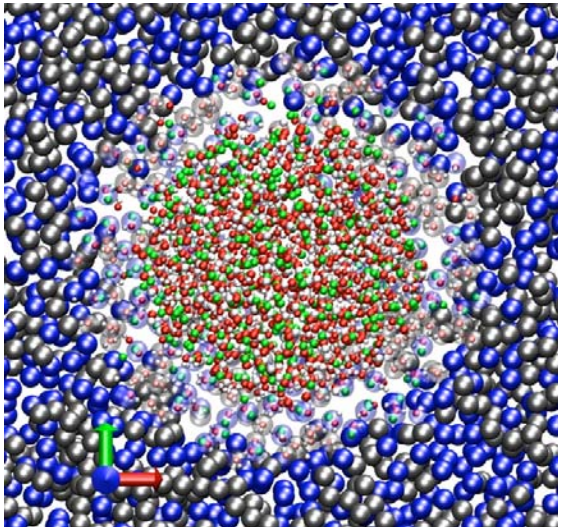
Soft Matter Properties: What can we learn from computer simulations?



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15th July @ 9:30 AM

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)

$$m\ddot{\mathbf{R}}_i = -\overrightarrow{\nabla} V\left(\{\mathbf{R}_i\}\right) - \gamma m \dot{\mathbf{R}}_i + \mathcal{F}_i(t)$$

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

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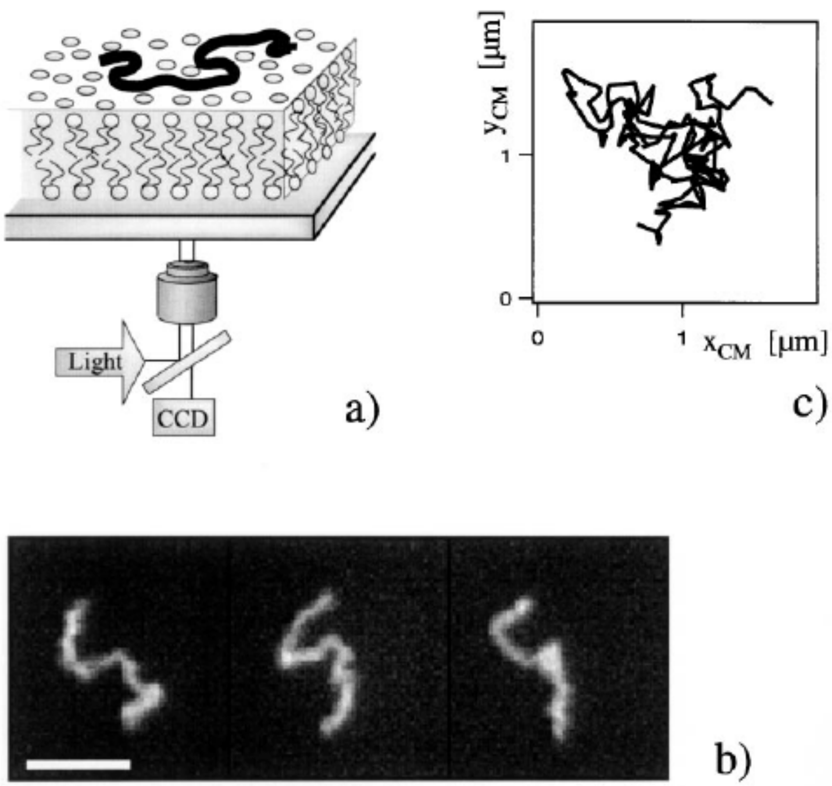
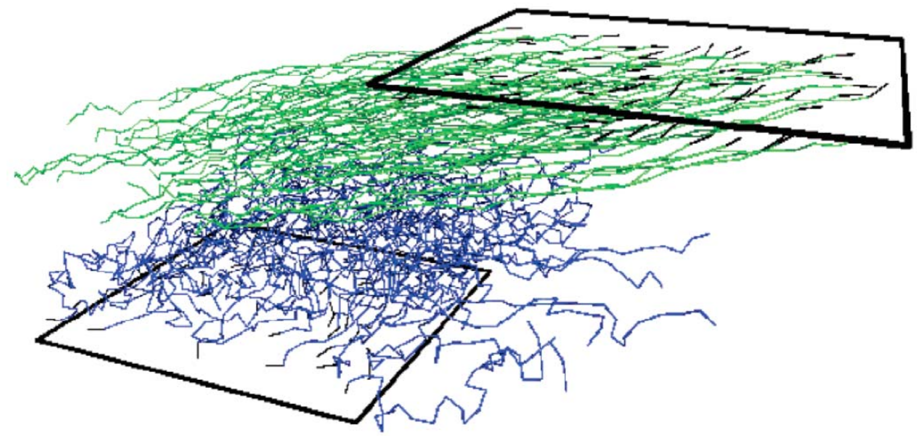
Why confined polymers?

Applications from Biology to Friction



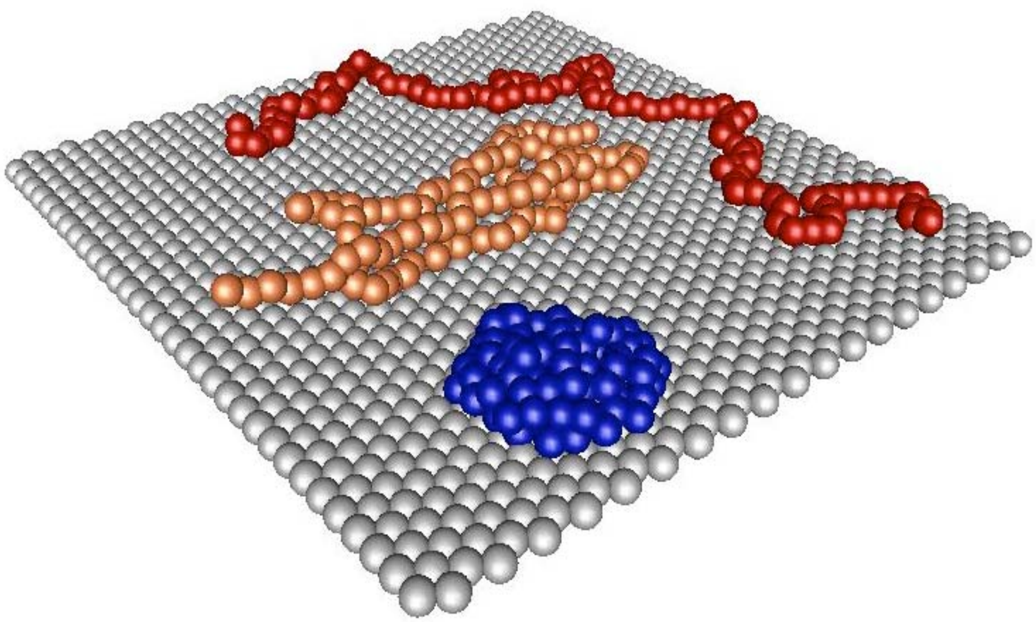
Maier et. al. PRL 18, 1911 (1999)



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

Popular Cases

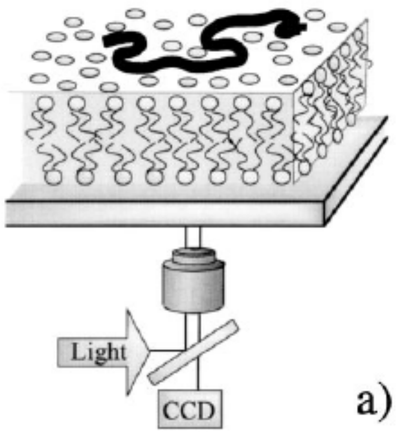
- Trapped chain in a tube.
- Polymer in narrow-slit.
- Polymer translocation through narrow-pore.
- Polymers confined and sheared between two walls.
- Adsorbed polymers.



