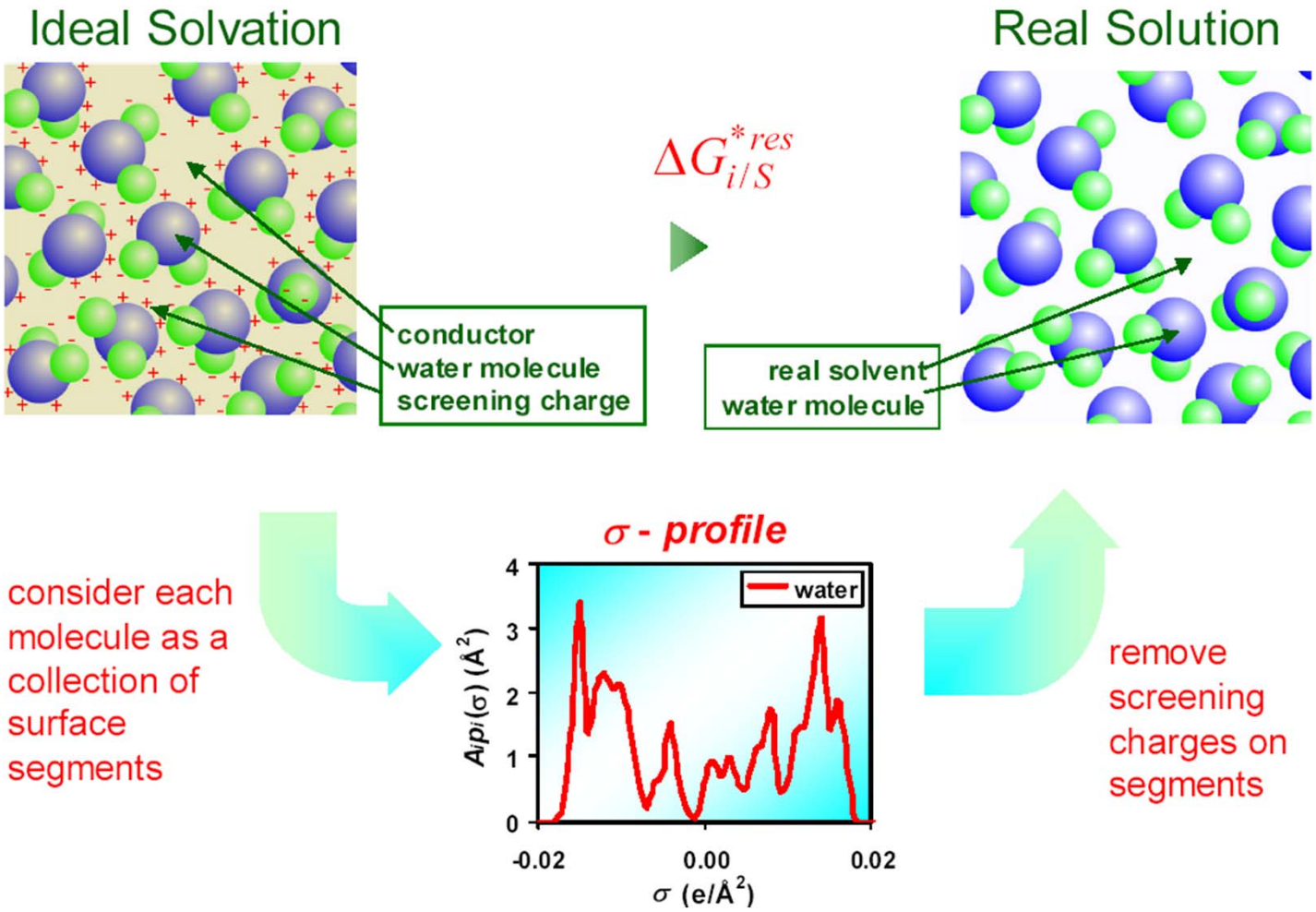
고려대학교

- Conductor-like Screening Model for Real Solvents
  - Developed by A. Klamt , Bayer (1995)
  - COSMOlogic GmbH, A. Klamt (1999)
    - 1994, Prof. W. Arlt (TU Berlin) Joined as a collaborator
    - 2001, ROYOKA Systems (Japan) have started long-term strategic collaboration
    - APEN Plus is planning to include COSMO –RS or related product in 2004

