POLYMER MODELING IN INDUSTRY
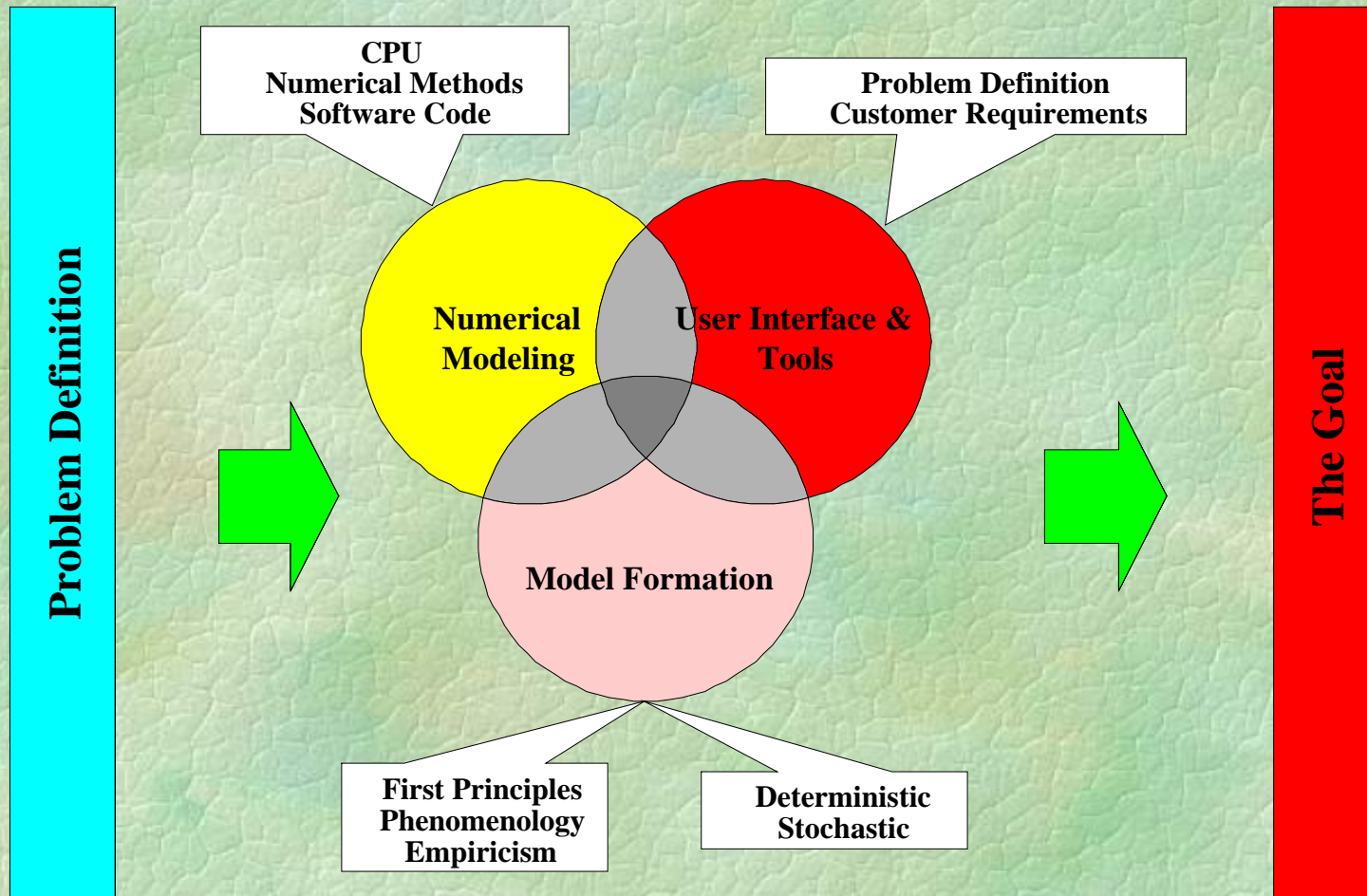
Jozef Bicerano, Ph.D.
Bicerano & Associates, LLC

For further details on most of the work summarized in these slides, see J. Bicerano, S. Balijepalli, A. Doufas, V. Ginzburg, J. Moore, M. Somasi, S. Somasi, J. Storer and T. Verbrugge, "Polymer Modeling at The Dow Chemical Company", *J. Macromol. Sci.-Polymer Reviews*, *44*, 53-85, 2004.

INTEGRATED MODELING APPROACH
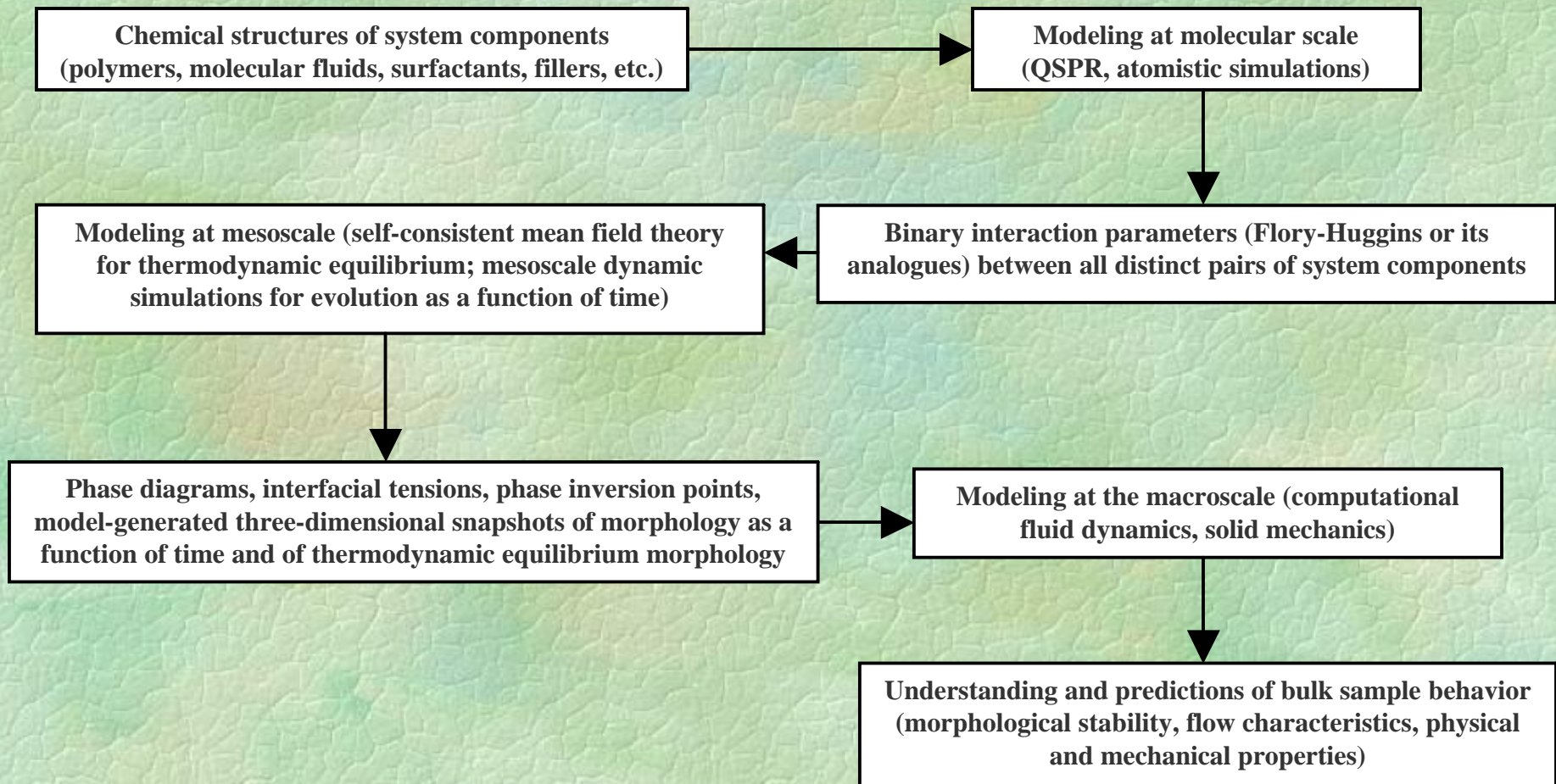
- New product and/or process development in industry requires attention to many (and often contradictory) considerations:
  - Formulation design.
  - Raw material costs.
  - Processing costs.
  - Product performance targets.
  - Market trends.
  - Governmental regulations.

- A multidisciplinary and integrated modeling approach is desirable since the relevant materials science encompasses many phenomena.

Multidisciplinary Nature of Industrial Modeling

Problem Definition

The Goal

CPU
Numerical Methods
Software Code

Problem Definition
Customer Requirements

Numerical Modeling

User Interface & Tools

Model Formation

First Principles
Phenomenology
Empiricism

Deterministic
Stochastic

"Holy Grail": Multiscale Modeling Paradigm

Chemical structures of system components
(polymers, molecular fluids, surfactants, fillers, etc.)

→

Modeling at molecular scale
(QSPR, atomistic simulations)

↓

Modeling at mesoscale (self-consistent mean field theory
for thermodynamic equilibrium; mesoscale dynamic
simulations for evolution as a function of time)

←

Binary interaction parameters (Flory-Huggins or its
analogues) between all distinct pairs of system components

↓

Phase diagrams, interfacial tensions, phase inversion points,
model-generated three-dimensional snapshots of morphology as a
function of time and of thermodynamic equilibrium morphology

→

Modeling at the macroscale (computational
fluid dynamics, solid mechanics)

↓

Understanding and predictions of bulk sample behavior
(morphological stability, flow characteristics, physical
and mechanical properties)

BRIEF REVIEWS OF SELECTED PROJECTS

- **Mechanical properties of thermoplastics (Jonathan Moore).**

- **Polymer/clay nanocomposites (Valeriy Ginzburg).**

- **Polyol templating (Sudhakar Balijepalli).**

- **Flow-induced crystallization and polymer process modeling (Antonios Doufas and Madan Somasi).**

- **High-throughput polymer design (Sweta Somasi and Jozef Bicerano).**

- **Controlled release of drugs from hydrophilic polymers (Sweta Somasi, Irina Graf, Steve Ceplecha, Daniel Simmons and Jozef Bicerano).**

- **Branched/network polymer structures (Tom Verbrugge).**

- **Water vapor transport in a polymer matrix composite (Joey Storer, Jozef Bicerano and Dave Moll).**

# MODELING MECHANICAL PROPERTIES OF THERMOPLASTIC POLYMERS

Microscopic Properties

Intra-Chain Energies

Inter-Chain Energies

σ ε

ε **Mechanical Property Models**   t

Crystallinity

Tie Chains

Long Chain Branching

σ

t

Experimental Data

via Finite Element Analysis
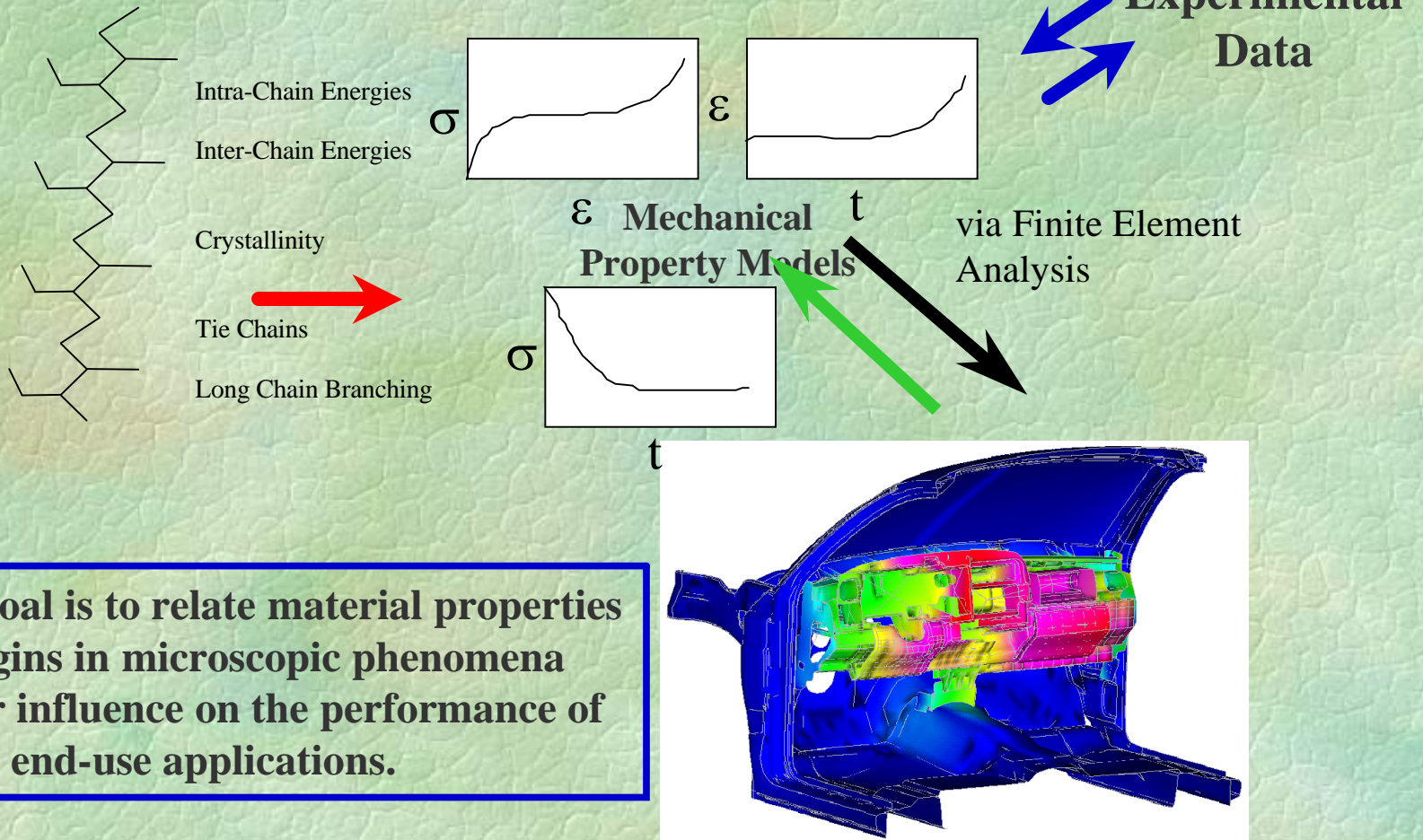
The basic goal is to relate material properties to their origins in microscopic phenomena and to their influence on the performance of products in end-use applications.