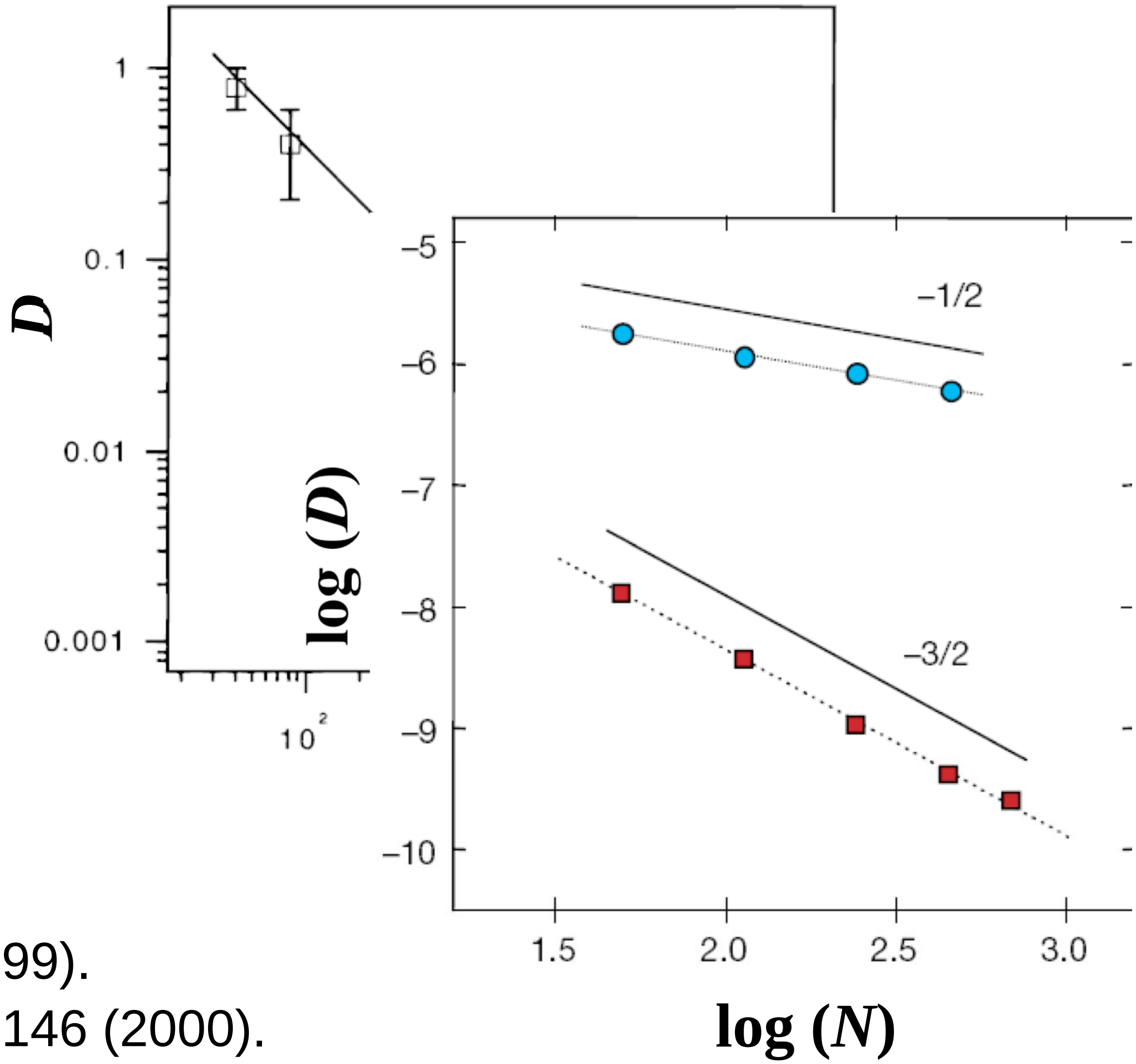
Case - I

Single flexible chain

Scaling of lateral diffusion as a function of chain length.



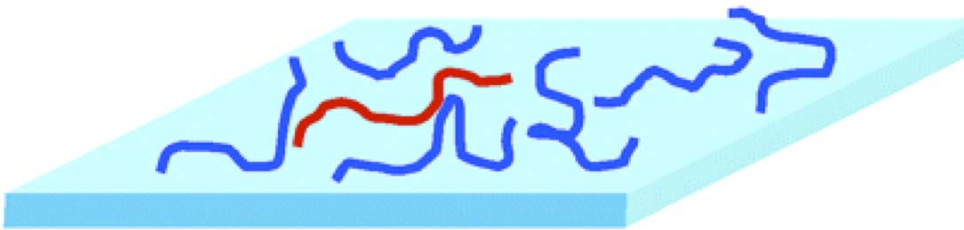
$$D \propto N^{-y}$$



Maier et. al. PRL 18, 1911 (1999).
Sukhishvili et. al. Nature 406, 146 (2000).

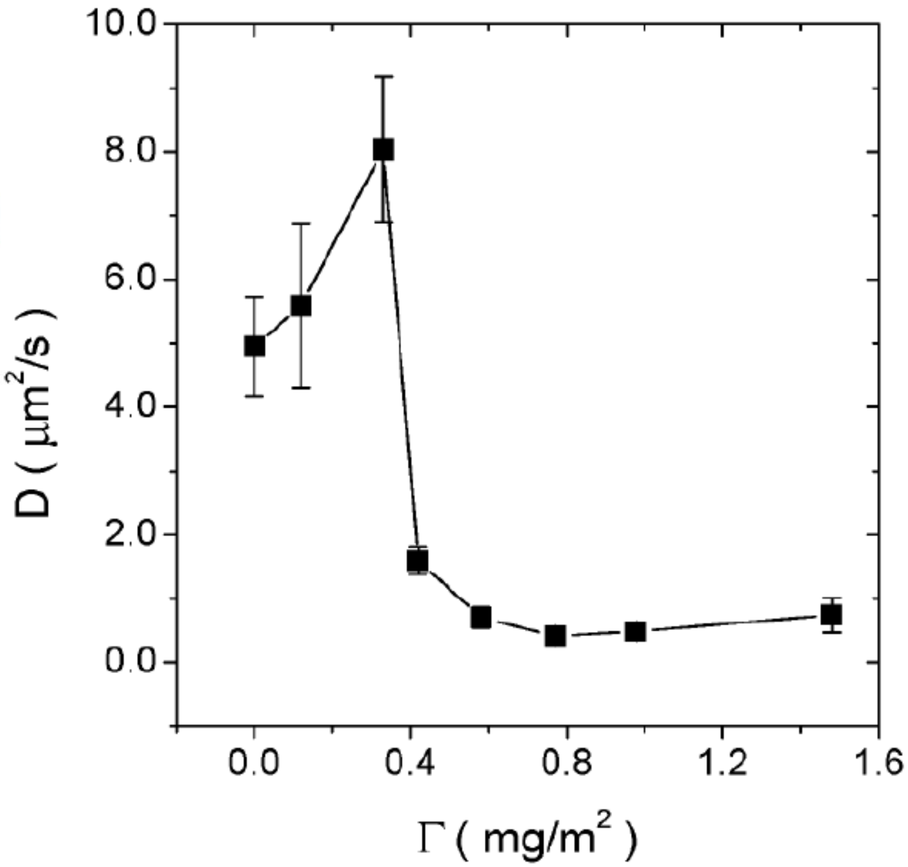
Case - II

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.

Milchev et. al., Macromolecules 29, 343 (1996).
Pandey et. al., Macromolecules 30, 1194 (1997).
Patra et. al., J. Chem. Phys. 111, 1608 (1999).

Simulations implemented energy barriers with infinite height.