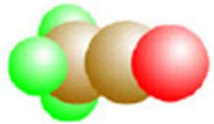
Basic idea of COSMO-RS



고려대학교



COSMO-therm



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Chemical potential calculation using statistical thermodynamics

$$p_S(\sigma) = \sum_{i \in S} x^i p^{X_i}(\sigma). \qquad p'_S(\sigma) = p_S(\sigma)/A_S = p_S(\sigma) \Big/ \sum_{i \in S} x^i A^{X_i}.$$

$$\ln\{\gamma_S(\sigma)\} = -\ln\left\{\int d\sigma' p'_S(\sigma')\gamma_S(\sigma')\exp\left(-\frac{a_{eff}e(\sigma,\sigma')}{RT}\right)\right\},$$

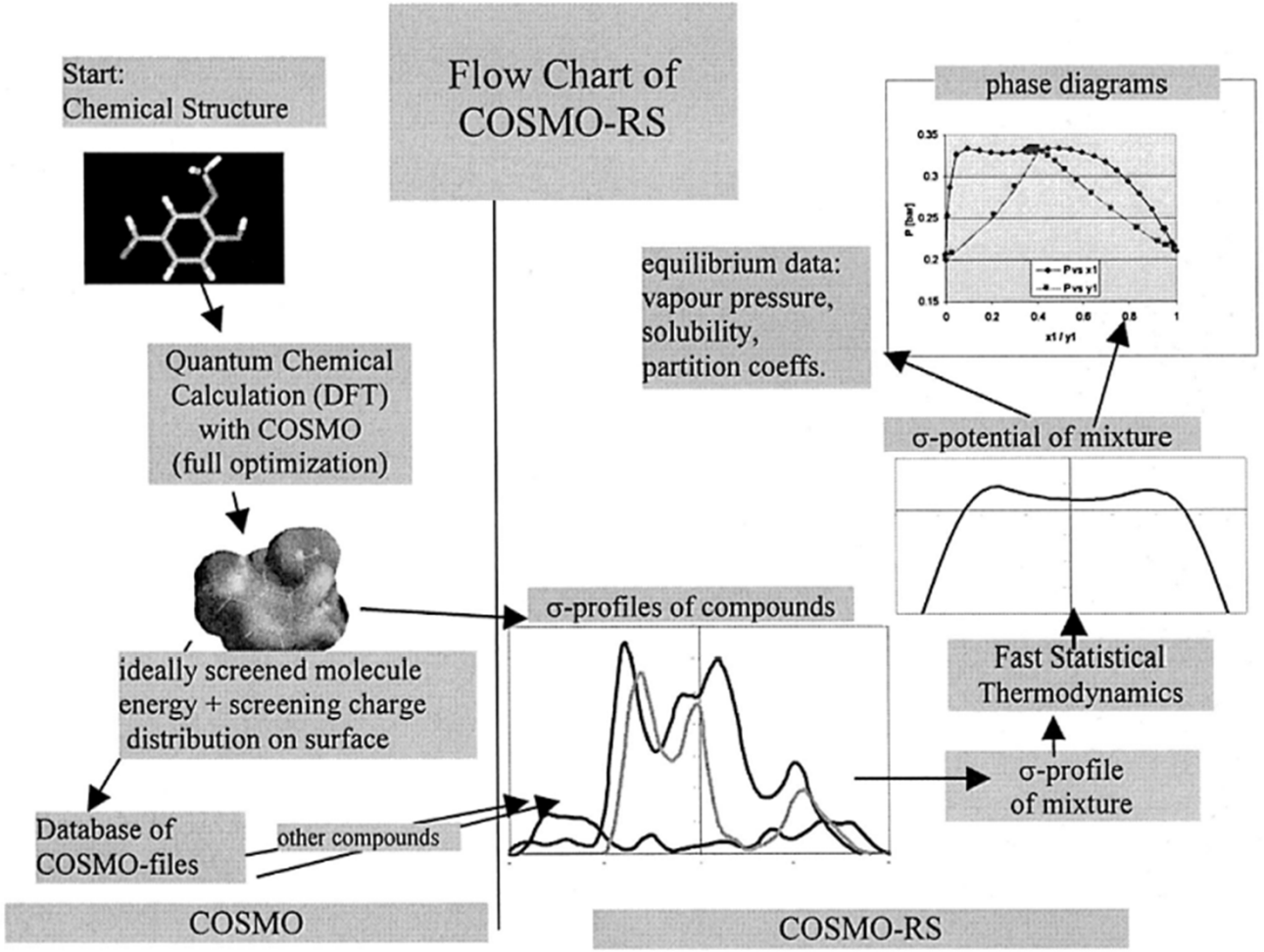
$$\mu_S(\sigma) = -RT\ln\left\{\int d\sigma' p_S(\sigma')\exp\left(\frac{\mu_S(\sigma') - a_{eff}e(\sigma,\sigma')}{RT}\right)\right\}.$$