Physical Picture for Glassy Thermoplastic Polymers

- **A mosaic of nanoscale clusters:**
  - Distribution of differing cluster viscoelastic characteristics.
  - Fluctuations of the Eyring-type activation energy for yielding induce dynamic inhomogeneities.

- **"Locally yielded" regions that no longer respond elastically (solid black clusters) become more abundant with increasing strain.**
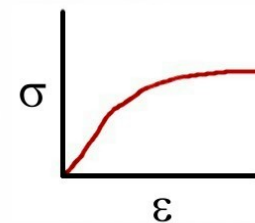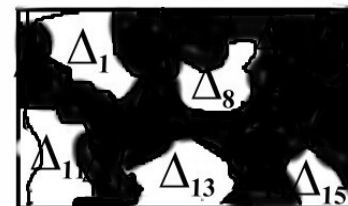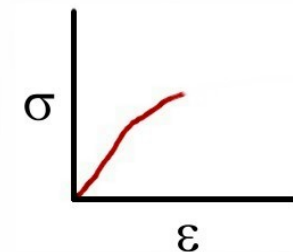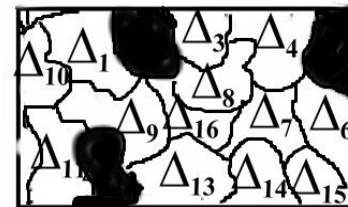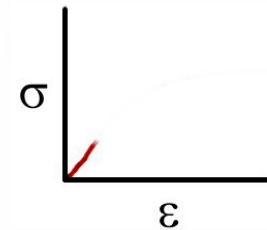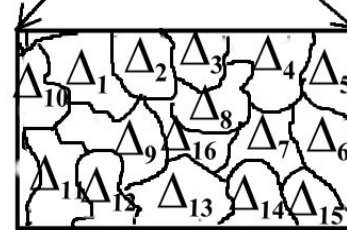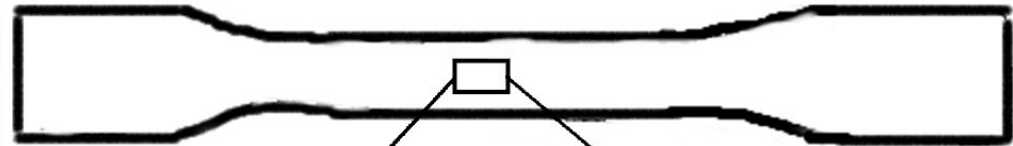
Distribution of Yield Characteristics Related to dσ/dε
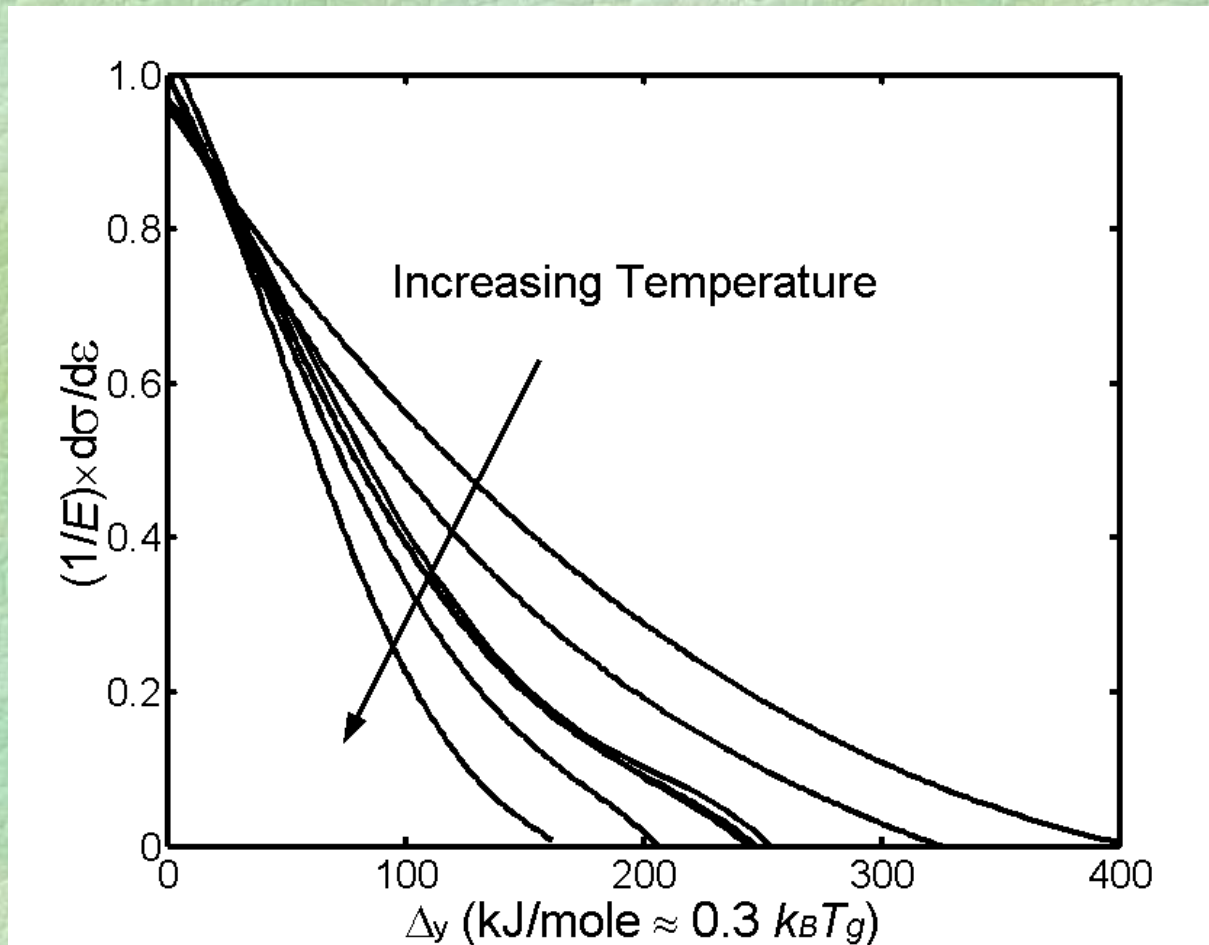
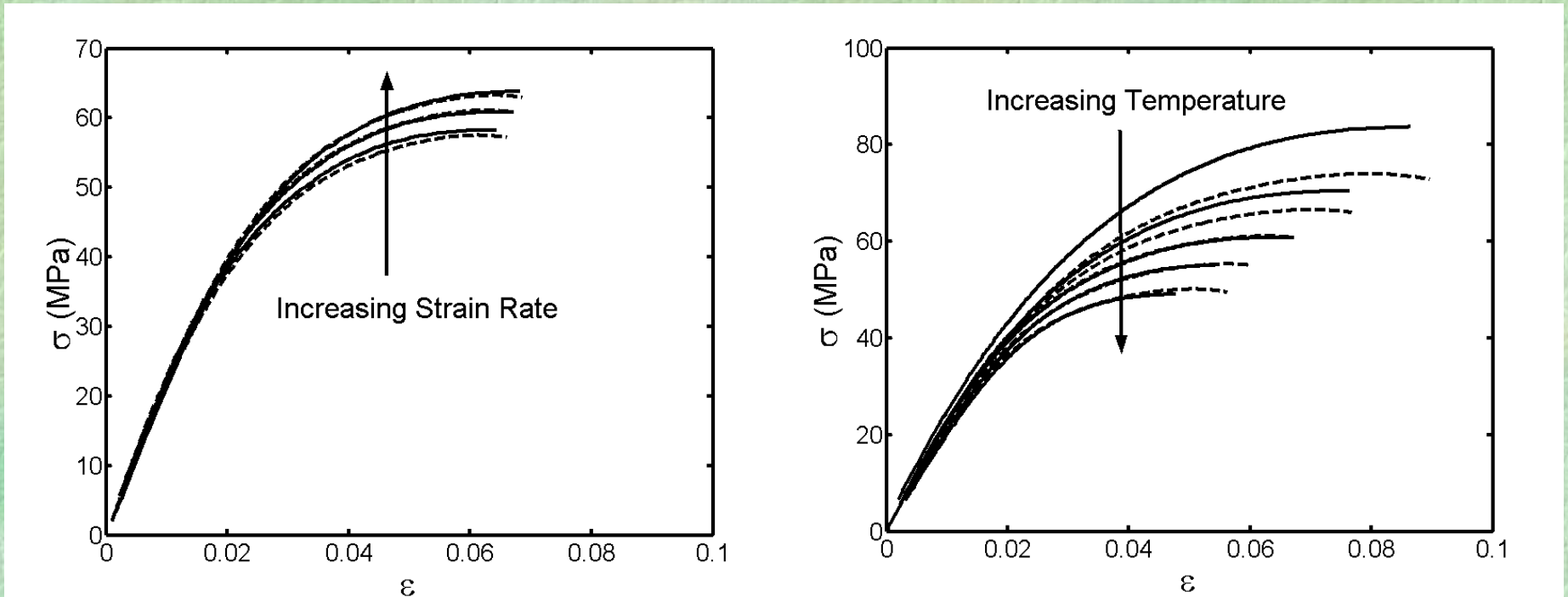Bisphenol-A polycarbonate

MFR ~ 10

233 < T (K) < 338

1.6×10^{-3} < strain rate (sec^{-1}) < 1.6×10^{-1}
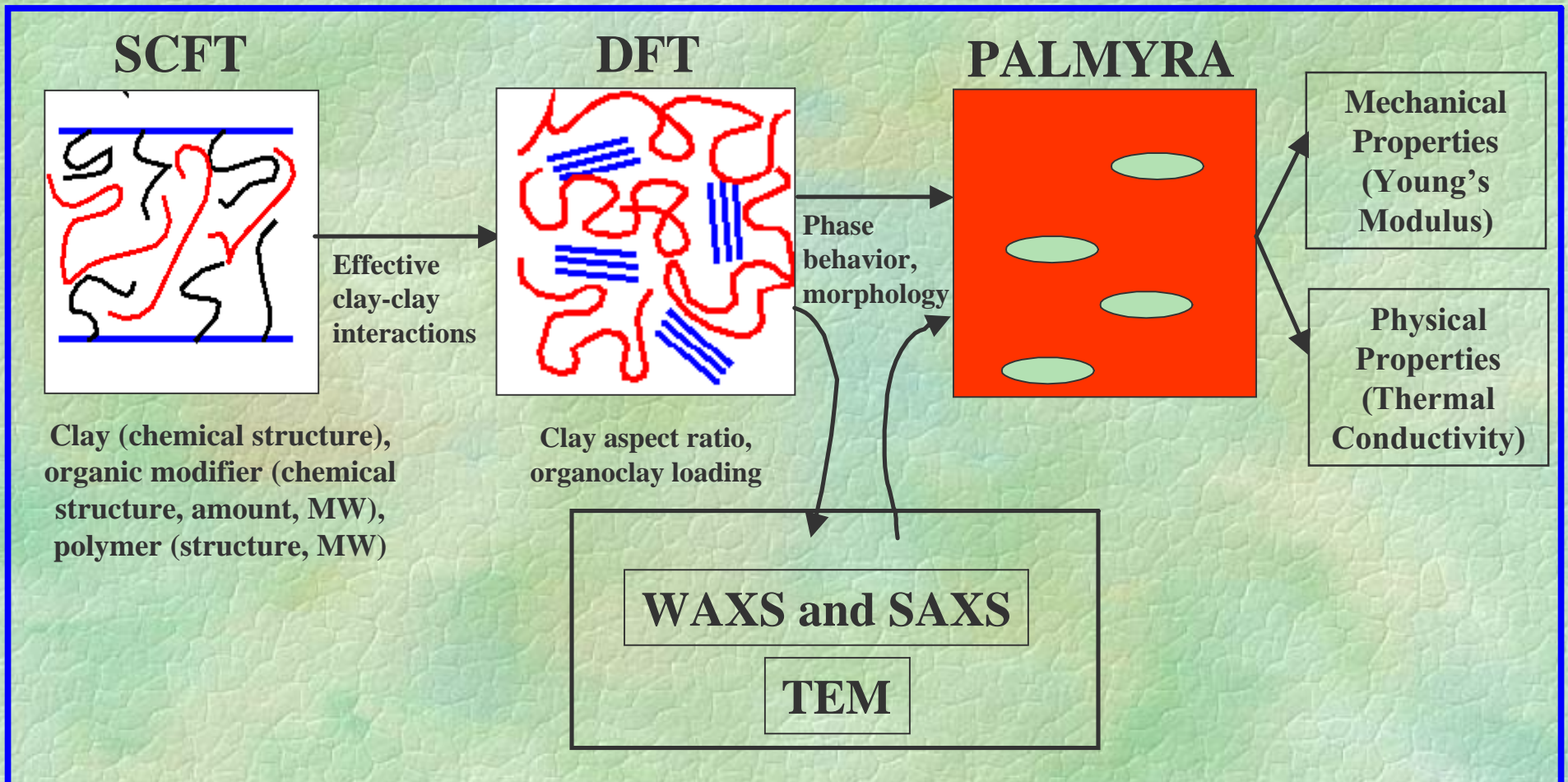
Strain Rate and Temperature Dependences

Dashed lines are calculated.
Solid lines are experimental data.

Thermoplastic Mechanical Property Modeling Summary

- **The model requires three stress-strain curves as input for calibration.**

- **It captures the stress-strain curves up to yield accurately at different rates and temperatures for bisphenol-A polycarbonate.**

- **Limited testing suggests that it works well for other glassy polymers, such as ABS, PC/ABS, and HIPS.**

- **It also provides insights into the fundamental issue of glass-former "fragility" in the glassy state and a practical means to assess dynamic inhomogeneities in polymeric glasses.**

- **For further details, see J. Moore, M. Mazor, S. Mudrich, J. Bicerano, A. Patashinski and M. Ratner, *ANTEC '02 Preprints*, Society of Plastics Engineers, 1961-1965 (2002).**

# MULTISCALE MODELING OF POLYMER/CLAY NANOCOMPOSITES

SCFT

Clay (chemical structure), organic modifier (chemical structure, amount, MW), polymer (structure, MW)

Effective clay-clay interactions

DFT

Clay aspect ratio, organoclay loading

Phase behavior, morphology

PALMYRA

Mechanical Properties (Young's Modulus)

Physical Properties (Thermal Conductivity)

WAXS and SAXS

TEM

Modeling Clay Intercalation or Exfoliation:
Mean-Field Theory of Polymers in the Galleries

Dispersing Unmodified (Virgin) Clay in Polymer:
- Calculate polymer-induced clay-clay interactions:
  - Entropy -- polymer pushed out
  - Enthalpy -- polymer pulled in
- Enthalpy needs to dominate
- Best way -- use polar head group
  (such as MaPP for PP/clay hybrids)

**For Success With Organically Modified Clays:**
- Organic modifier chains should be sufficiently long.
- Organic modifier and polymer should be miscible.
- Polymer should be attracted to clay surface.