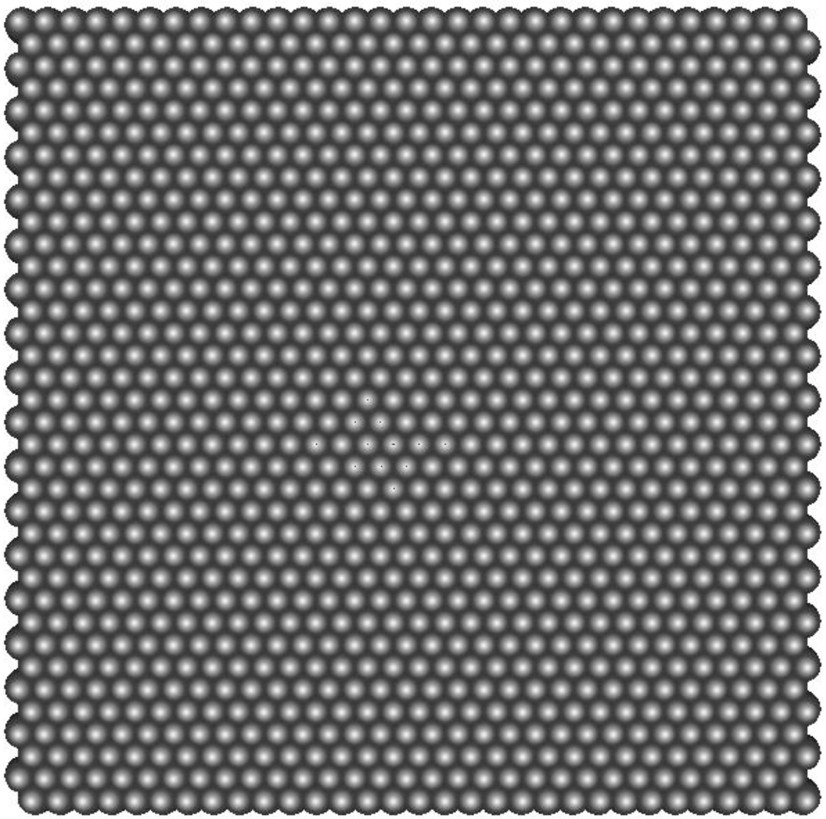
Azuma and Takayama, J. Chem. Phys. 111, 8666 (1999)
Desai et. al., J. Chem. Phys. 124, 084904 (2006).

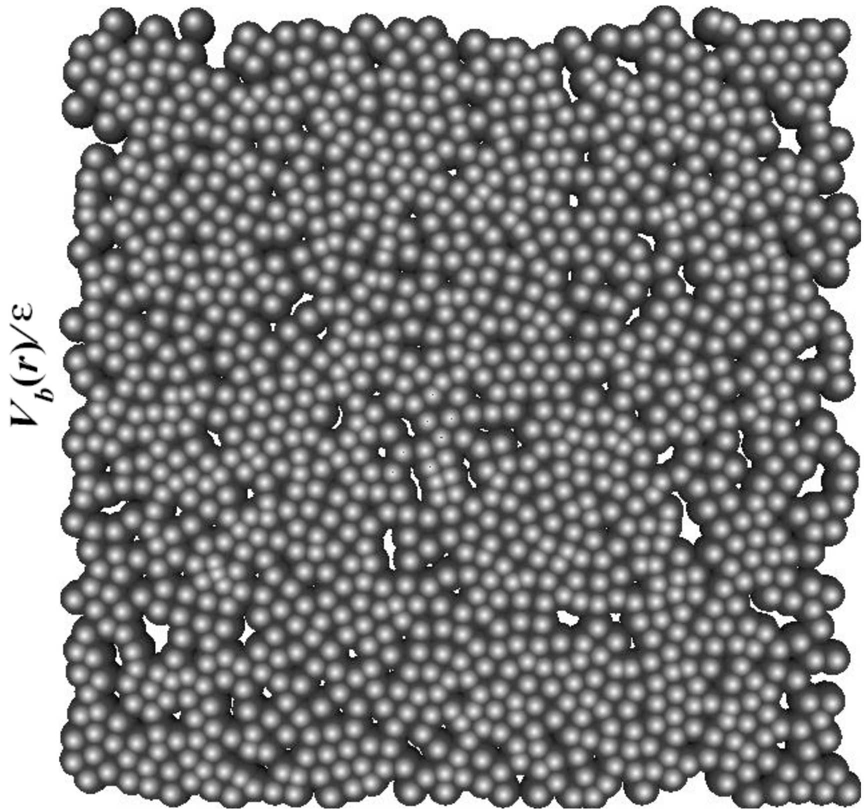
Not sure how to compare these simulation results with real laboratory experiment.

-At atomic level corrugation barrier exists !

Our modeling

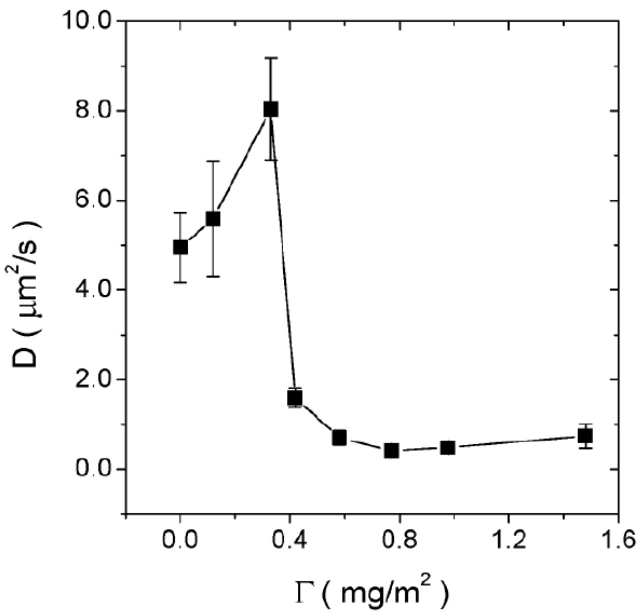
Kremer-Grest Model: Bead spring chain



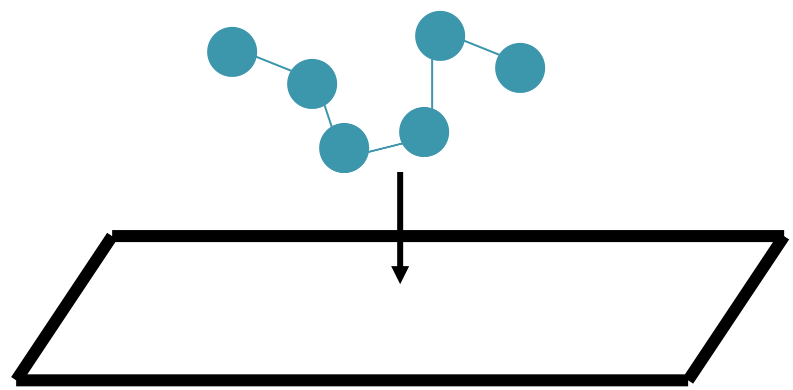


Kremer and Grest, J. Chem. Phys., 92, 5057 (1990).

How does the surface diffusion depends on surface coverage?



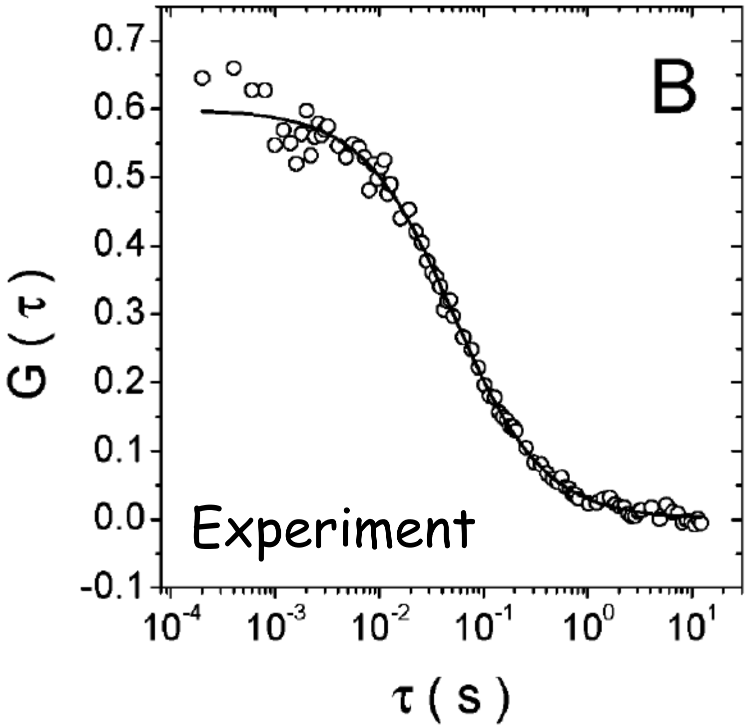
Experimental observation of lateral diffusion as a function of surface coverage



