IMA/MCIM Industrial Problems Seminar

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Mathematics and Materials: The Role of Mathematics in a Materials Development Laboratory

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Outline

- Materials Modeling Technology at 3M
- Fractals and Pavement Marking Materials
- Mesoscopic Simulations and Block Copolymer Materials
- Monte Carlo Methods and Complex Fluids
- Summary
**Vision/Values**

**Vision**
- The most innovative enterprise
- The preferred supplier

**Values**
- Satisfying our customers with superior quality, value and service
- Providing investors with an attractive return
- Respecting our social and physical environment
- Being a company employees are proud to be a part of
Technologies
Materials Modeling Technology at 3M

- **Advanced Materials Technology Center**
  - drives strong 3M global growth short-term and long-term through building and applying expertise in chosen materials-related technology areas, anticipating new technology platforms aligned with major 3M growth opportunities

- **Materials Modeling Technology Group**
  - accelerate 3M innovation by using mathematical and computational models of materials
  - provide an integrated approach among the various length scales and time scales of materials behavior
Materials Modeling

- Molecular Modeling
- Polymer Modeling
- Constitutive Modeling
- Transport Modeling

TIME
- years
- hours
- minutes
- seconds
- microsec
- nanosec
- picosec
- femtosec

DISTANCE
- 1 Å
- 1 nm
- 10 nm
- micron
- mm
- yards

Engineering Design
- (Unit Process Design)

Finite Element Analysis
- (Process Simulation)

Mesoscale Dynamics
- \( \sigma = E\varepsilon \)

Atomistic Simulations
- MD/MC

Quantum Mechanics
- \( H\Psi = E\Psi \)

Trends
- nanotechnology,
- microfluidics,
- MEMS, etc
Fractals and Pavement Marking Materials

- Important to understand road adhesion
- Difficulty: a variety of roads
Fractals and Materials

- **Topography Data**
  - Height \( z \) as a function of area \( (x,y) \)

- **Fractal Methods to determine topographical parameters with physical interpretation**
  - Patchwork Method (US 5 307 292)
  - Christopher Brown et al, Wear (1993)

- **Hypothesis**
  - Adhesive Strength is related to the relative area at the scale of interaction
Adhesive Strength

- Depends on a finite number of bonds requiring a certain space and each having a certain strength
- Overall Strength
  \[ S_t = N \frac{S_s}{A_p} \]
- # of Interactions
  \[ N = m \frac{A_{ts}}{A_s} \]
- Overall Strength
  \[ S_t = m \left( \frac{A_{ts}}{A_p} \right) \left( \frac{S_s}{A_s} \right) \]
The Patchwork Method
(US 5 307 292)

- Topography Data
  - Height (z) as a function of area (x,y)
- Tile surface with triangles of constant area (x,y,z)
- Relative area is number of triangles X triangle area X projected area
- Plot (log-log) relative area vs triangle area
- Repeat with a different triangle area

![Graph showing relative area vs triangle area](image)

- Relative area
- Triangle area
- Slope
- Crossover scale
Road Surface Analysis

- Laser Profilometry Data
  - Height (z) as a function of area (x,y)
- Data bound by the resolution of the instrument
  - 25 microns
Mesoscopic Simulations and Block Copolymer Systems

- Block Copolymer are important industrial polymers
- “Blocks” with different chemistry
- Use as compatibilizers
  - go to the interface and “blend” different materials
- Different blocks do not “like” each other
  - microphase separation
  - morphology drives performance
Mesoscopic Simulations and Block Copolymer Systems - Polymers

Monomer $-CH_2-CH_2-$

Polymer $-CH_2-CH_2--CH_2-CH_2--CH_2-CH_2--CH_2-$

Polyethylene

Modern Computer Methods
1.-Atomistic
2.-Coarse-Grained
3.-Field Theoretic

Bead-Spring Model
The Gaussian Chain

Bond length has the Gaussian Distribution

\[ \varphi\{r_n\} = \left[ \frac{3}{2\pi b^2} \right] \exp\left( \frac{-3r^2}{2b^2} \right), \langle r^2 \rangle = b^2 \]

\[ \Psi\{r_n\} = \prod_n \varphi(r_n, r_{n+1}, \ldots, r_{n+n_c}) \]

\[ G(R, R'; N) = \left( \frac{2\pi Nb^2}{3} \right)^{-3/2} \exp\left( -\frac{3(R - R')^2}{2Nb^2} \right) \]