Immiscible

Intercalated

Exfoliated
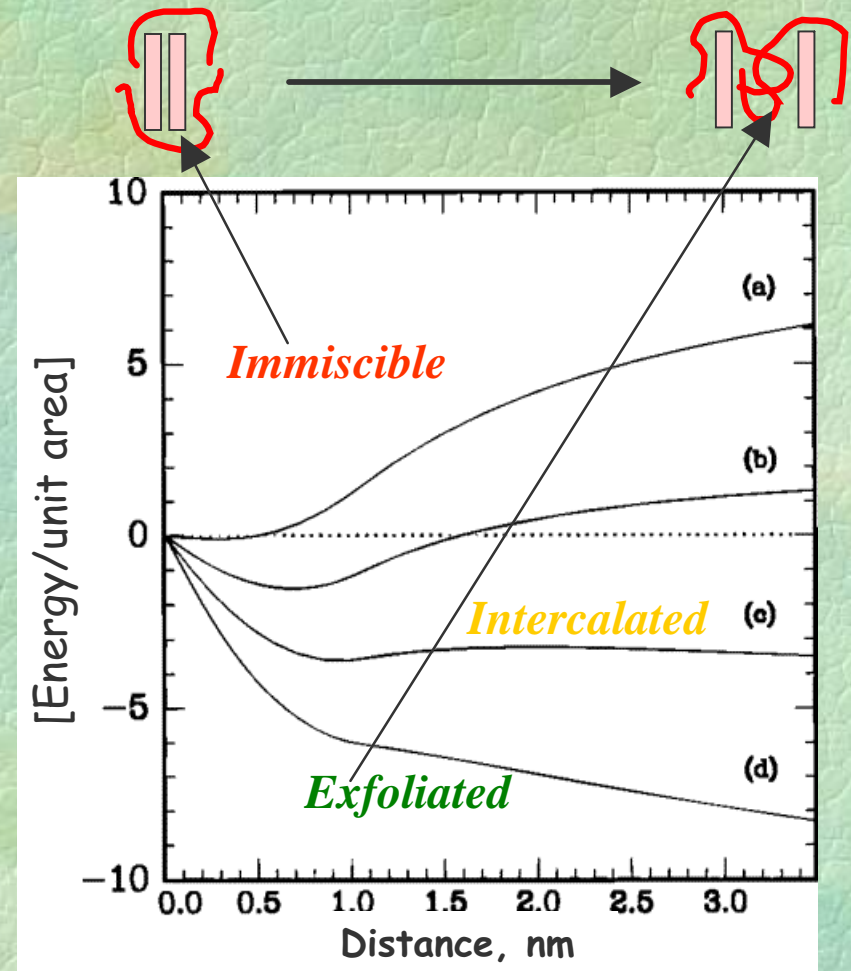
Vaia and Giannelis, *Macromolecules*, *30*, 7990-7999 (1997).

Modeling Clay Dispersion Morphology

Clay-Clay Potentials (SCMFT)

Immiscible

Exfoliated

F/A

H

ε=0
ε=3.5
ε=4
ε=5
ε=6
ε=7
ε=8
ε=10
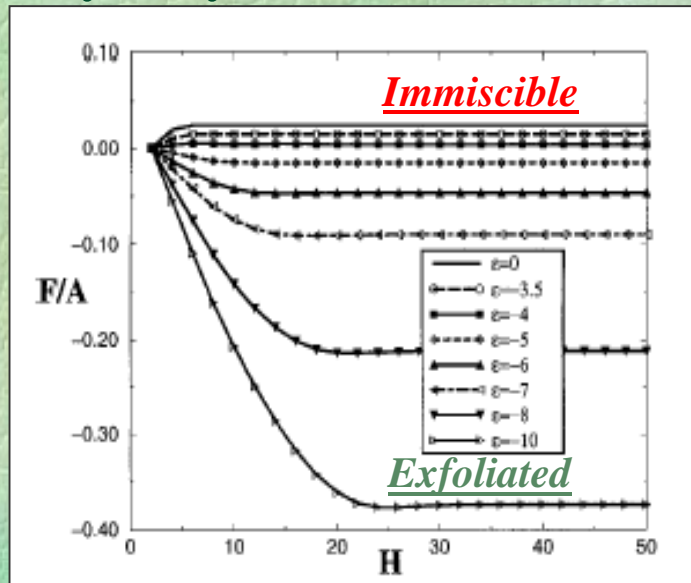
Increase in
End-Functionalized
Polymer Adsorption
Enthalpy (units: kT)
Onto Clay Surface

Dispersion Phase Behavior (DFT)

Two-Phase
(Part. Exf., Part. Stacks)

Isotropic
Exf.

Aligned
Exf.

Aligned
Int.

Iso. Gel

Clay Stacks

Organoclay Loading
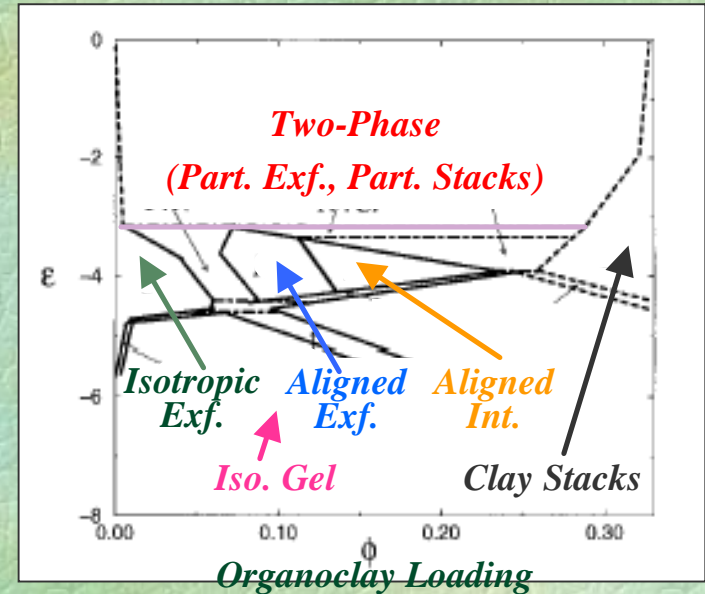
Ginzburg and Balazs, *Adv. Mater.*, **12**, 1805-1809 (2000).

- Clay surface coverage and organoclay loading determine the equilibrium morphology, but in practice the morphology is often non-equilibrium.
- Morphology can be deduced experimentally from WAXS, SAXS and TEM.

Verifying Dispersion Morphology Using WAXS

System 1: **<10% single layers, the rest in stacks of 20-30 platelets each with interlayer separation ~ 3.7 nm**
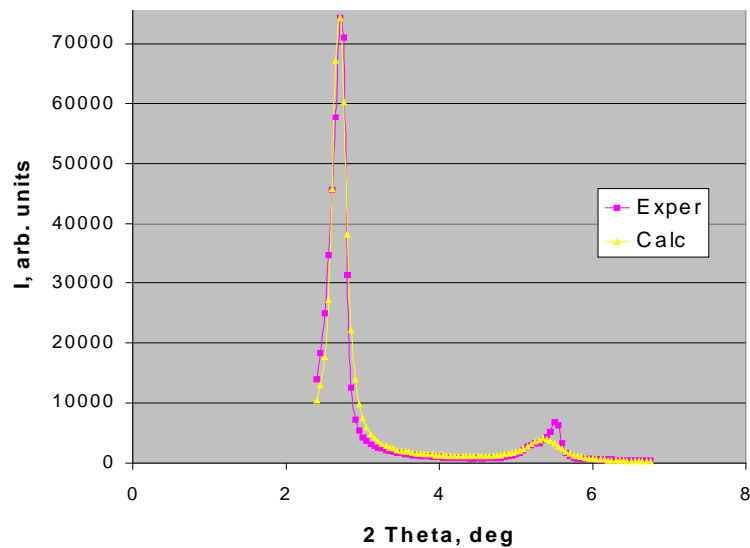

System 2: **~50% single layers, the rest in stacks of 6-8 platelets each with interlayer separation ~ 3.9 nm**
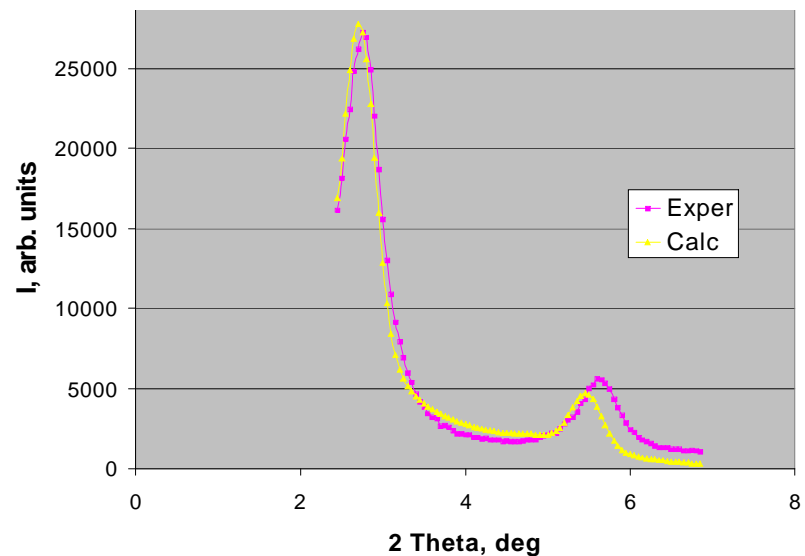
Calculations based on a model by Vaia and Liu, *Polymeric Materials: Science & Engineering*, *85*, 14-15 (2001).

- ▪ **XRD fitting model can determine degree of exfoliation in clay dispersions.**
- ▪ **Results in qualitative agreement with transmission electron micrographs.**

Predicting Mechanical Properties of Nanocomposites Using Finite Element Models
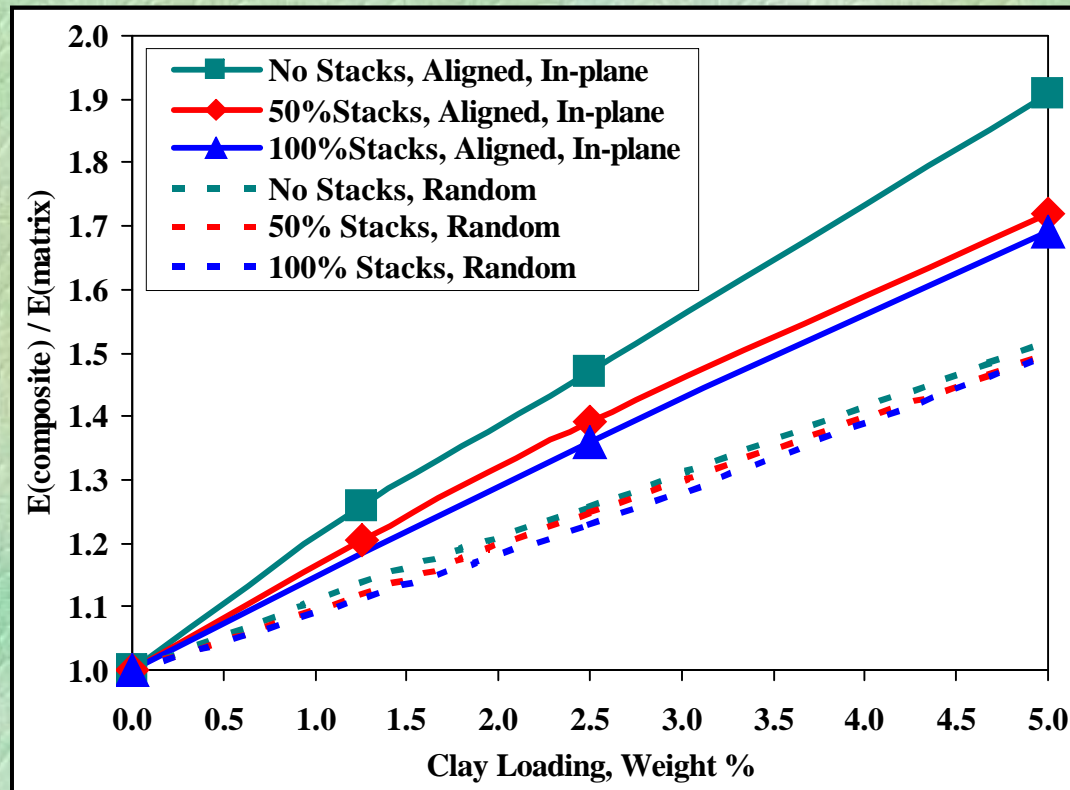
- • **For randomly oriented disks, no significant dependence of Young's modulus on exfoliation.**

- • **For aligned disks, in-plane modulus improves with increased exfoliation.**

See also: **D. A. Brune and J. Bicerano, *Polymer*, *43*, 369-387 (2002), where closed-form equations were used to model more idealized morphologies.**

- ▪ **Young's modulus depends strongly on extents of platelet exfoliation and alignment.**
- ▪ **Similar methods are applicable to predicting other properties.**

Nanocomposite Modeling Summary

- **Implemented multiscale modeling framework relating properties of nanocomposites to their formulations:**
  - Polymer/Clay Miscibility -- Mean-Field Theory of Polymers.
  - Phase Behavior of Dispersions -- DFT of Colloids.
  - Morphology Verification -- XRD Analysis and Modeling.
  - Property Prediction -- Finite Element Analysis.
- **Modeling framework was applied successfully to:**
  - Design compatibilizer formulations to improve clay dispersion in aqueous and other solutions, as well as in polymer melts.
  - Estimate mechanical properties of specific nanocomposites.