Degree of polymerization: fixed

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

Measurement of lateral diffusion coefficient: Experiment and Simulations

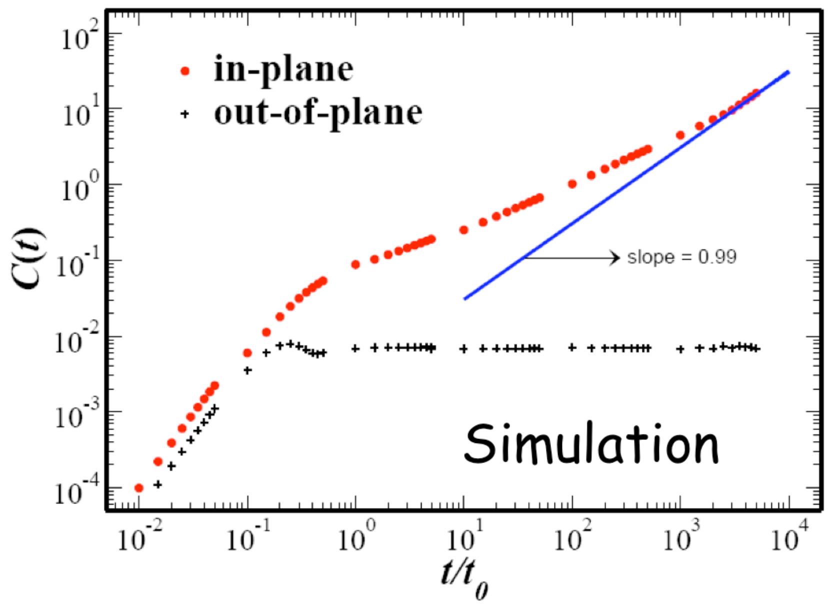


$$G(t) = G(0)\frac{1}{1 + 8Dt/W_0^2}$$

Einstein relation

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

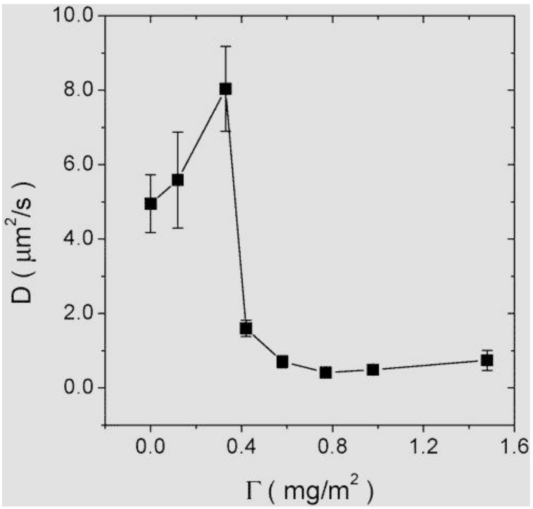
$$C(t) = \frac{1}{2N}\sum_{\alpha=1}^{2}\sum_{i=1}^{N}\left\langle [R_{i\alpha}(t+t') - R_{i\alpha}(t')]^2 \right\rangle$$



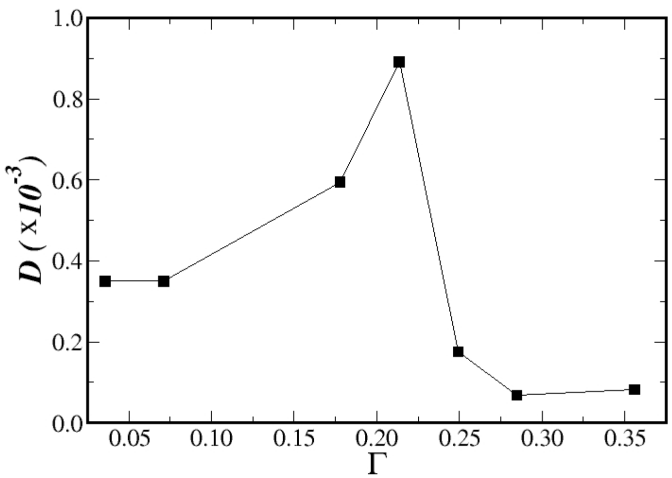
Zhao and Granick, JACS comm.126, 6242 (2004).

Experiment vs Simulations

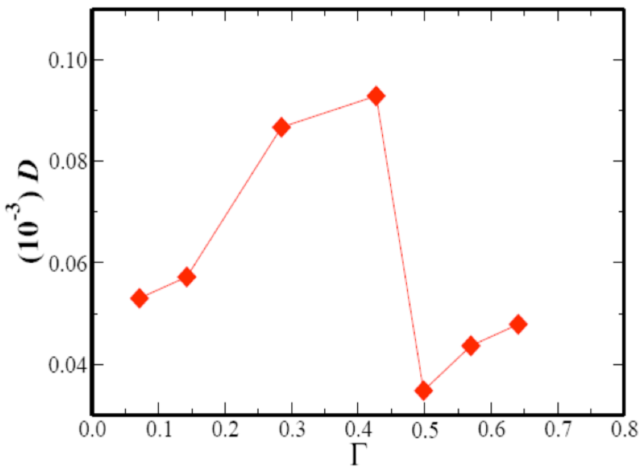
Λ−shape anomaly



Experiment



Simulation: Crystalline



Simulation: Amorphous

D : Lateral Diffusion Coefficient

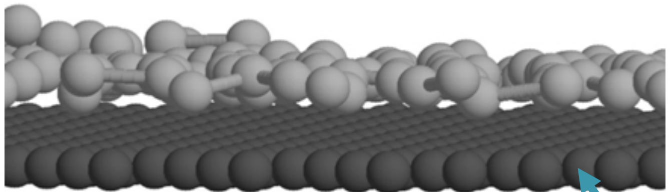
Γ: Number of monomers per unit surface area

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

Mukherji and Müser, Phys. Rev. E, 74, 010601(**R**) (2006).

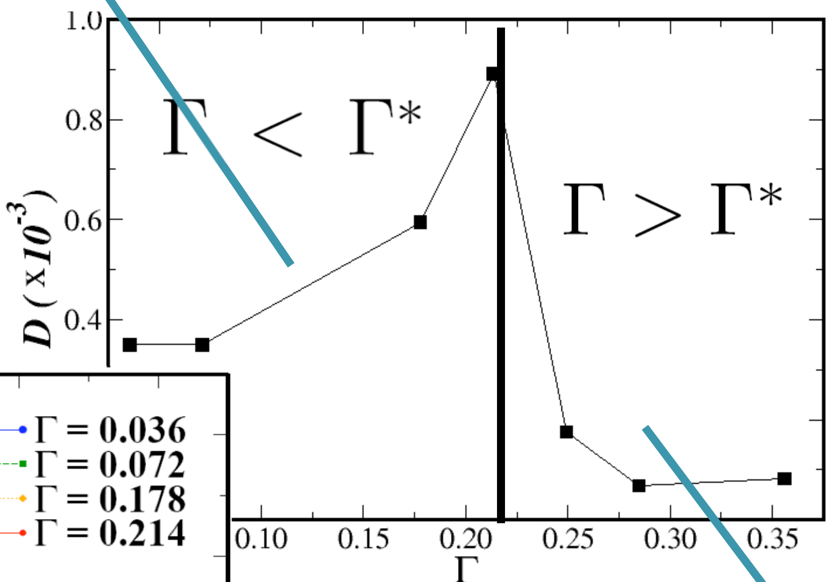
Mukherji and Müser, Macromolecules, 40 (5), 1754 (2007).

Why discontinuity?