$$\mu_S^X = \mu_{resS}^X + \mu_{combS}^X = \int p^X(\sigma)\mu_S(\sigma)d\sigma + \mu_{combS}^X,$$

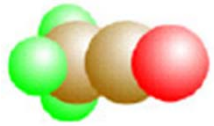
$$\mu_{combS}^X = -RT\left\{\lambda \ln A_S + L_1^{SG} + \frac{z}{2}\frac{V^X}{V_0}L_2^{SG}\right\}$$

Guggenheim –Starvermann Term

Flow chart of COSMO-therm



Applications



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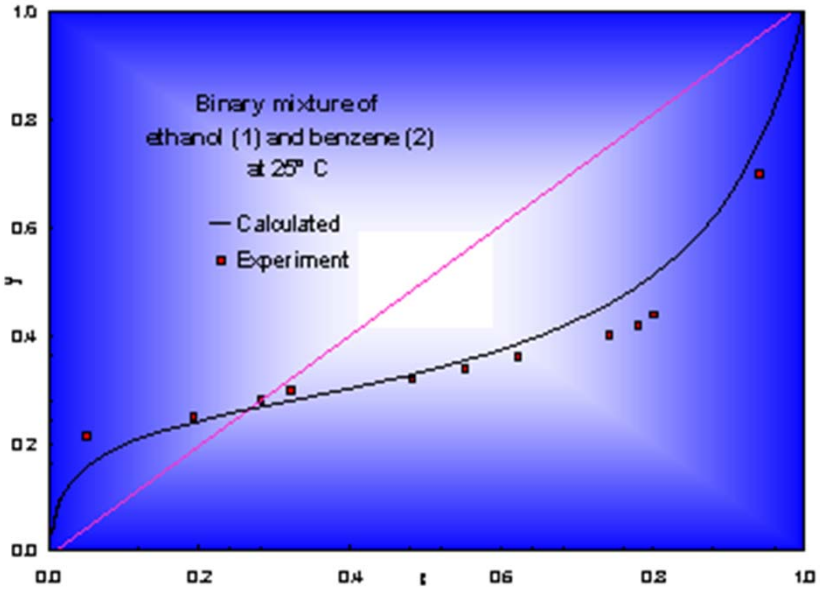
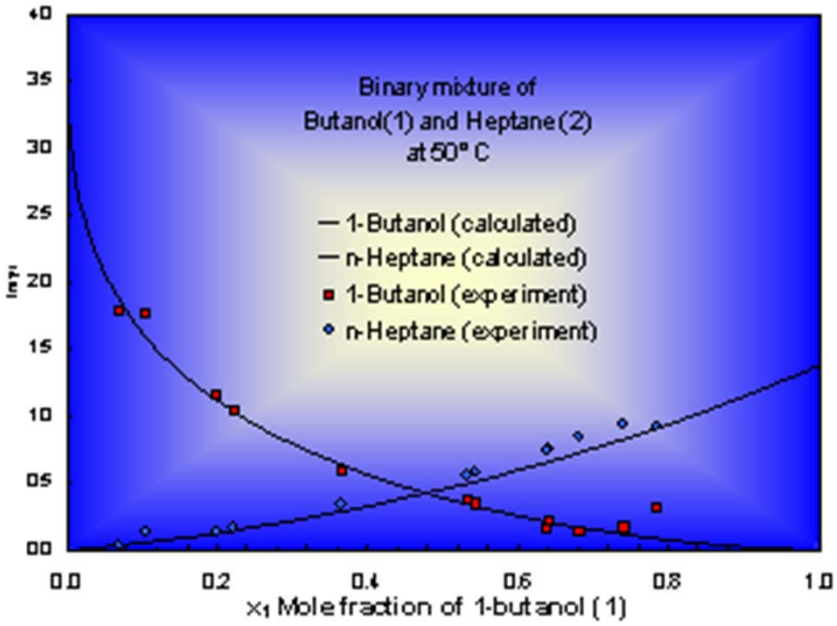
- **Vapor-Liquid Phase Diagram**
- **Activity Coefficients**
- **Excess Properties**
- **Isomeric Effects**
- **Temperature Dependency**