POLYOL TEMPLATING

- **Predict phase diagram, including transitions.**


- **Many applications in nanotechnology.**
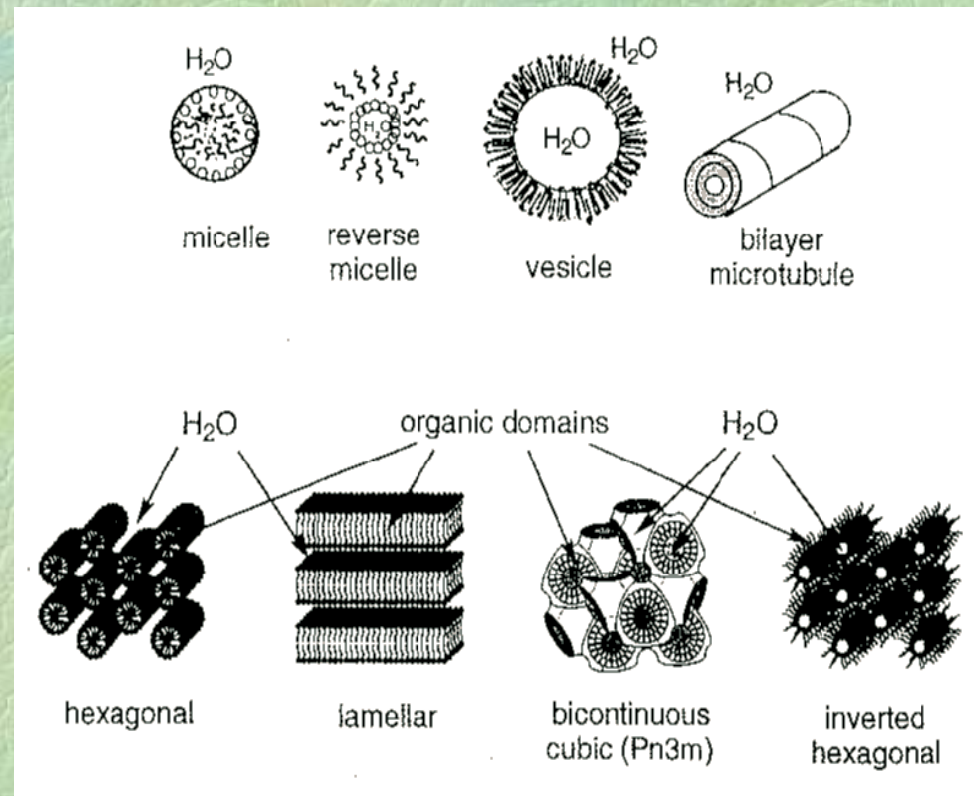
Assumptions in Lattice Mean-Field Model
(developed by Per Linse *et al.*, Lund University)

- Space divided into equal-sized lattice sites in two dimensions.

- One species per lattice site.

- Flexible polymers.

- Mean-field approximation, with nearest neighbor interactions accounted for via Flory-Huggins interaction (χ) parameters.

- Aqueous solutions of PEO and PPO homopolymers display a lower critical solution temperature.

- EO and PO segments are each modeled in terms of "polar" and "apolar" internal states.

Main Features of Phase Diagram for
an AB-EO Triblock / Water System
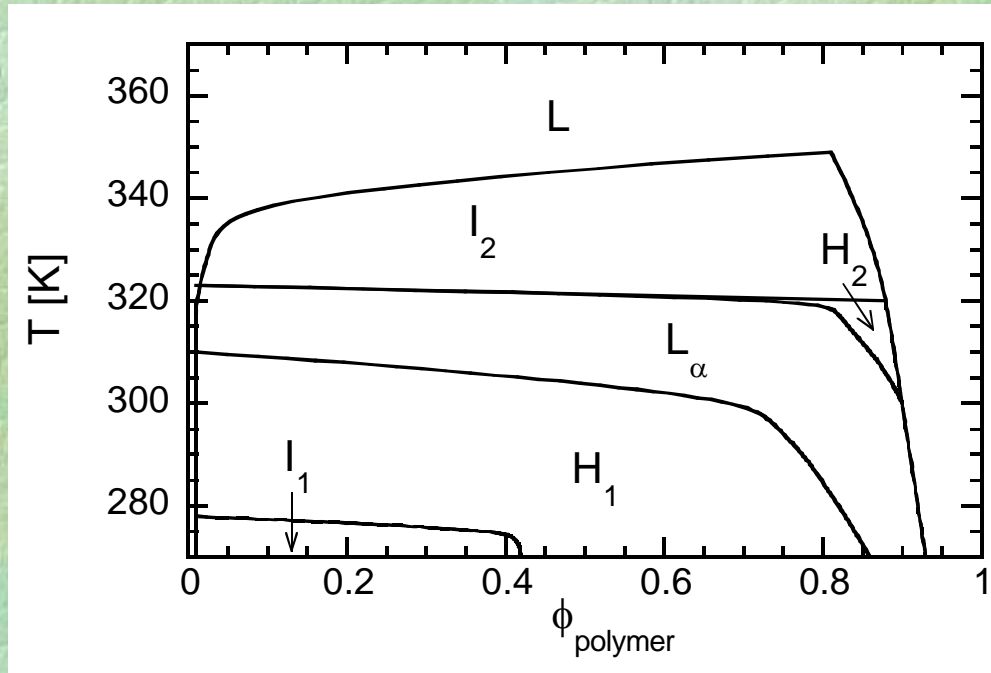
- *Lyotropic Phase Transitions:* **Caused by concentration changes (for example, $H_1 \rightarrow L_\alpha$ as $\phi_{polymer}$ is increased).**

- *Thermotropic Phase Transitions:* **Caused by temperature changes (for example, $H_1 \rightarrow L_\alpha \rightarrow I_2$ as T is increased).**

Ordered Phases:		*Disordered Phase:* L
Micellar cubic:	I_1	
Hexagonal:	H_1	
Lamellar:	L_α	
Reverse hexagonal:	H_2	
Reverse micellar cubic:	I_2	

Thermotropic Behavior From Increasing Effective Hydrophobicity With Temperature

Low temperature

hydrophobic   hydrophilic

- **Water-continuous phases with high curvature dominate.**
- **Lamellar phase is narrow.**
- **No stable "reverse" (polymer-continuous) phase is found.**
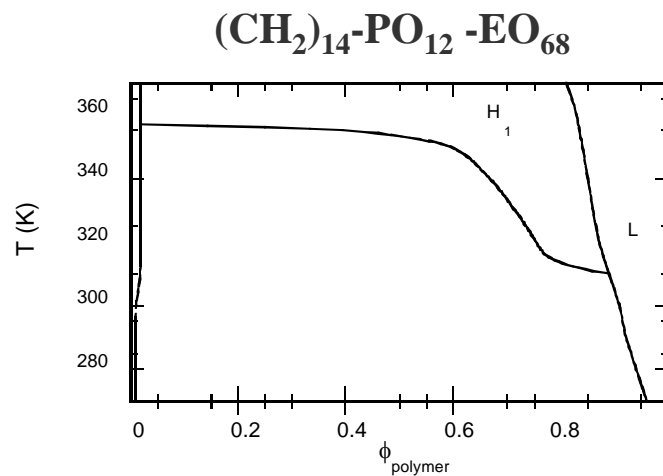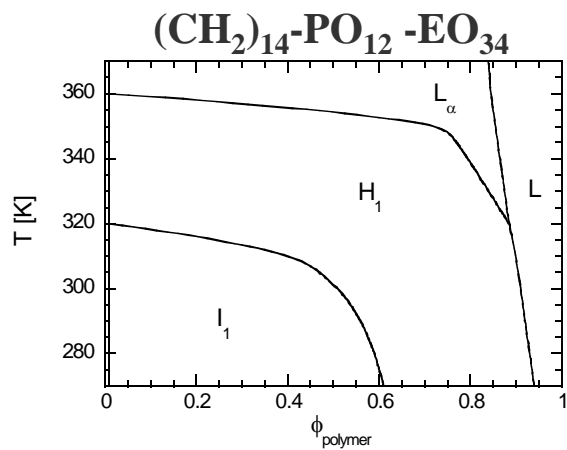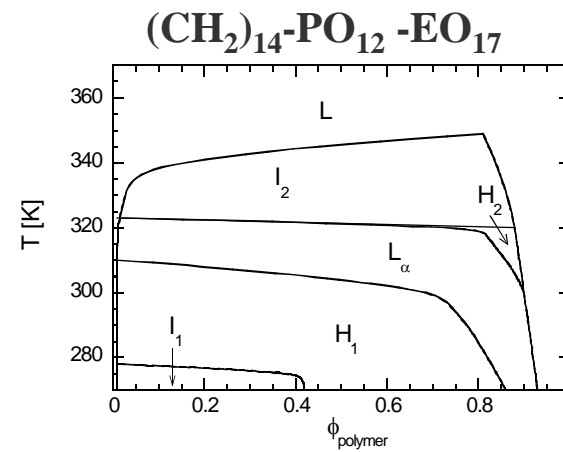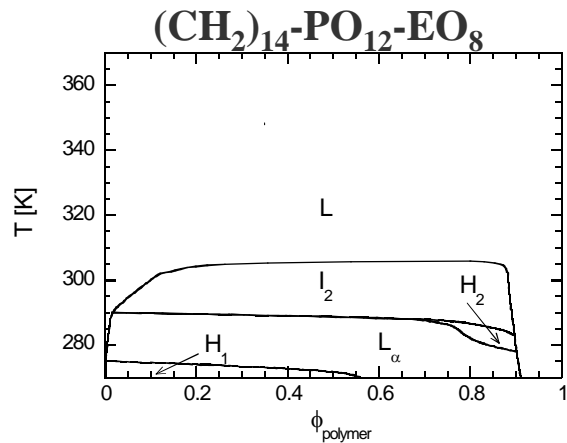
Intermediate temperature

hydrophobic   hydrophilic
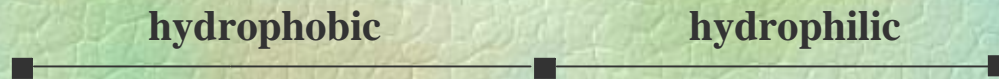
- **Lamellar phase is stable.**

High temperature

hydrophobic   hydrophilic

- **"Reverse" (polymer-continuous) phases become more stable.**

Block Length Effects on Thermotropic Transitions
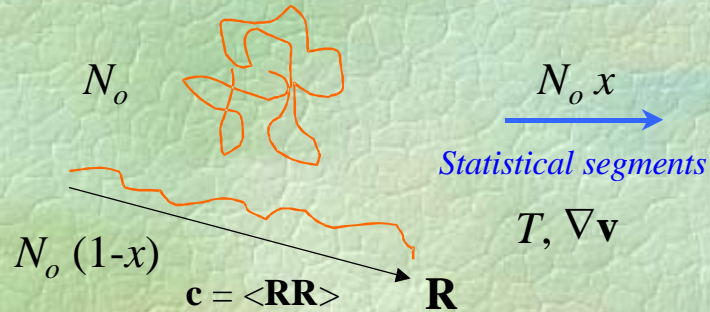

Increasing the EO block length extends the temperature stability of ordered phases and favors water-continuous phases.
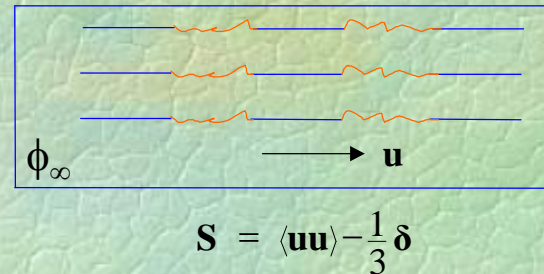
Polyol Templating Summary

- **Lattice mean-field theory was used to predict the lyotropic and thermotropic phase transitions of polyol surfactants with water, as functions of chemical composition, block length and concentration.**

- **This work is discussed in greater detail in several publications:**
  - **N. P. Shusharina, S. Balijepalli, H. J. M. Grünbauer and P. Alexandridis, *ACS Polymer Preprints*, *43(2)*, 354-355 (2002).**
  - **N. P. Shusharina, P. Alexandridis, P. Linse, S. Balijepalli and H. J. M. Grünbauer, *Eur. Phys. Jour. E*, *10*, 45-54 (2003).**
  - **N. P. Shusharina, S. Balijepalli, H. J. M. Grünbauer and P. Alexandridis, *Langmuir*, *19*, 4483-4492 (2003).**
  - **P. Alexandridis, N. P. Shusharina, K.-T. Yong, K.-K. Chain, S. Balijepalli and H. J. M. Grünbauer, *ACS Polymer Preprints*, *44(2)*, 218-219 (2003).**

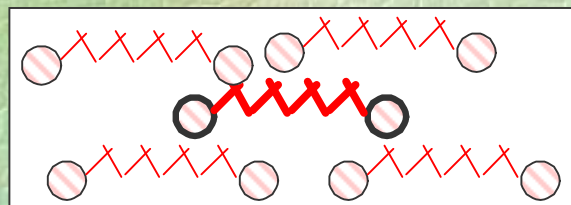# MICROSTRUCTURAL / CONSTITUTIVE FLOW-INDUCED CRYSTALLIZATION MODEL
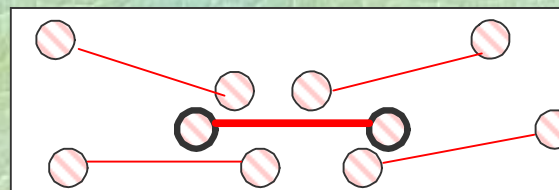
Amorphous phase

Semi-crystalline phase

N_o

$N_o x$

Statistical segments

$T, \nabla \mathbf{v}$

ϕ_∞

$\mathbf{u}$

Mesoscale picture

$N_o (1-x)$

$\mathbf{c} = \langle \mathbf{RR} \rangle$ $\mathbf{R}$

$S = \langle \mathbf{uu} \rangle - \frac{1}{3}\boldsymbol{\delta}$

FIC

Kinetic theory

Model

Modified Giesekus Model

Rigid Rod Model

$$c_{(1)} = -\frac{1}{\lambda_a(T)} \frac{k_B T}{K_0} \left((1-\alpha)\boldsymbol{\delta} + \alpha \frac{K_0}{k_B T} E c \right) \left(\frac{K_0}{k_B T} E c - \boldsymbol{\delta} \right)$$

$$S_{(1)} = -\frac{\sigma}{\lambda_{sc}(x, T)} S + \frac{1}{3}(\nabla v + (\nabla v)^T) - 2(\nabla v)^T : \langle uuuu \rangle$$