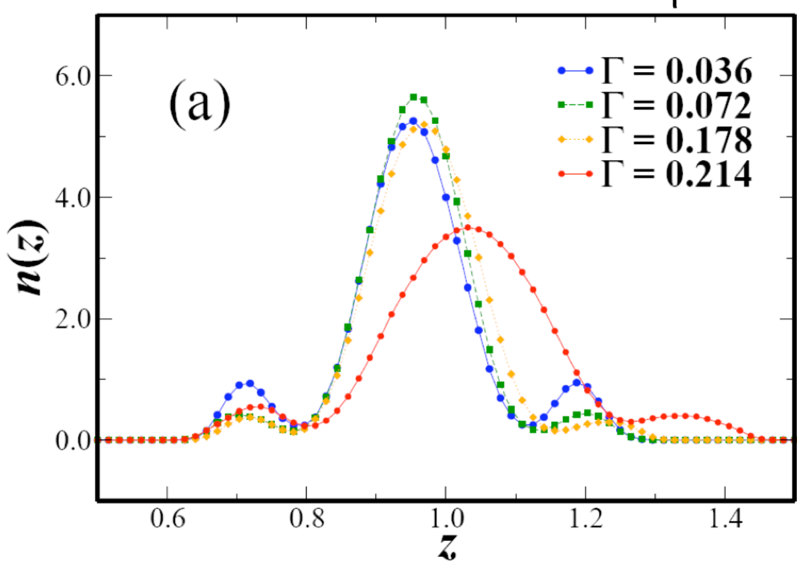


Single layer

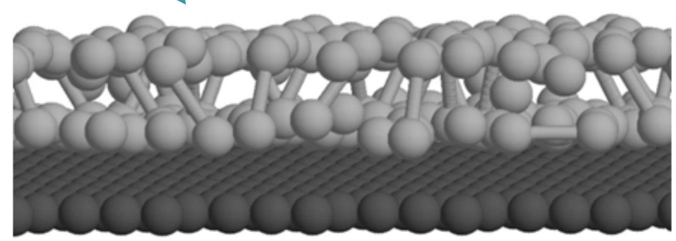
Structural transition



Note: Fluctuation mediated increase.

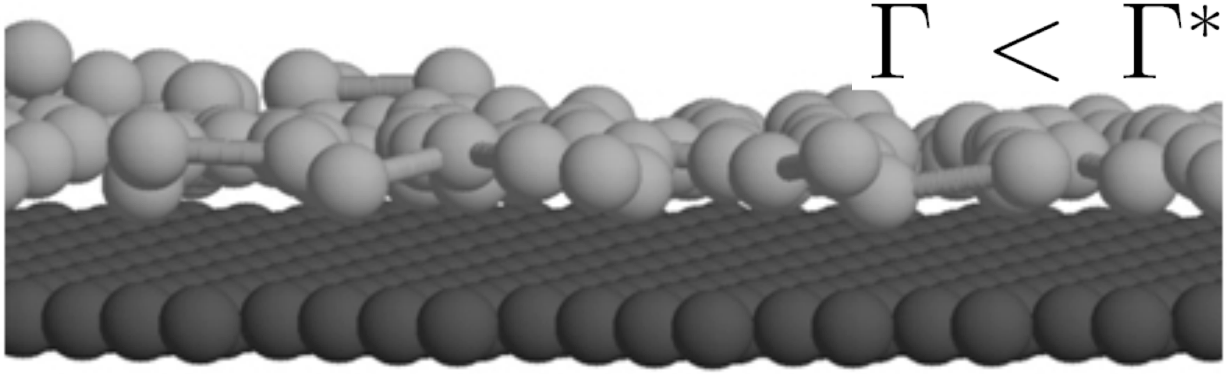


Double layer



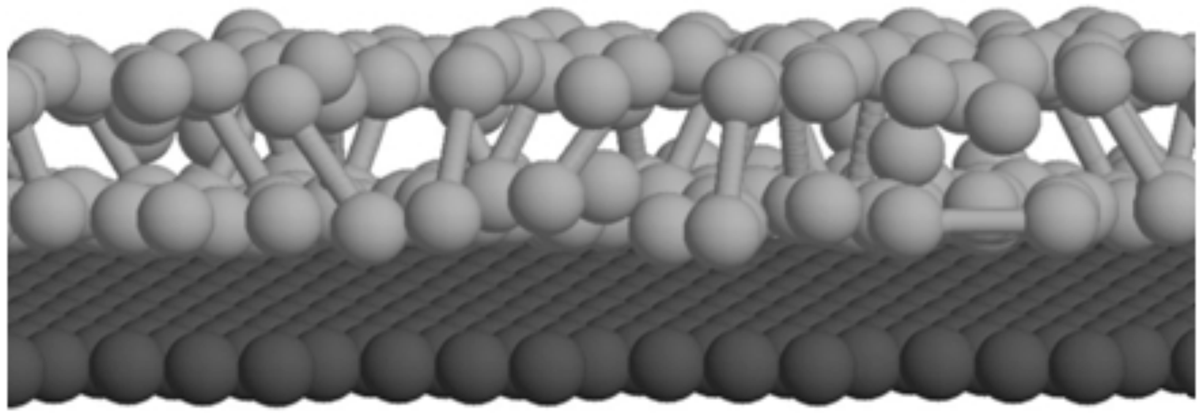
Molecular snapshot (side view)

$\Gamma < \Gamma^*$



$\Gamma > \Gamma^*$ **Note:** Load effect is mere 20%

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

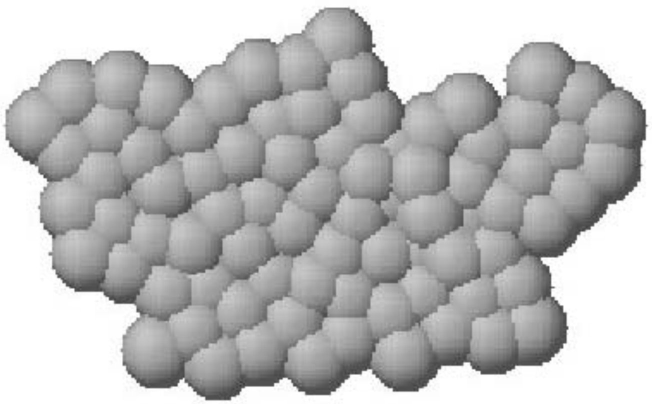


Mukherji and Müser, Phys. Rev. E, 74, 010601(**R**) (2006).

Molecular snapshot (bottom view)