- **Water Solubility**
- **Brood-Brain Partitioning**
- **Intestinal Absorption**

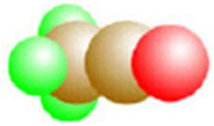
VLE applications





Find more results at
http://www.cosmologic.de

Purpose of This Lecture

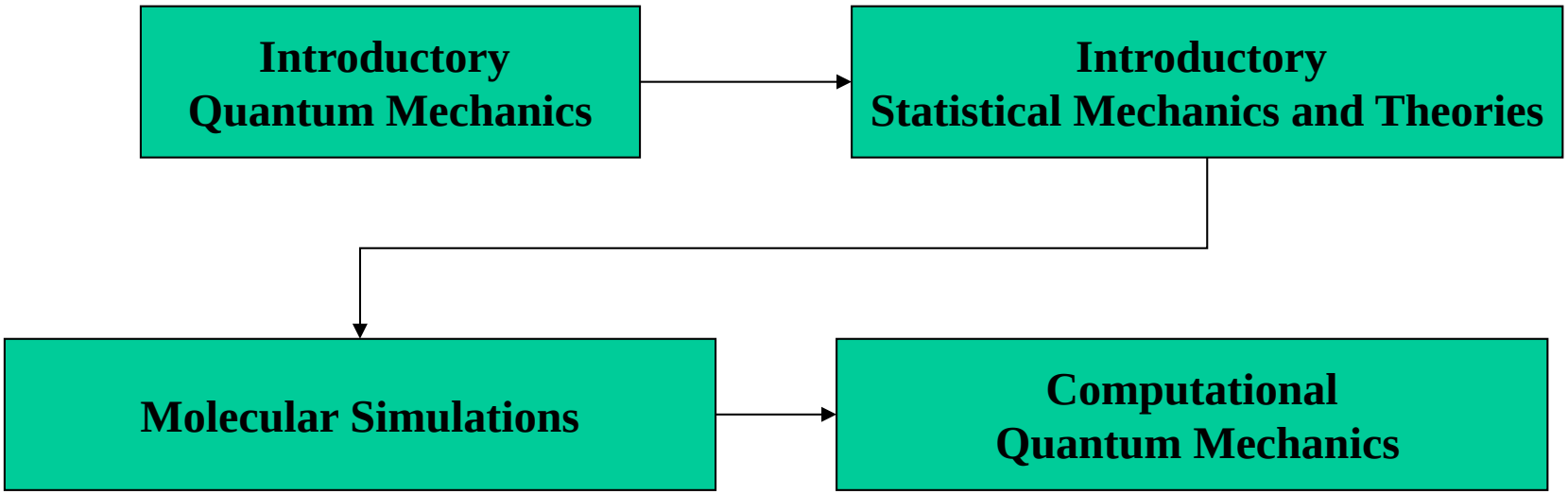


고려대학교

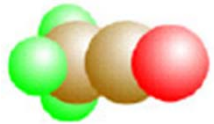
- To be able to use molecular modeling softwares
  - Computational Quantum Chemistry Tools
    - HF, MP2, MP4, …
  - Computer Simulation Tools
    - MC, MD, ..
- Brief introductory lectures on…
  - Introductory Quantum mechanics
  - Principles of Statistical Mechanics
  - Molecular Simulations
  - Computational Quantum mechanics

Subjects …

고려대학교



Grading…



고려대학교

- 시험 : 1회 (학기말) 50 %
- 발표 : 1회 (학기말) 50 %
- 출석 : 학교 기준 만족