Flexible molecules, represented here as non-linear elastic dumbbells with finite extensibility (Peterlin approximation to get closed form equation).
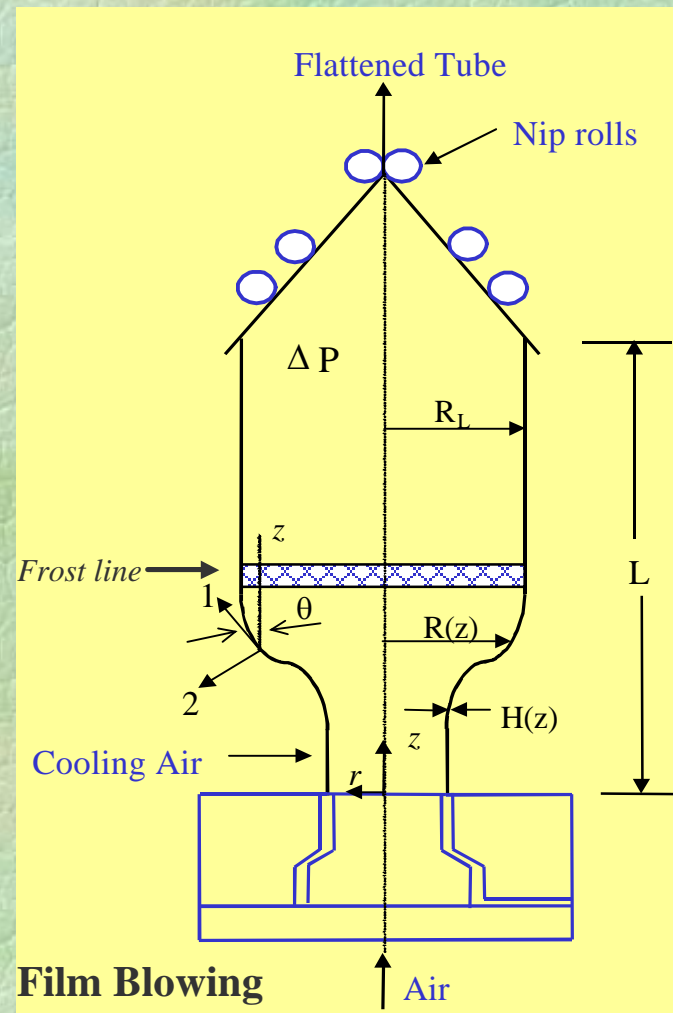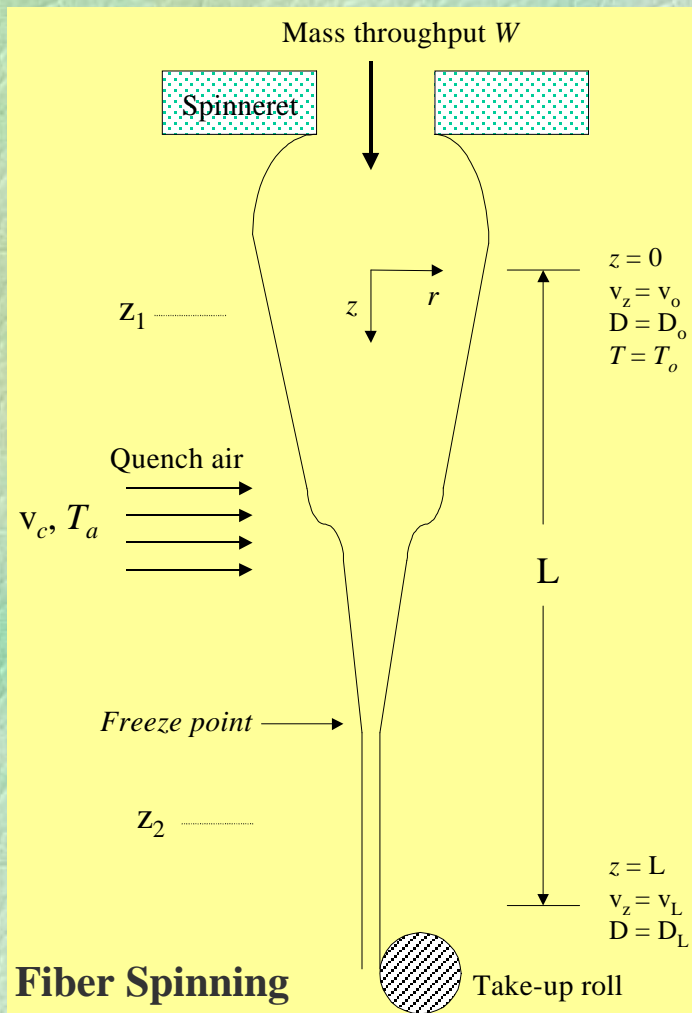
Rigid rods (with anisotropic drag) that orient and grow at the expense of flexible portions of chains.

Modeling Fiber Spinning and Film Blowing Processes

Mass throughput W

Spinneret

$z = 0$
$v_z = v_o$
$D = D_o$
$T = T_o$

z_1

Quench air

v_c, T_a

z r

L

Freeze point

z_2

$z = L$
$v_z = v_L$
$D = D_L$

Fiber Spinning

Take-up roll

Flattened Tube

Nip rolls

ΔP

R_L

Frost line

z

1

θ

R(z)

2

H(z)

z

Cooling Air

r

L

Film Blowing

Air

Must solve the coupled mass, momentum and energy conservation and constitutive/crystallization equations numerically.

Fiber Spinning Model Validation
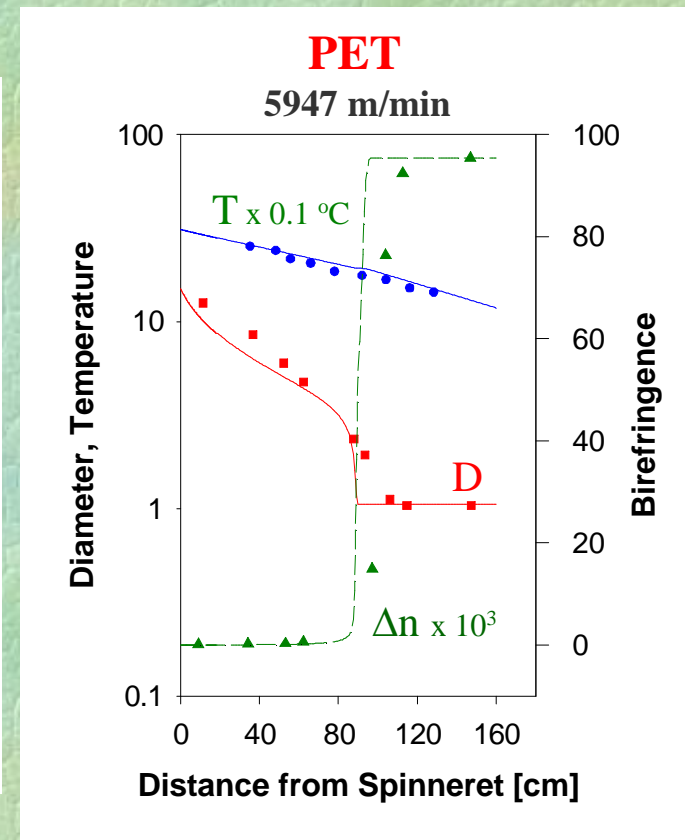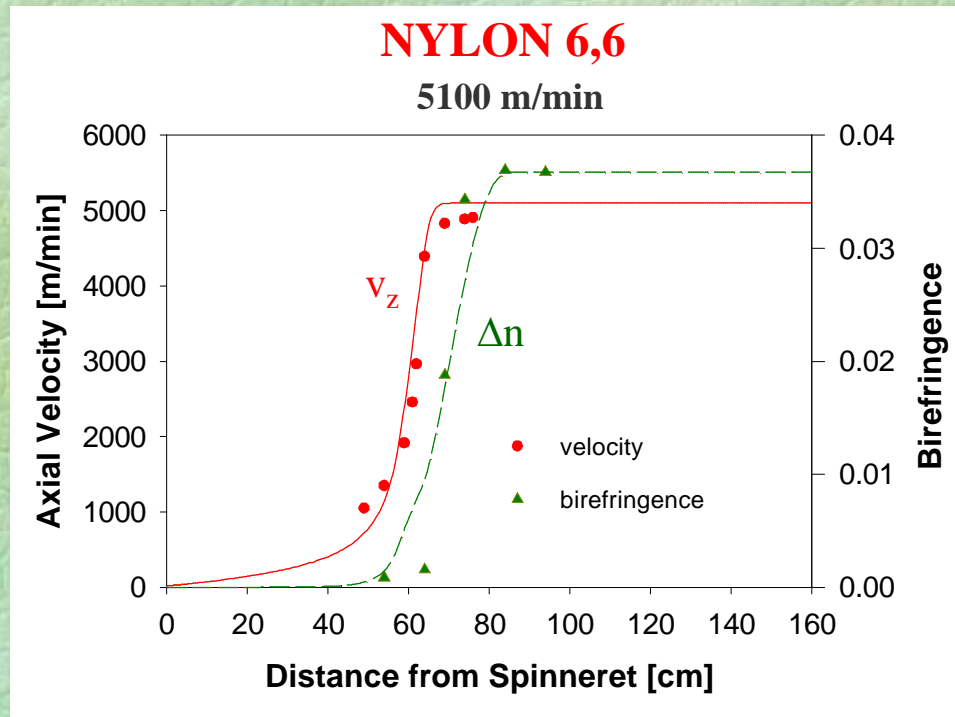
The model predictions are in good agreement with high-speed spinning data for the velocity, diameter (necking), temperature, and flow birefringence of Nylon and PET.

Linear Stability Analysis for Fiber Spinning

To predict the onset and evolution of instabilities (*draw resonance*), the system of equations is linearized around the steady state and the time evolution of prescribed disturbances is monitored. This evolution is dictated by the eigenvalues of the system.
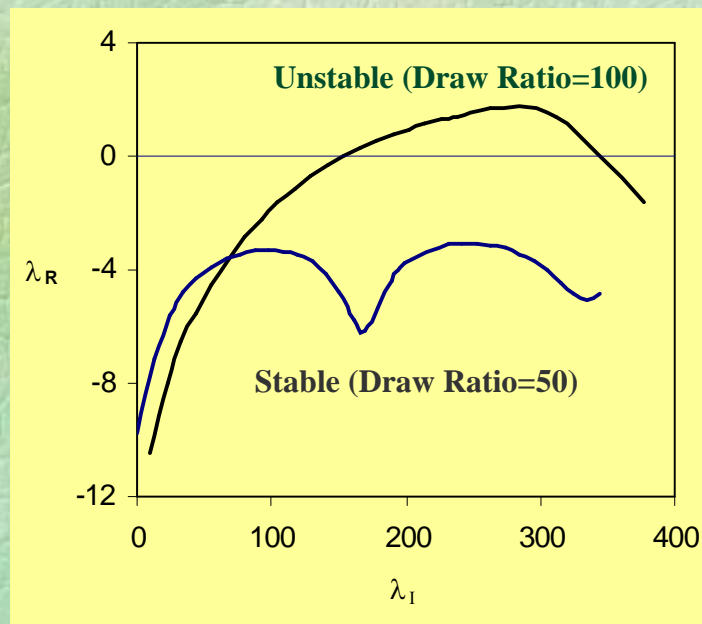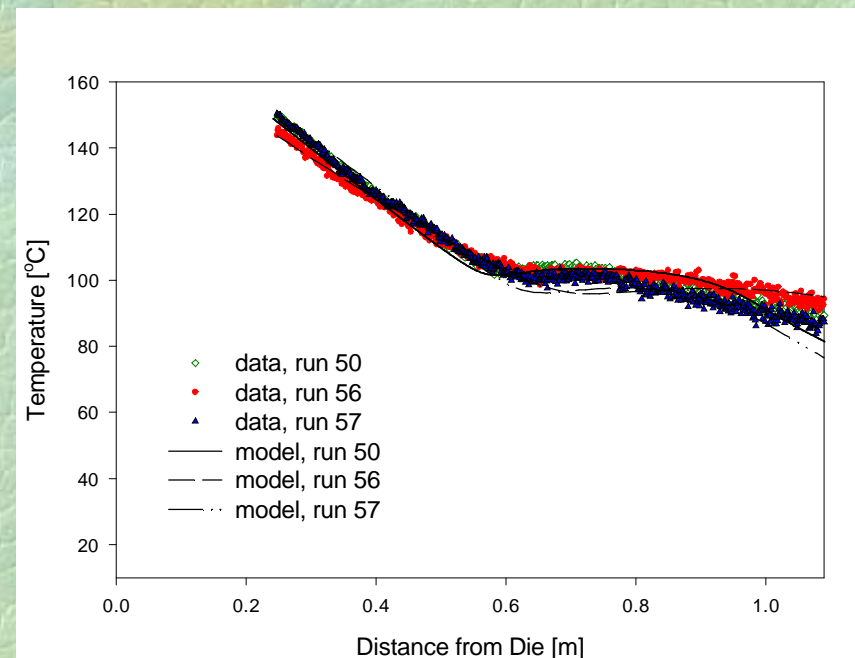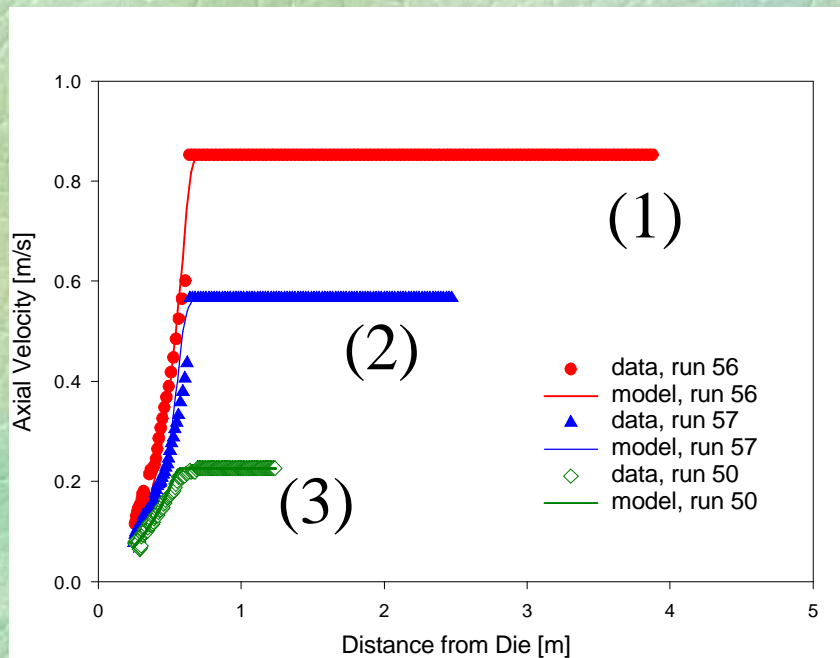

Eigenspectrum for two different take-up speeds
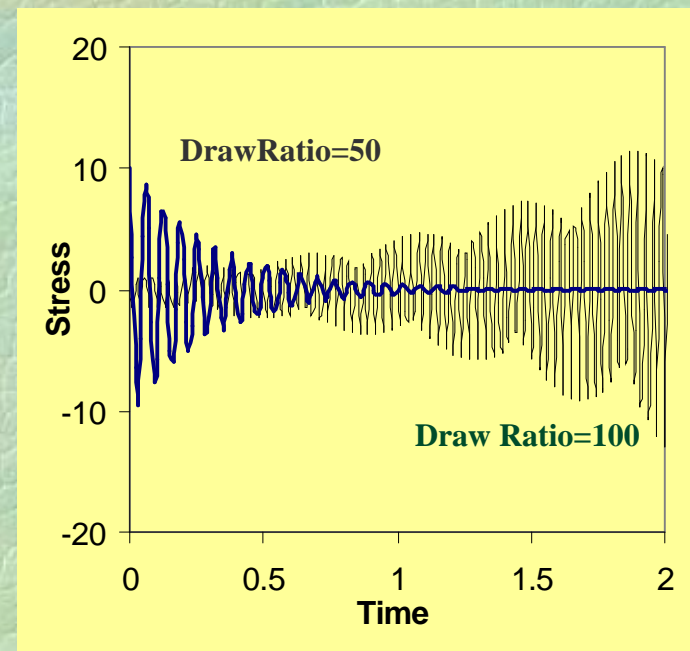
Stress disturbance evolution at *end of spinline* at most dominant eigenvalue for the two take-up speeds

Blown Film Model Validation

Prediction of bubble velocity and temperature profiles

The model can predict film velocity and temperature profiles accurately and capture the plateau of the film temperature due to crystallization.