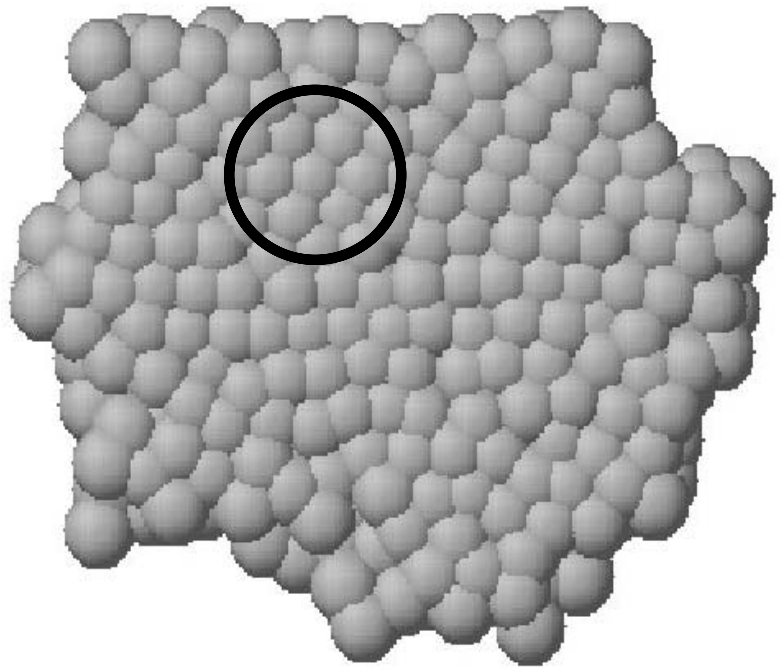
Incompatible intrinsic length scale

$\Gamma < \Gamma^*$



Single layer

$\Gamma > \Gamma^*$



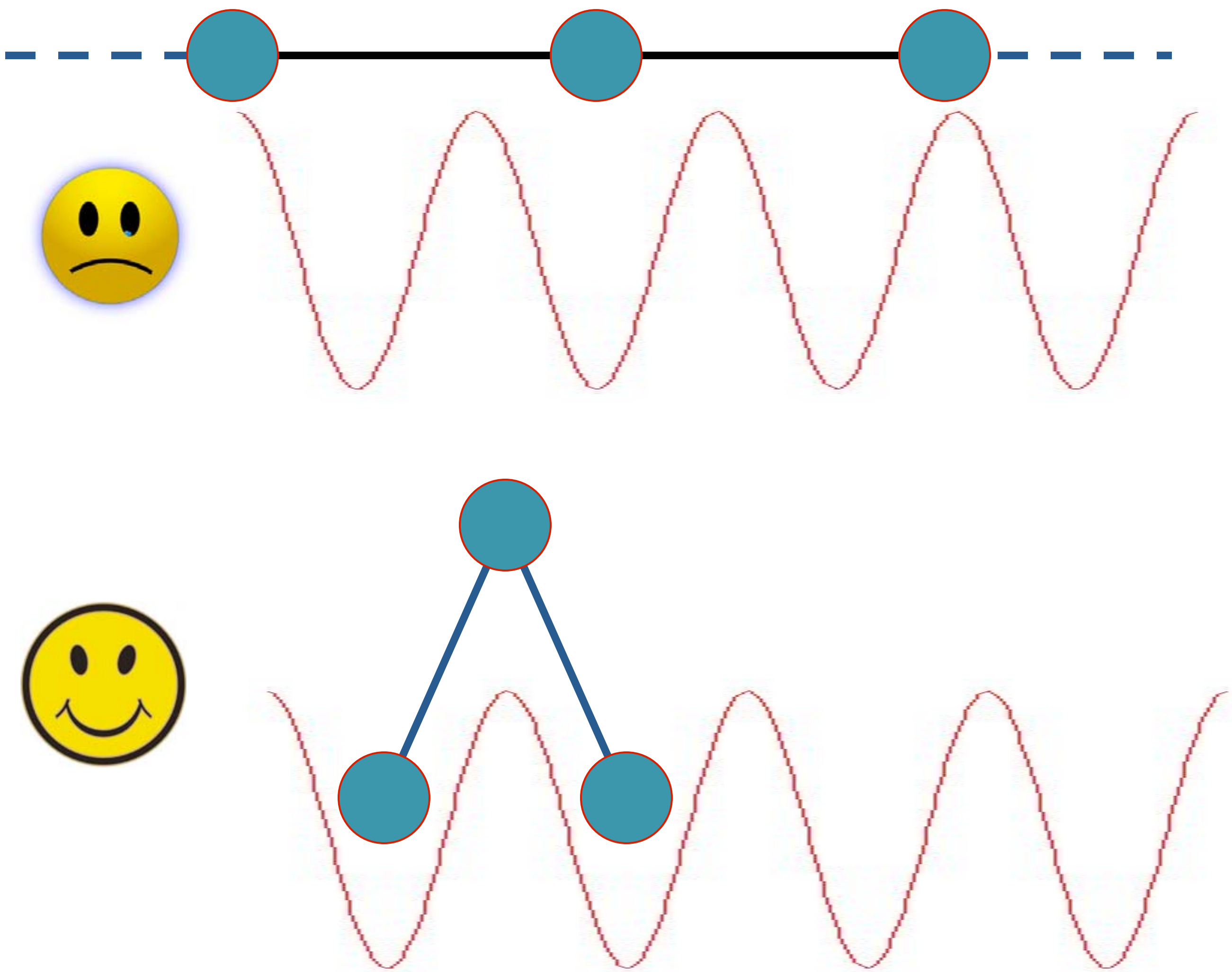
Double layer

Compatible intrinsic length scale

As viewed from the substrate

Mukherji and Müser, Phys. Rev. E, 74, 010601(**R**) (2006).

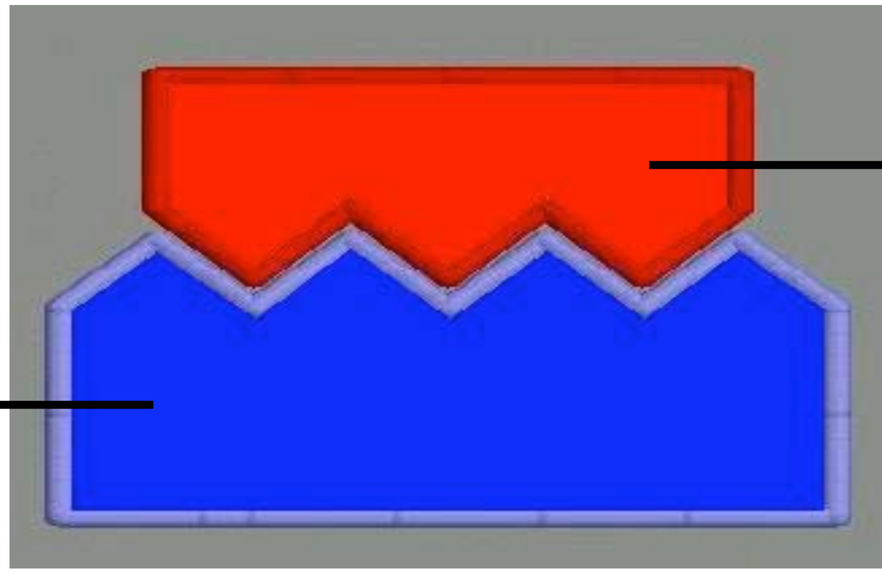
Double layer formation



$\Gamma < \Gamma^*$

$\Gamma > \Gamma^*$

Theoretical interpretation

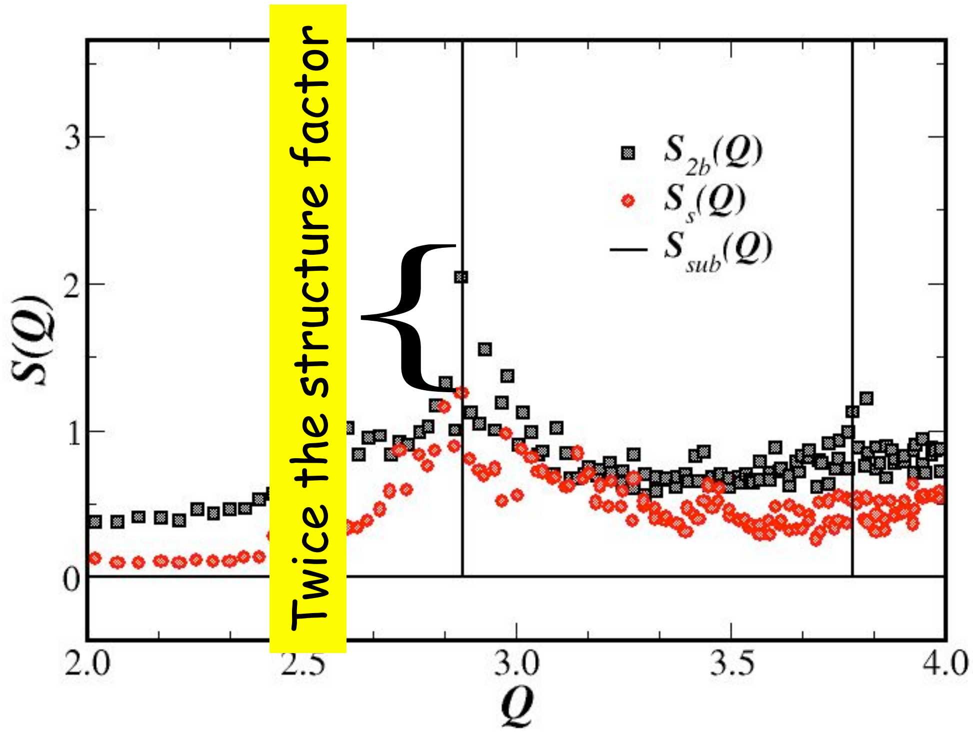


Corrugation barrier:

$$\Delta E \propto \sum_{Q} S_{sub}(Q) S_{slider}(Q) \exp(iQx)$$

Müser, Wenning and Robbins, Phys. Rev. Lett., 86, 1295 (2001).