Flexible Polymer
Density Functional Theory

Langevin Equation for diffusive dynamics of density fields:

\[
\frac{\partial \rho_A(r)}{\partial t} = \nabla \cdot \left( M \nabla \rho_A \nabla (\mu_A - \mu_B) \right) + \eta \\
\frac{\partial \rho_B(r)}{\partial t} = \nabla \cdot \left( M \nabla \rho_B \nabla (\mu_B - \mu_A) \right) - \eta
\]

\(\rho\sim\) density  
M~mobility  
\(\nu\sim\) volume  
\(\mu\sim\) potential  
\(\eta\sim\) noise

The polymer architecture is included in the partition function

A free energy density functional is constructed which includes a nonideal contribution (\(\chi\))

The noise distribution satisfies the fluctuation-dissipation theorem
Crank-Nicolson Scheme

- The system of equations is solved via a Crank-Nicolson scheme
- It is used to determine how the system evolves in time (not space)
- These methods are good for solving ordinary differential equations because they have a higher order of convergence than one-step explicit or implicit methods
The Impact of Level of Noise on the Dynamics

The variance of the noise is proportional to:

$$2\Delta\tau / \Omega$$

$\tau$~time step
$\Omega$~noise expansion parameter

If the noise is too low (small $\tau$ or large $\Omega$)- **NO RESULTS**
If the noise is high (larger $\tau$ or smaller $\Omega$)- **DYNAMICS**
Sometimes at very low time steps, the results are **unstable**
Phase Diagram

\[ \chi_N \]

- spheres
- cylinders
- bicontinuous
- lamellar

Disordered region

\[ \phi_A = 0.5 \]

Isodensity Profiles

- lamellar
- spheres
- cylinders
Monte Carlo and Complex Fluids

Molecular Modeling
- Molecular Modeling

Polymer Modeling
- Polymer Modeling

Constitutive Modeling
- Constitutive Modeling

Transport Modeling
- Transport Modeling

monolayers

surfactants

micelles & vesicles

design of materials

Spherical micelle

Bilayer

Reverse Micelles
Monte Carlo Methods-The Canonical Ensemble

Isolated System composed of $M$ subsystems each $V, N, T$

$$\nu_i \quad \text{# of subsystems in ith state}$$

$$M = \sum_i \nu_i, \quad E_T = \sum_i E_i \nu_i, \quad \Omega(\{\nu\}) = \frac{M!}{\prod_i \nu_i}$$

The Partition Function

$$Q_N = \sum_i e^{-\beta E_i} \quad \text{(thermodynamics)}$$

$$p_i = \frac{e^{-\beta E_i}}{Q_N} \quad \text{(ith probability)}$$

$$U = \sum_i E_i p_i = -\left(\frac{\partial \ln Q_N}{\partial \beta}\right)_{N,V}$$

$$P = \sum_i P_i p_i = -\left(\frac{\partial \ln Q_N}{\partial V}\right)_{N,\beta}$$
Monte Carlo Scheme

- Select a particle at random and calculate the energy of its configuration $U(\text{old})$
- Displace the particle at random. Calculate new $U(\text{new})$
- The probability $\alpha = \alpha(\text{old}) = \alpha(\text{new})$ so that
- The Move is accepted with a probability of
  $$\min(1, \exp[-\beta (U(\text{new}) - U(\text{old}))])$$
- If rejected the old configuration is kept
Strategy

- Electrostatic
- Surface interactions

\[ g_{\text{head}} \]

\[ g_{\text{tail}} \]

\[ n_c - 2 \]

MC Simulations

Free energy model

Molecular Modeling

Polymer Modeling

Constitutive Modeling

Transport Modeling
Composition Effect on Micelle Size

Reduction in area with increase in mole fraction $\text{Sal}^-$ is consistent with experiments of Lin et al. *J. Phys. Chem.*, 1994

Micelle sizes are consistent with experimental observations.
For pure CTA\(^+\), the head groups in a spherical micelle have a lower free energy. Increasing Sal\(^-\) shields repulsive interactions making cylindrical conformations more favorable. Ordering in the micelles also influences free energy.
Summary

- Mathematics is at the core of our Materials Development
- We are in constant need of “smarter” and “faster” algorithms to probe material behavior