Blown Film Model Validation (continued)
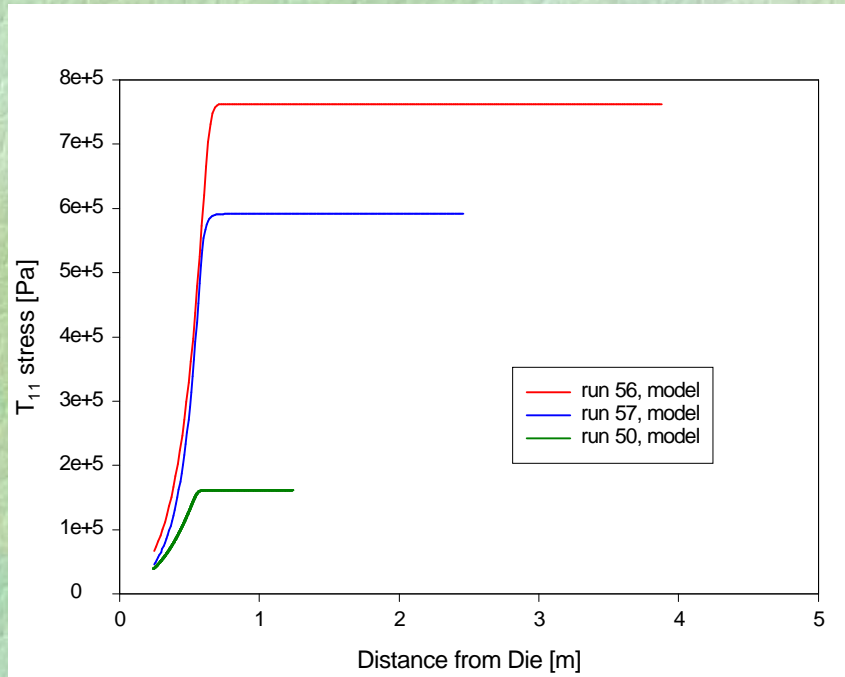
- **Predicted axial stress profiles T_{11} along bubble tangential direction.**

- **Locking-in of the macroscopic and molecular relative extensions in hoop direction ("3", CD) and evolution of relative crystallinity along film line.**

Flow-Induced Crystallization Modeling Summary

- **Model is mesoscopically-based, applicable to a variety of kinematics (uniaxial or biaxial extension, shear), and able to simulate polymer processes of great industrial and academic interest quantitatively.**
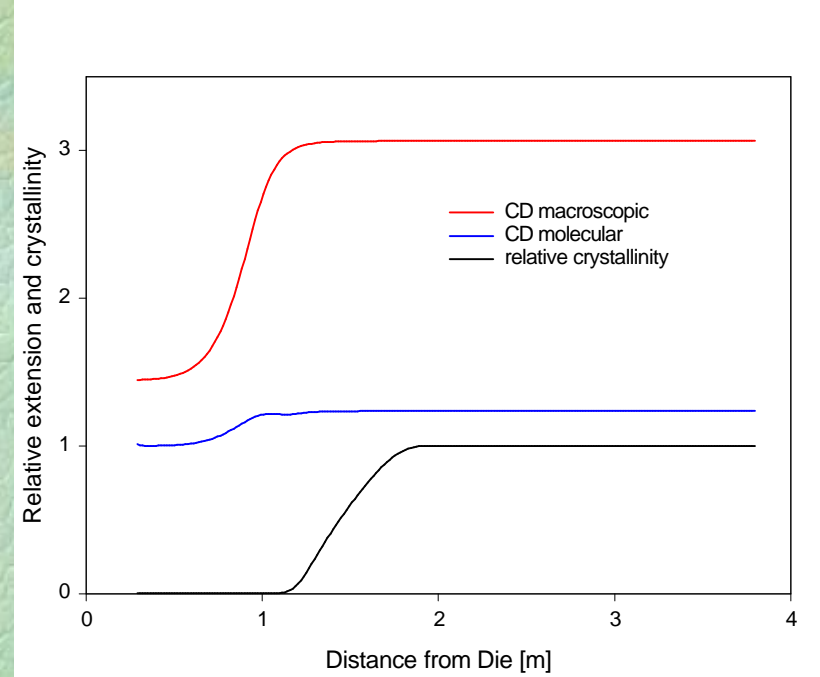
  - **Predicts necking and the associated softening (decrease of the extensional viscosity at high draw ratios) behavior in fiber spinning for the first time.**

  - **Predicts stresses in and microstructures of fibers and films at the freeze point, which are closely related to the mechanical and physical properties.**

  - **Predicts effects of fabrication conditions and molecular architecture on draw resonance during non-isothermal fiber spinning.**

  - **Predicts rheometric data (such as Meissner, Rheotens, shear) in absence of crystallization.**

- **See the many publications of Doufas *et al.* for further details.**

HIGH-THROUGHPUT POLYMER DESIGN

Conventional "Forward Engineering" Approach

Researcher guesses some candidate repeat units that may perhaps give polymers satisfying performance criteria for target application.

→

Properties are predicted to select the best candidates for synthesis, which are limited to being just a subset of the researcher's initial guesses.

More Powerful "Reverse Engineering" Approach

High-throughput (combinatorial) methods are used to generate a vast "library" of repeat unit structures, and properties are predicted for the polymers of these repeat units.
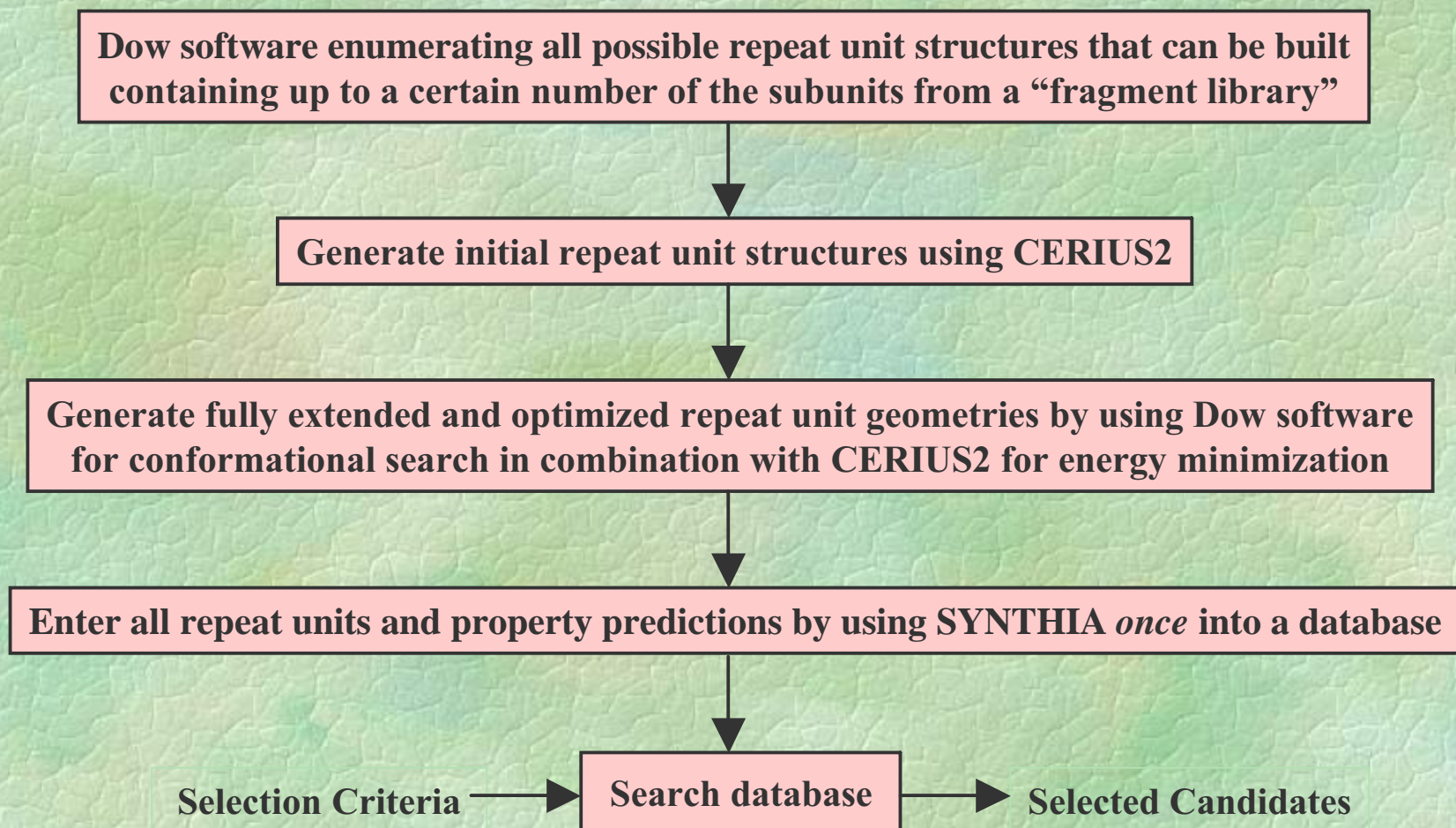
→

The best candidates for synthesis are identified from this huge repeat unit library, possibly providing attractive candidates that the researcher would never have thought of.

- ▪ The approach attempted at Dow was based on J. Bicerano, *Prediction of Polymer Properties*, third edition, Marcel Dekker, New York (2002), as implemented in the SYNTHIA software module marketed by Accelrys, Inc.

CERIUS2/SYNTHIA Approach

Dow software enumerating all possible repeat unit structures that can be built containing up to a certain number of the subunits from a "fragment library"

Generate initial repeat unit structures using CERIUS2

Generate fully extended and optimized repeat unit geometries by using Dow software for conformational search in combination with CERIUS2 for energy minimization

Enter all repeat units and property predictions by using SYNTHIA *once* into a database

Selection Criteria → Search database → Selected Candidates

High-Throughput Polymer Design Summary

SYNTHIA was endowed with combinatorial modeling capabilities!

Enumeration Program	$\rightarrow$	Builds repeat units for CERIUS2
Backbone Program	$\rightarrow$	Changes torsion angles to 180° or 0° and stores all such conformations
CERIUS2	$\rightarrow$	Minimizes energies of conformations
Compare Program	$\rightarrow$	Compares conformations, finds one with maximum extension, saves it
SYNTHIA	$\rightarrow$	Predicts properties at T= 200K to 500K for stored conformations, saves output in database-compatible XML format
Database	$\rightarrow$	Stores conformations and predictions in a readily searchable format (work not completed on this component of system)

High-Throughput Polymer Design: Work in Progress

- **Bicerano & Associates, LLC, is working with DTW Associates, Inc., to develop a much more effective new modeling approach to high-throughput polymer design.**

- **This approach will be implemented as a new module (HTPD) which will be made commercially available in DTW's Polymer-Design Tools™ suite of software tools.**

CONTROLLED RELEASE OF DRUGS FROM HYDROPHILIC POLYMERS

Swelling of tablet and formation of gel

Dissolution of polymer

Drug Filler

HPMC

Water

Diffusion of water, drug and filler
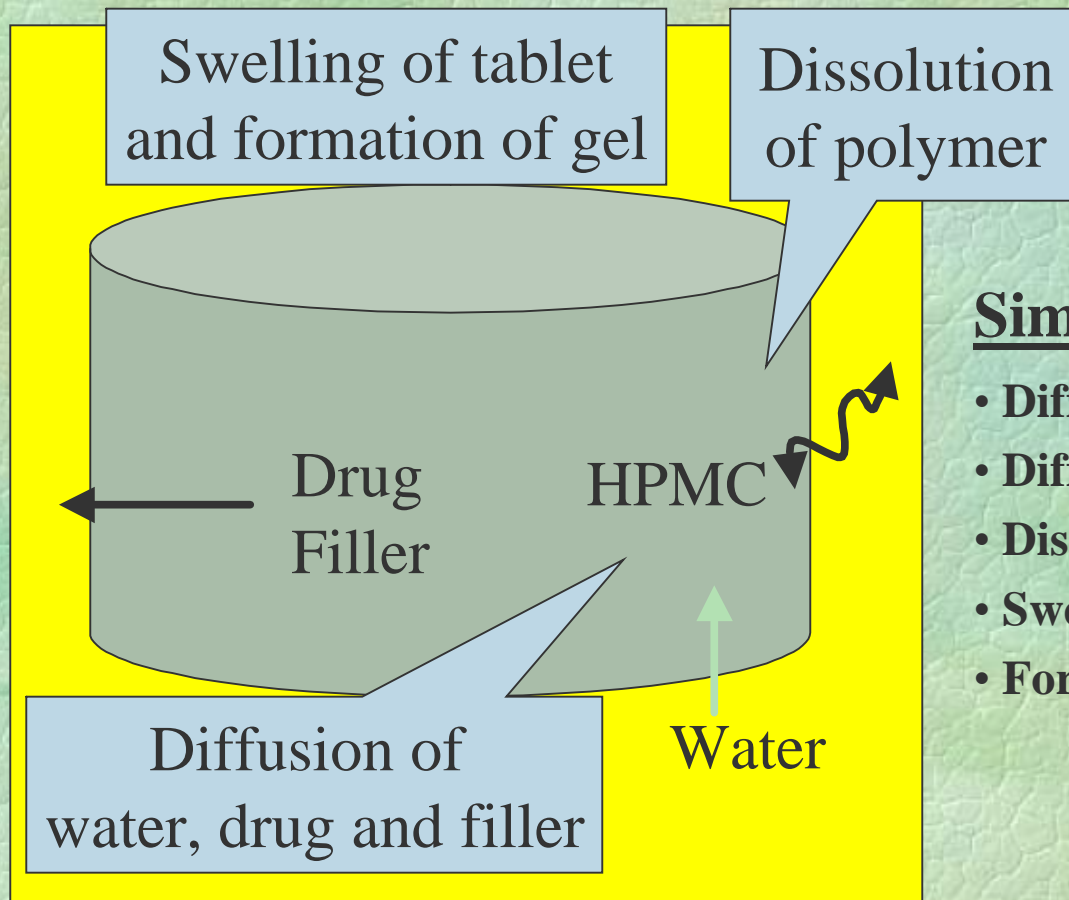
Simultaneous Processes:

- Diffusion of water into tablet.
- Diffusion of drug/filler out of tablet.
- Dissolution of polymer matrix.
- Swelling of tablet as water enters.
- Formation of gel.