Structure factor



Corrugation barrier: S(*Q*=*G*)

$$\Delta E \propto S(G)$$

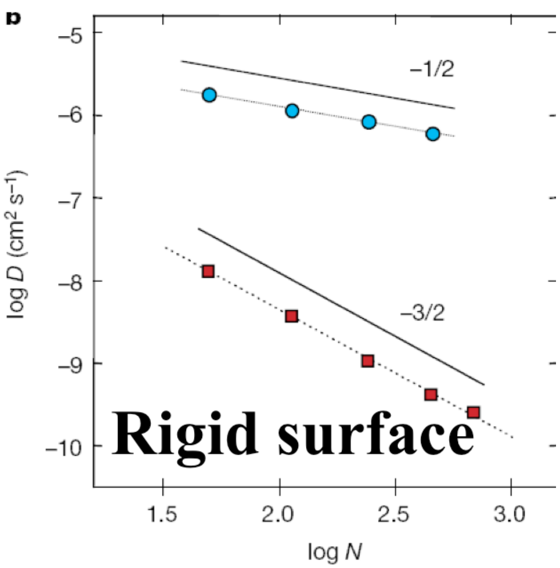
Arrhenius-type activation picture:

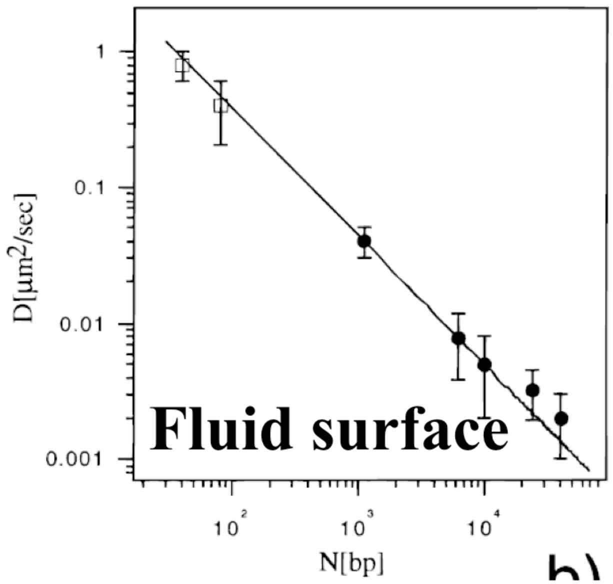
$$D \propto \exp(-\alpha S(\mathbf{G})/k_B T)$$

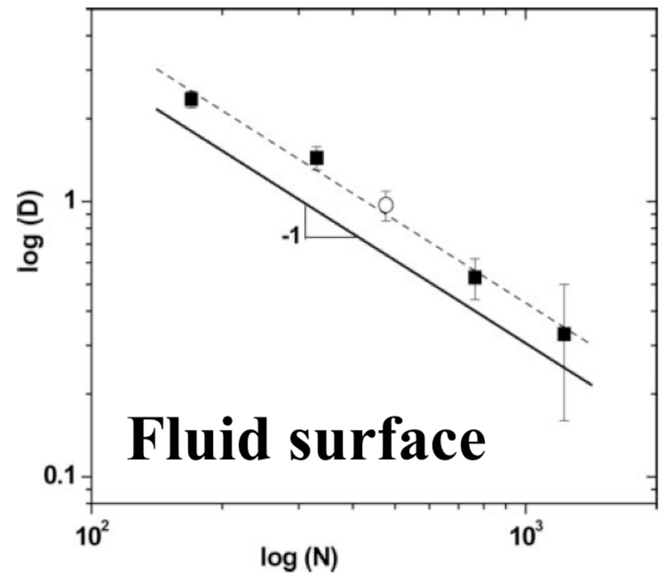
S_{2b}(Q): Bottom layer of double layer structure
S_s(Q) : Single layer structure
S_{sub}(Q): Substrate’s Bragg peak

Mukherji and Müser, Phys. Rev. E, 74, 010601(**R**) (2006).

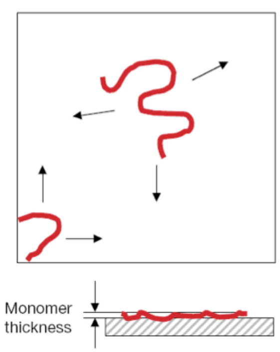
Single polymer dynamics

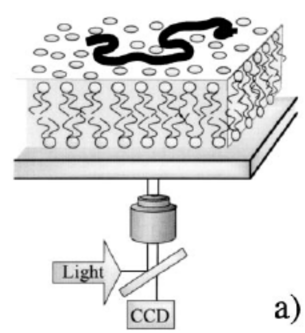


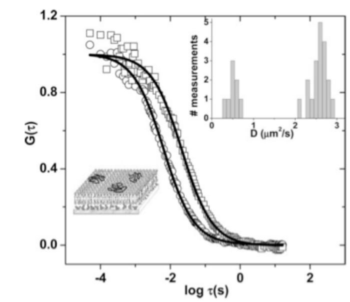




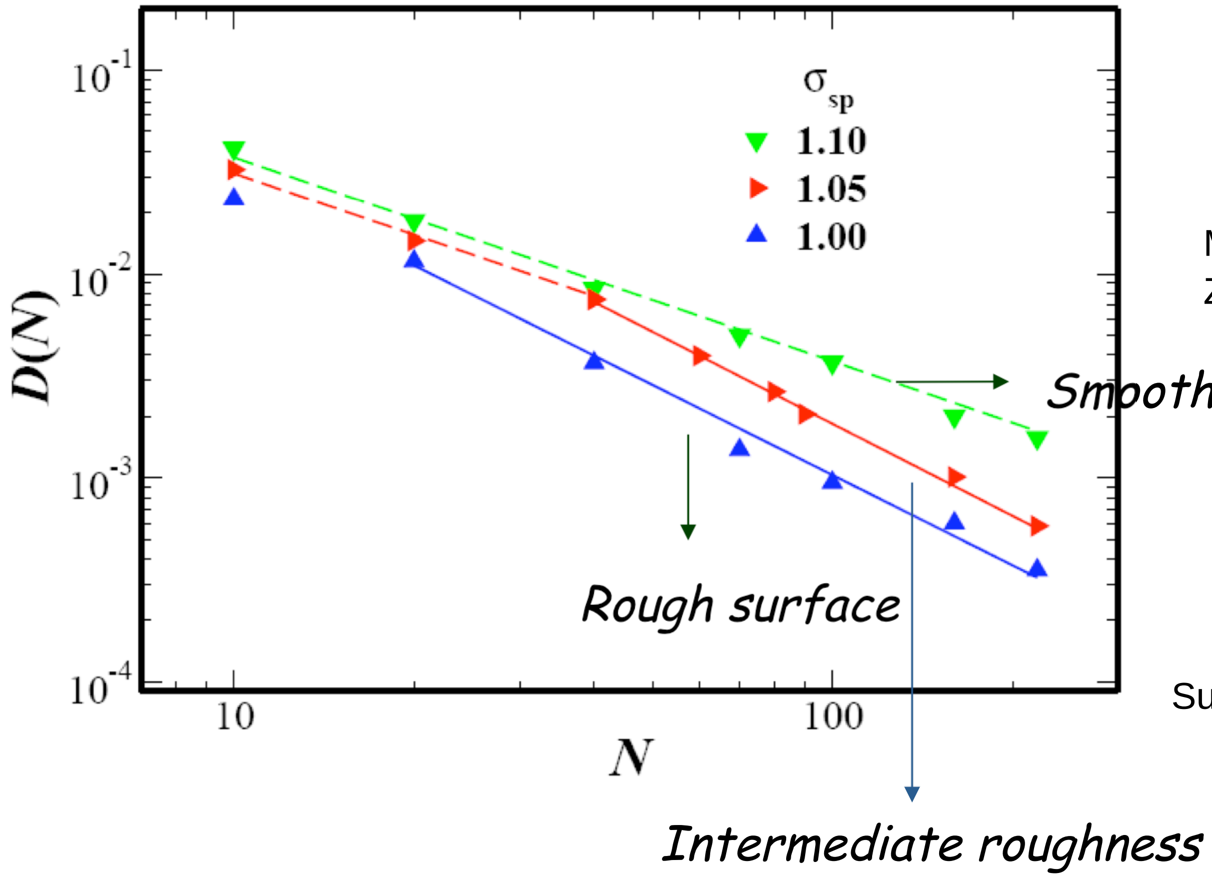
Sukhishvili et. al. Nature 406, 146 (2000). Maier et. al. PRL 18, 1911 (1999). Zhang et. al. PNAS 102, 9118 (2005).







