Soft Matter Properties: What can we learn from computer simulations?

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Why computer simulation?

- Experiments give us very interesting results
- Analytical theory is extremely difficult

We will perform molecular dynamics or computer experiments (solving Newton’s equations of motions)

\[ m\ddot{R}_i = - \nabla V (\{R_i\}) - \gamma m\dot{R}_i + \mathcal{F}_i(t) \]

Langevin Equation of motion
Outline

- Polymer in high geometric confinement
  (coarse-grained modeling)

- Advanced functional materials
  (coarse-grained modeling and experiments)

- Liquid mixtures
  (Adaptive Resolution Scheme)
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Why confined polymers?

Applications from Biology to Friction

Kreer et. al. Langmuir 17, 7804 (2001)

Maier et. al. PRL 18, 1911 (1999)
Popular Cases

- Trapped chain in a tube.
- Polymer in narrow-slit.
- Polymer translocation through narrow-pore.
- Polymers confined and sheared between two walls.
- Adsorbed polymers.
Single flexible chain

Scaling of lateral diffusion as a function of chain length.

\[ D \propto N^{-y} \]

Maier et. al. PRL 18, 1911 (1999).
Case - II

Mono-dispersed polymers

Lateral diffusion as a function of surface coverage

\[ D = c f (\Gamma) \]

Zhao and Granick, JACS comm. 126, 6242 (2004).
Problems with prior simulations

Surface: an attractive/repulsive hard wall.


Simulations implemented energy barriers with infinite height.


Not sure how to compare these simulation results with real laboratory experiment.

-At atomic level corrugation barrier exists!
Our modeling

Kremer-Grest Model: Bead spring chain

How does the surface diffusion depend on surface coverage?

Experimental observation of lateral diffusion as a function of surface coverage

Degree of polymerization: fixed

Zhao and Granick, JACS comm. 126, 6242 (2004).
Measurement of lateral diffusion coefficient: Experiment and Simulations

**Einstein relation**

\[ D = \frac{1}{2} \lim_{t \to \infty} \frac{\partial C(t)}{\partial t} \]

\[ C(t) = \frac{1}{2N} \sum_{\alpha=1}^{2N} \sum_{i=1}^{N} \left< [R_{i\alpha}(t + t') - R_{i\alpha}(t')]^2 \right> \]

- **Experiment**
  \[ G'(t) = G(0) \frac{1}{1 + 8Dt/W_0^2} \]

- **Simulation**

Zhao and Granick, JACS comm.126, 6242 (2004).
Experiment vs Simulations

\( \Lambda \)-shape anomaly

Experiment

Simulation: Crystalline

Simulation: Amorphous

\( D \) : Lateral Diffusion Coefficient

\( \Gamma \) : Number of monomers per unit surface area

Zhao and Granick, JACS comm.126, 6242 (2004).


Why discontinuity?

Single layer

Note: Fluctuation mediated increase.

Structural transition

Double layer
Molecular snapshot (side view)

\[ \Gamma < \Gamma^* \]

\[ \Gamma > \Gamma^* \textbf{ Note: Load effect is mere 20\%} \]

Something more is going on, not only simple external adhesive load effect!

Molecular snapshot (bottom view)

\[ \Gamma < \Gamma^* \]

Single layer

\[ \Gamma > \Gamma^* \]

Double layer

As viewed from the substrate

Double layer formation

\[ \Gamma < \Gamma^* \]

\[ \Gamma > \Gamma^* \]
Theoretical interpretation

Corrugation barrier:

\[ \Delta E \propto \sum_Q S_{\text{sub}}(Q)S_{\text{slider}}(Q) \exp(iQx) \]

Structure factor

Corrugation barrier: $S(Q=G)$

$\Delta E \propto S(G)$

Arrhenius-type activation picture:

$$D \propto \exp(-\alpha S(G)/k_BT).$$

$S_{2b}(Q)$: Bottom layer of double layer structure

$S_s(Q)$: Single layer structure

$S_{sub}(Q)$: Substrate’s Bragg peak

Single polymer dynamics

Experiments vs simulations

Maier and Radler, PRL 18, 1911 (1999).
Zhang et. al. PNAS 102, 9118 (2005).
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  (Adaptive Resolution Scheme)
What are these functional materials?

- Light weight high performance matrices
- Outstanding chemical and corrosion resistance
- Good thermal and adhesive properties
- Extremely strong (~GPa)

- Extremely brittle (~1% strain)
Improving toughness

- Ductility can be increased by decreasing bond density.

Jang et. al., Adv. Mat. 18, 2123 (2006)

Reducing bond density enhances plastic deformation at the same time significantly reduces tensile strength.

How to improve ductility/toughness of a neat thermoset matrix?
Simulation details

KISS method: Keep it simple and stupid

Coarse-grained model:
• Non-bonded = LJ interactions
• Bonded = WCA + Quartic

Stevens, Macromolecules 34, 2710 (2001).

Network cure:
• 4 functional monomers
• 95% cure

Stress-strain behavior

Possible origin of strain hardening

Why voids?

- Bond orientation is random: 4 from 12 neighbors.
- Proto-voids already present.
- Strain disrupts non-bonded interaction.
- Void volume increases with strain (until bonds break).

What if we prevent void formation?

Experiment
IR spectra

Wavenumber (cm$^{-1}$)
Solvent evaporation and Tg
Toughness
Voids: SEM pictures
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Thermodynamic properties from structural details (Grand-canonical ensemble)

\[ G_{ij}(r) = 4\pi \int_{0}^{\infty} \{g_{ij}(r) - 1\} r^2 dr \]

for \( r \rightarrow \infty \)

\[ G_{ij}(r) = V \left[ \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{\langle N_j \rangle} \right] \]
Problems with closed boundary simulations NVT (Methanol + Water)
Effective Grand-canonical MD scheme
Adaptive Resolution Molecular Dynamics Scheme

Liquid mixture: AdResS Scheme

Mukherji, van der Vegt, Delle Site, and Kremer (to be submitted).
- Computer simulation can be effectively employed to study microscopic properties of soft matter.

- Surface roughness and interlocking of adsorbed layer dictates the dynamics of slider.

- Computer simulation could suggest a means to toughen epoxy network via formation and growth of micro-voids.

- An effective Grand-Canonical type simulation scheme was employed to study highly structured liquid mixtures.
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