Literature Model (Siepmann and Peppas)

Main Advantages:

- **Physically reasonable, yet mathematically simple.**

- **Well tested with different drugs, polymer grades, and release media.**

- **Parameters which are not drug dependent are published and can be used directly, so that only two parameters must be determined by fitting to data.**

Water $\qquad \dfrac{\partial c_w}{\partial t} = \nabla \cdot (-\hat{\rho}_t D_w \nabla c_w)$

Drug $\qquad \dfrac{\partial c_d}{\partial t} = \nabla \cdot (-\hat{\rho}_t D_d \nabla c_w)$

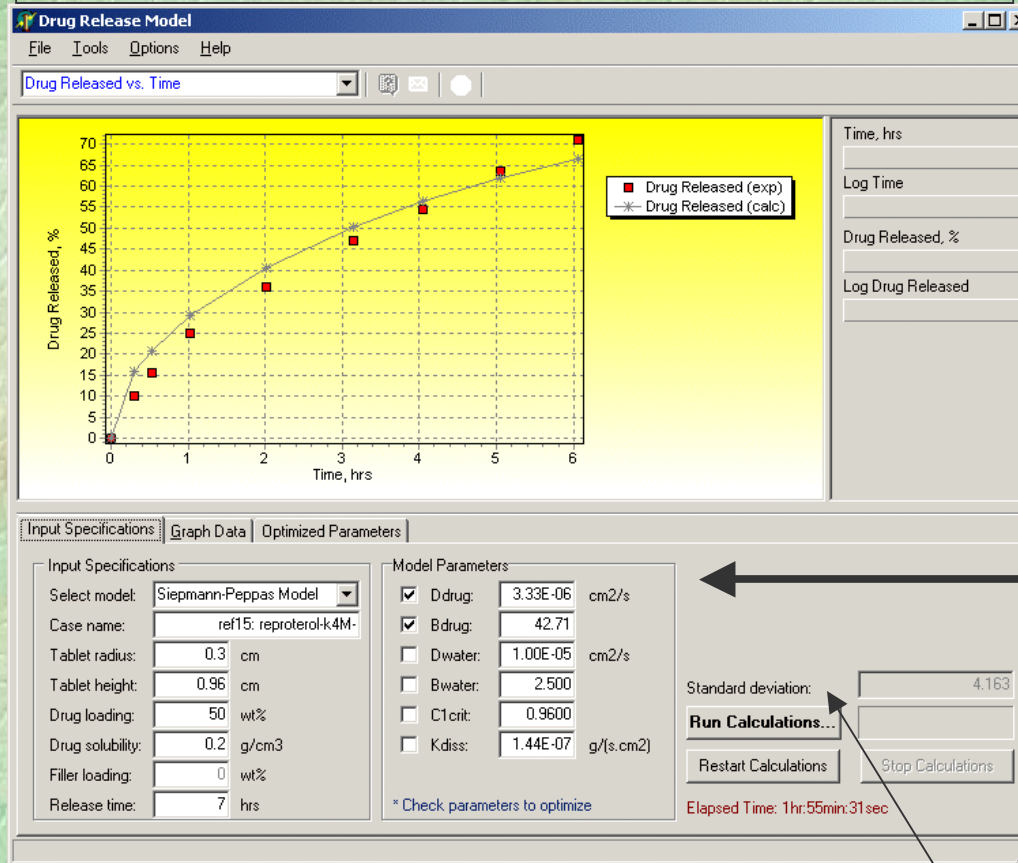Polymer $\qquad \dfrac{\partial c_p}{\partial t} = -K_p a_s$

Diffusivity

$$D_c = D_{0c} \exp(-\beta_c (1 - \frac{c_w}{c_s}))$$

Solve these equations and at each time step compute volume and remesh.

User Interface

**Can export results to Excel & many other features!**

Graphical representation of experimental results and model predictions

Interface to choose input parameters (tablet size, loading, etc.)

Interface to either input values for model parameters or choose them to be fitted by using a state-of-the-art particle swarm optimizer

Standard deviation – to determine goodness of fit.

Results With Siepmann-Peppas Model
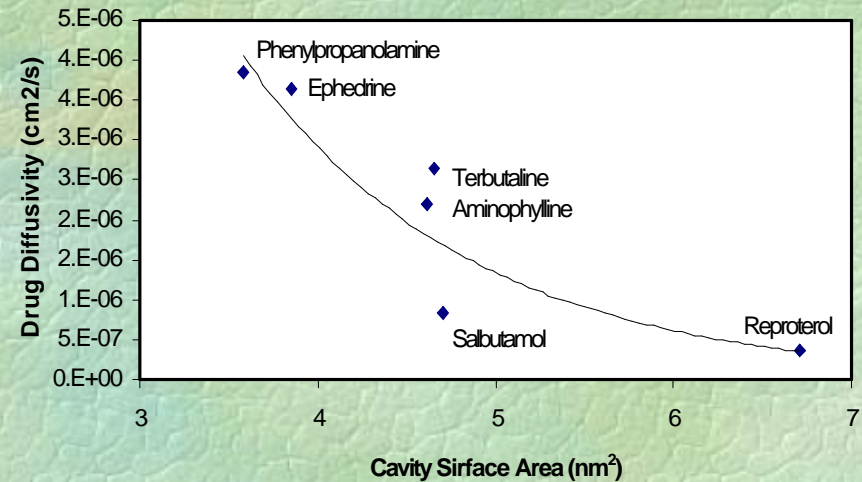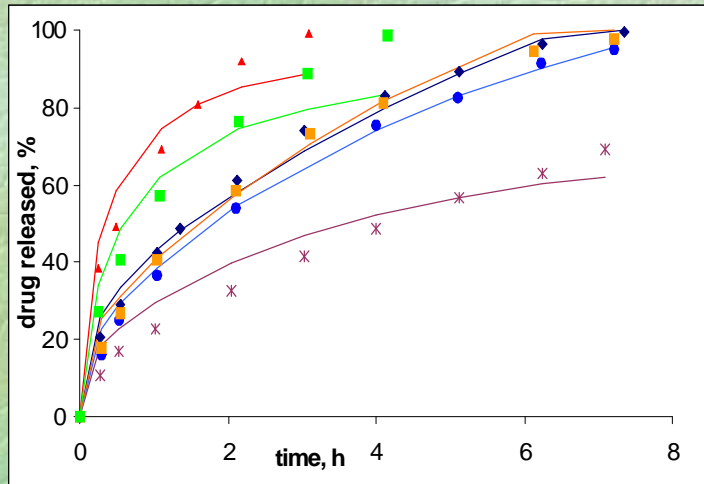
Fitted controlled release data for six different drugs of same family (water-soluble bronchodilators) from a literature reference, from a hydroxypropylmethylcellulose matrix (50% drug loading by weight), by using the Siepmann-Peppas model.

The drug diffusivity shows dependence on "cavity surface area" (also known as the "solvent-accessible surface area") of the drug molecules.
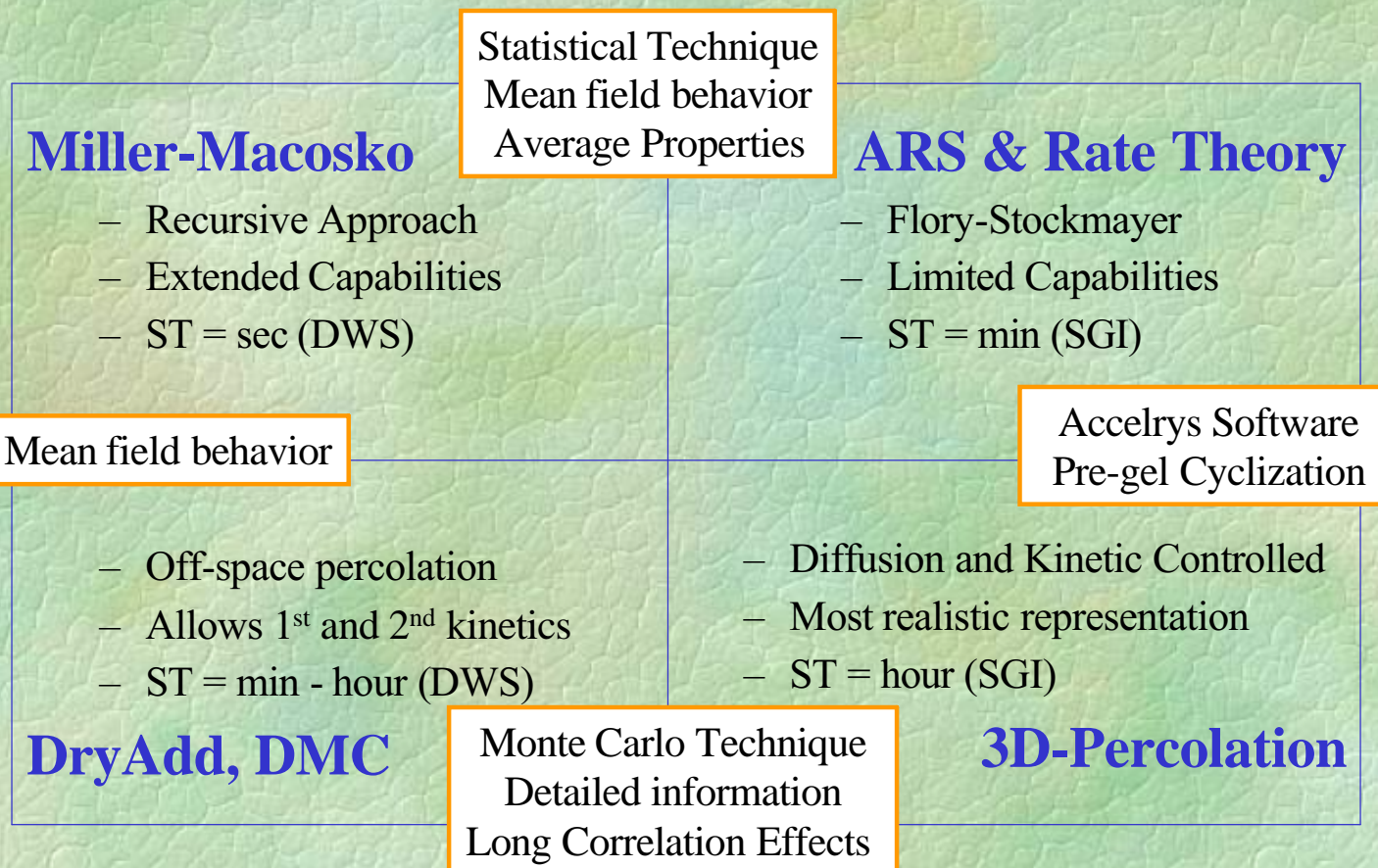
MODELING BRANCHED/NETWORK POLYMERS

- **This work is aimed towards understanding the following relations:**

reactant structures

reaction conditions

→ network structure → network properties

- **One can then predict industrially important parameters (such as the time to gel, critical gel ratio, polymer molecular weight and viscosity buildup).**

- **One can also gain insights on aspects of branched and/or network architectures where analytical tools fail (such as the compositions and sequence distributions of the elastic chain segments between crosslinks, dangling ends, loops).**

- **Most importantly, success in this effort can shorten the product development time by providing models to guide the experimental work.**

Available Theories

Different theories originate from different assumptions about non-ideal behavior.

| Statistical Technique |
| Mean field behavior |
| Average Properties |

Miller-Macosko

– Recursive Approach
– Extended Capabilities
– ST = sec (DWS)

ARS & Rate Theory

– Flory-Stockmayer
– Limited Capabilities
– ST = min (SGI)

Mean field behavior

Accelrys Software
Pre-gel Cyclization

– Off-space percolation
– Allows 1st and 2nd kinetics
– ST = min - hour (DWS)

– Diffusion and Kinetic Controlled
– Most realistic representation
– ST = hour (SGI)

DryAdd, DMC

Monte Carlo Technique
Detailed information
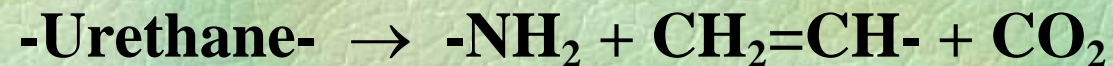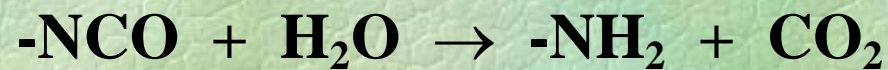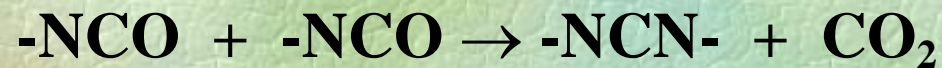Long Correlation Effects

3D-Percolation

Thermoplastic Polyurethane Pultrusion: Process

- Pultrusion is a continuous process where the developing composite is "pulled through" the fabrication equipment by a gripper/puller system.

- Polymer pellets are heated and melted, and fibers are "impregnated" with molten polymer, depolymerization at urethane bonds and side reactions being favored in these steps.

- Subsequent rapid cooling results in polymerization reactions becoming favored again.

5 sec

10 sec

20 mm

Half part thickness

Half part width

Half part thickness

Half part width
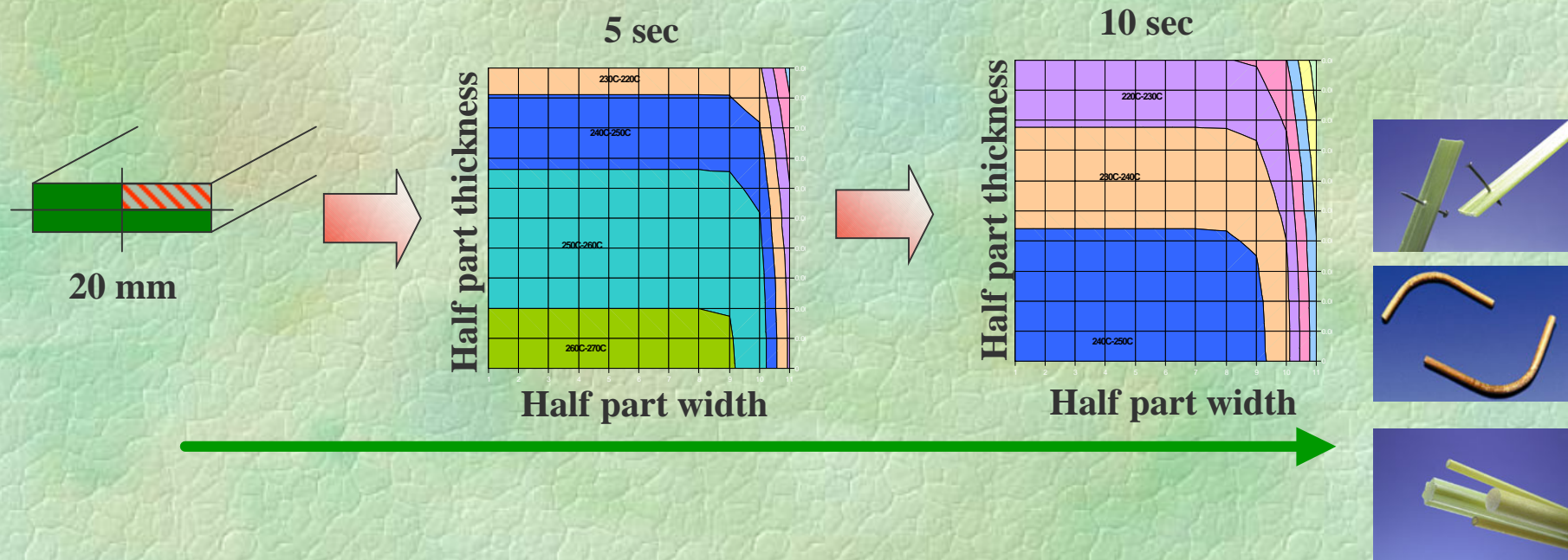
Thermoplastic Polyurethane Pultrusion: Reactions

$$-OH \; + \; -NCO \; \leftrightarrow \; -Urethane-$$

$$-NCO \; + \; -NH_2 \; \rightarrow \; -Urea-$$

$$-NCO \; + \; -NCO \rightarrow -NCN- \; + \; CO_2$$

$$-NCO \; + \; H_2O \; \rightarrow \; -NH_2 \; + \; CO_2$$

$$-Urethane- \; \rightarrow \; -NH_2 + CH_2=CH- + CO_2$$

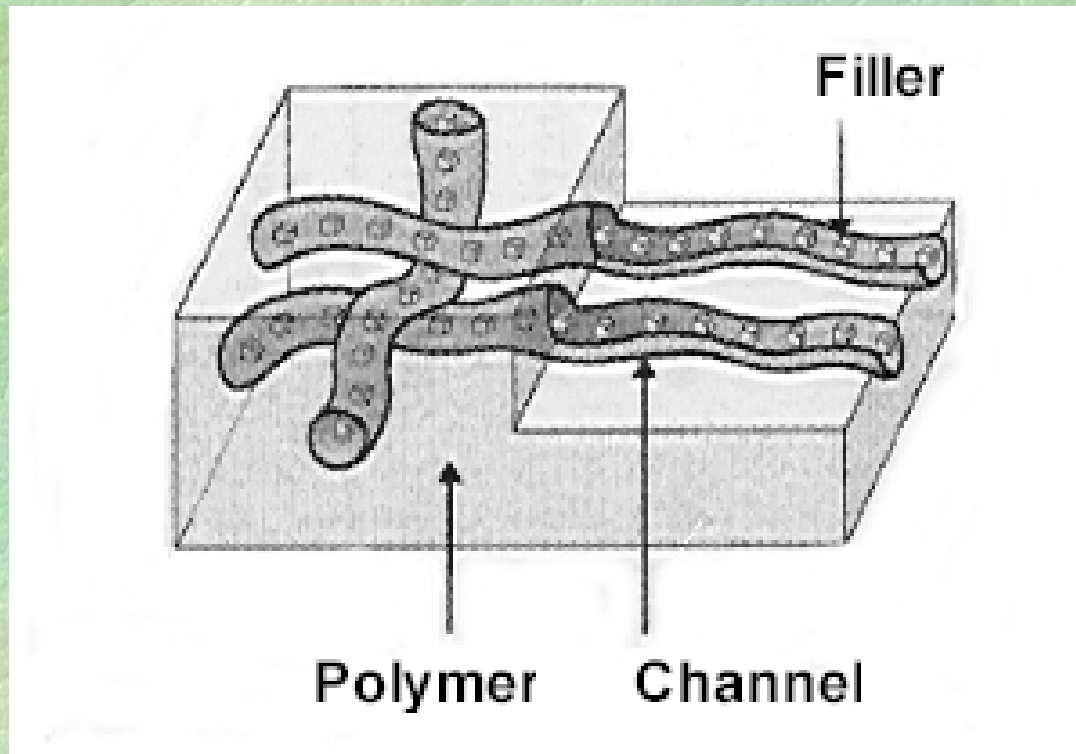# Thermoplastic Polyurethane Pultrusion: M_w Prediction
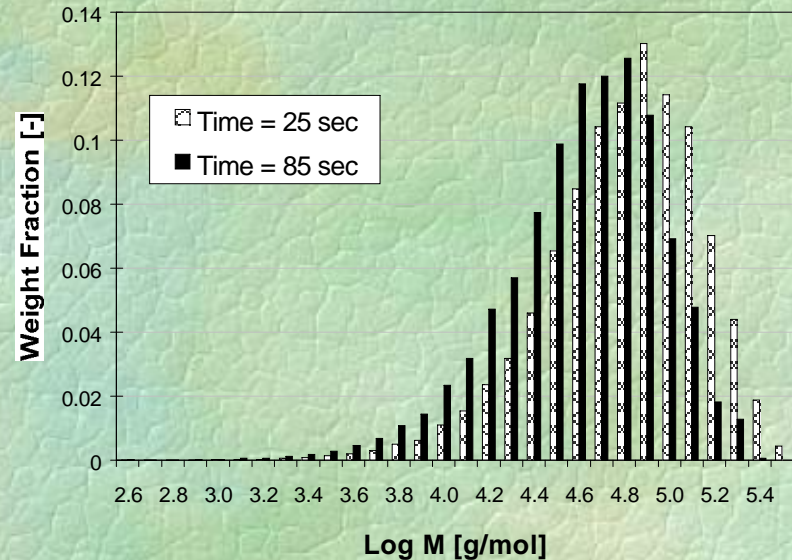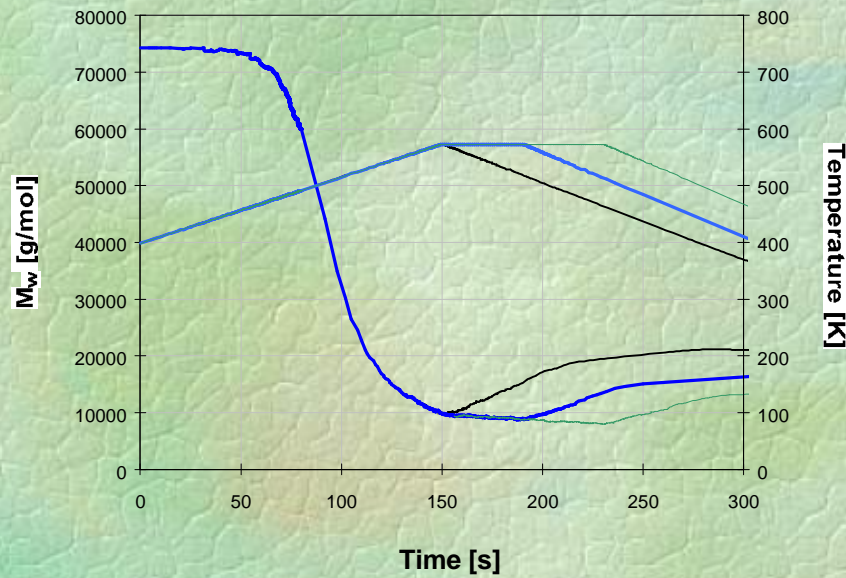
- Applied temperature profiles (left) all exhibit the same temperature rise and fall rates, but differ in length of the plateau that the temperature resides at prior to cooling and that determines the extruder residence time.
- The assumed reaction mechanism was implemented with the dynamic Monte Carlo method.
- The starting M_w was ~75 kg/mole, and a shorter residence time was found to favor a higher final M_w.
- Snapshots of weight distributions of formed polymers at time 25 sec and 85 sec are shown at the right.
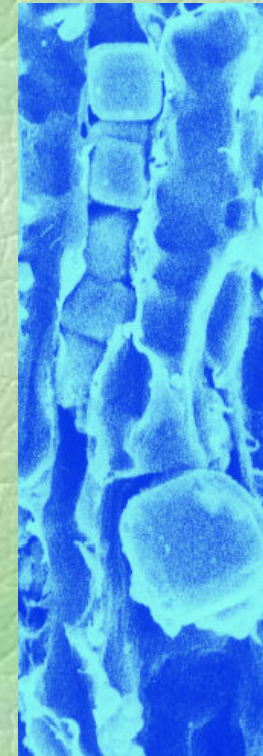- See T. A. M. Verbrugge and C. F. J. den Doelder (to be published) for further details.

MODELING WATER VAPOR TRANSPORT

- **Determine the filler [Linde Type A (LTA) zeolite] loadings needed to "activate" a polyolefin/desiccant blend for water vapor transmission.**

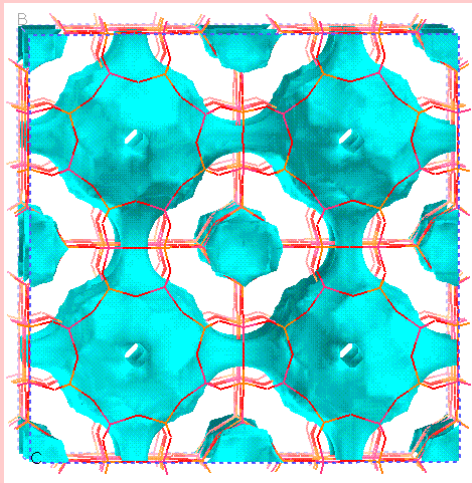**Schematic Illustration of Initial Morphological Hypothesis**   **Micrograph**

Accessible Volume Calculation

- **Compute accessible volume of LTA.**
  - Assume probe radius r=1.4 Å or 0.75 Å (representing roughly the longest and shortest dimensions of a water molecule).
  - Use the CERIUS2 crystal library and internal volume calculator.
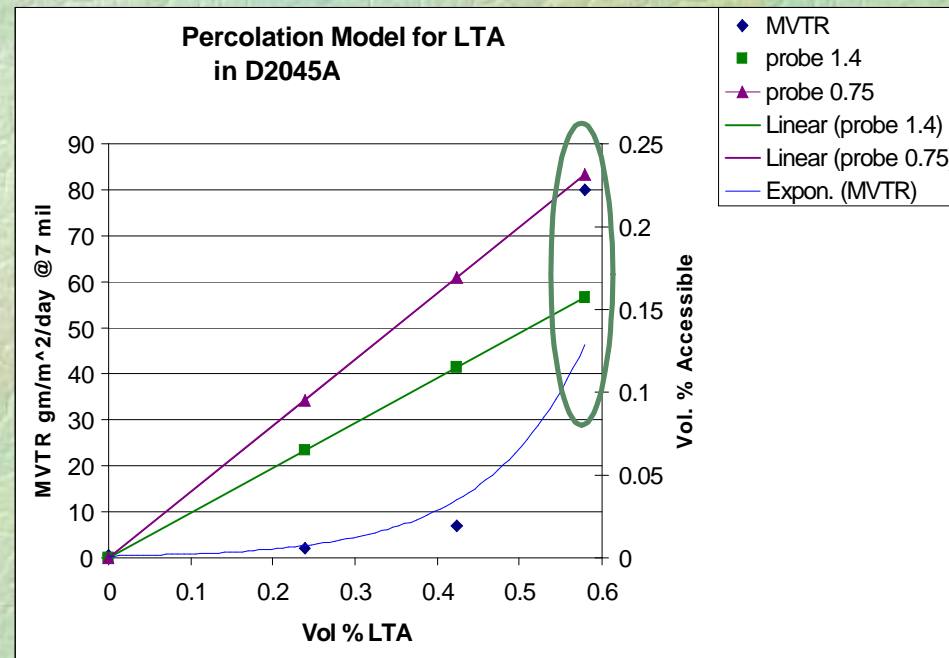 - Multiply by volume % of LTA loaded into polymer.

Occupiable volume (r=1.4 Å)   **Accessible Volume (r=1.4 Å)**
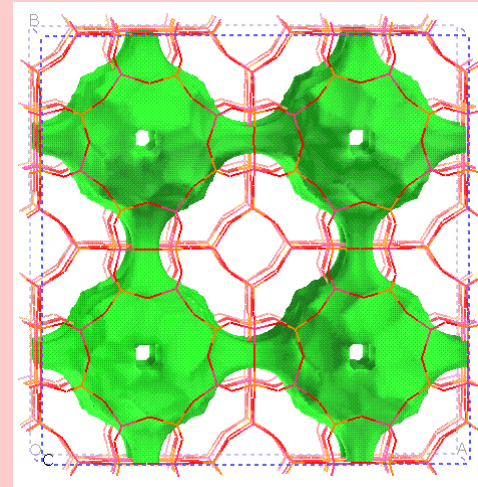
Water Vapor Transport Modeling Summary

- **The observed water vapor transmission rates were compared with the calculated water-accessible LTA zeolite volume fraction in the blends.**

- **The sudden onset of water vapor transmission was seen to coincide simply with the percolation threshold for water accessibility with a probe radius of 1.4 Å, without the need to assume the existence of a "channel" morphology.**

SUMMARY AND CONCLUSIONS

- **Polymer modeling has reached the state of maturity where it can serve as a powerful component of an industrial R&D program on polymer product and process development.**

- **Such work, at its most effective, attempts to address all of the essential formulation, process and product issues within a multidisciplinary and multiscale modeling paradigm.**

- **A few polymer modeling projects from Dow Chemical were reviewed to illustrate some of the many types of industrially relevant problems that can be solved.**