Experiments vs simulations



$$D \propto N^{-1}$$

Maier and Radler, PRL 18, 1911 (1999).
Zhang et. al. PNAS 102, 9118 (2005).

$$D \propto N^{-3/2}$$

Sukhishvili et. al. Nature 406, 146 (2000).

Mukherji, Bartels and Müser, Phys. Rev. Lett., 100, 068301 (2008).

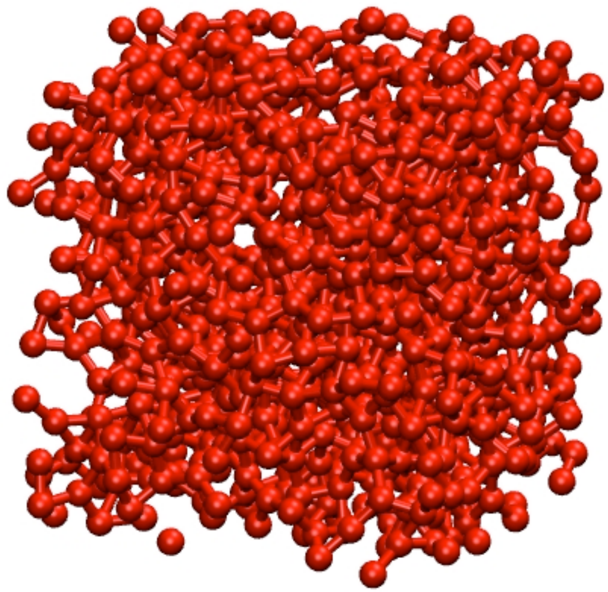
Outline

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

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

- Liquid mixtures
(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 ?

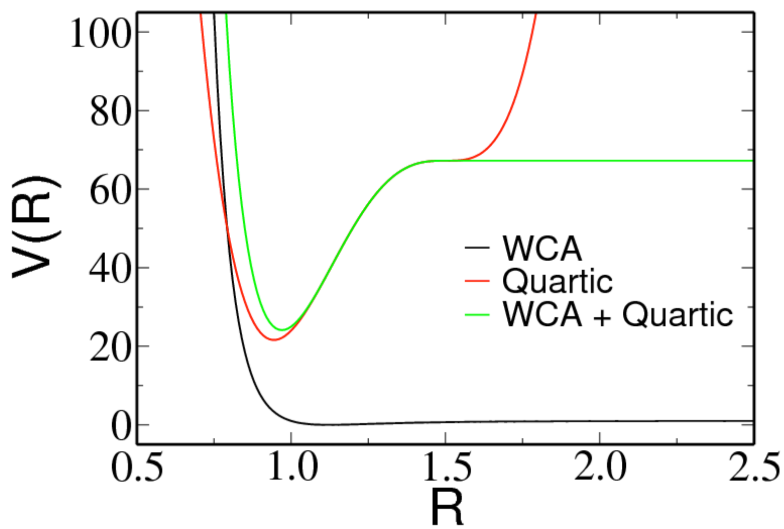
Simulation details

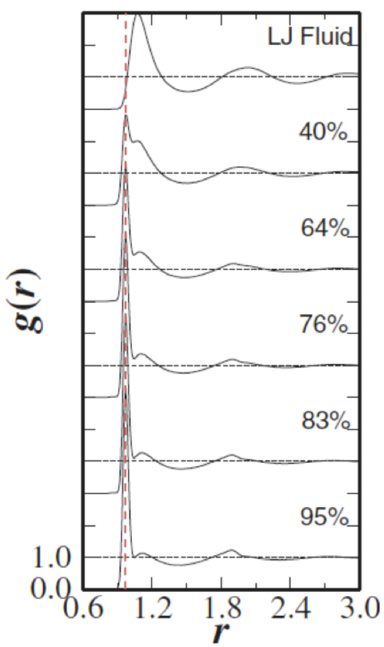
KISS method: Keep it simple and stupid

Coarse-grained model:

- •Non-bonded = LJ interactions
- •Bonded = WCA + Quartic

Stevens, Macromolecules **34**, 2710 (2001).

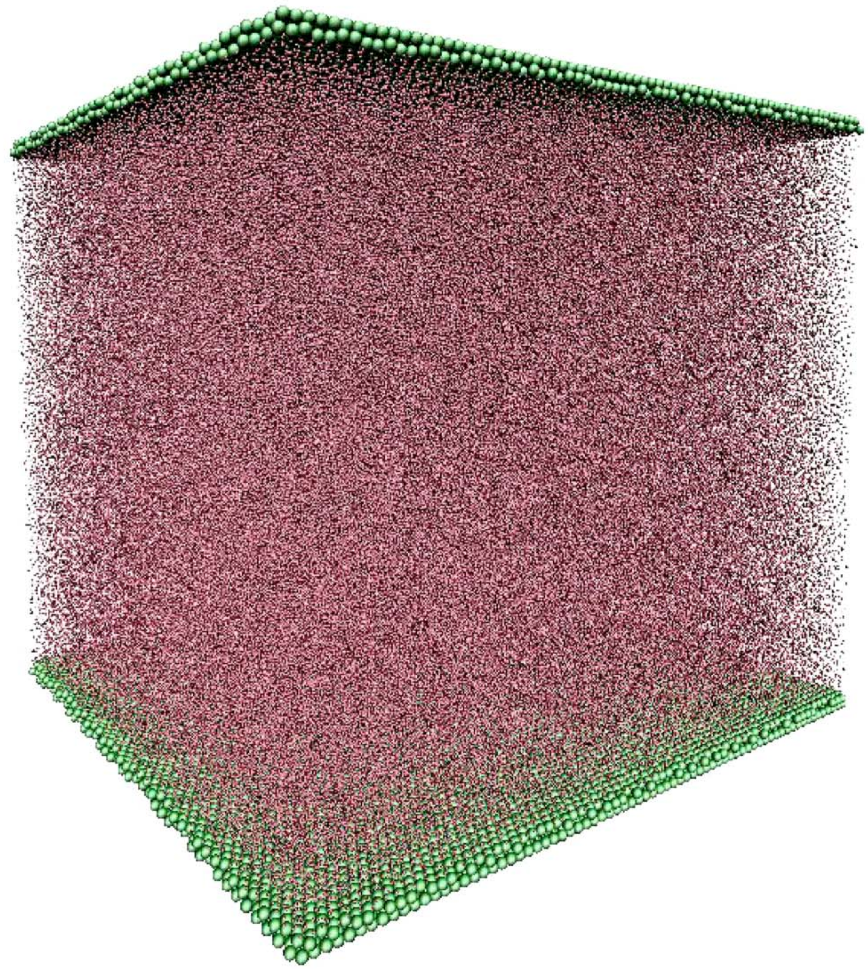




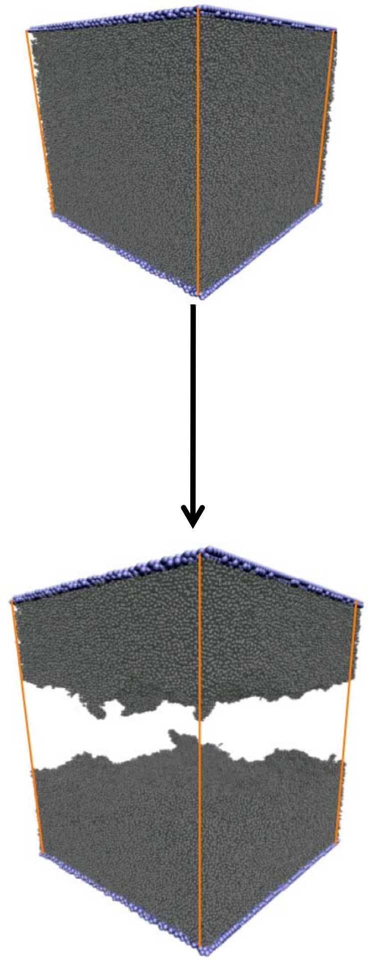
Network cure:

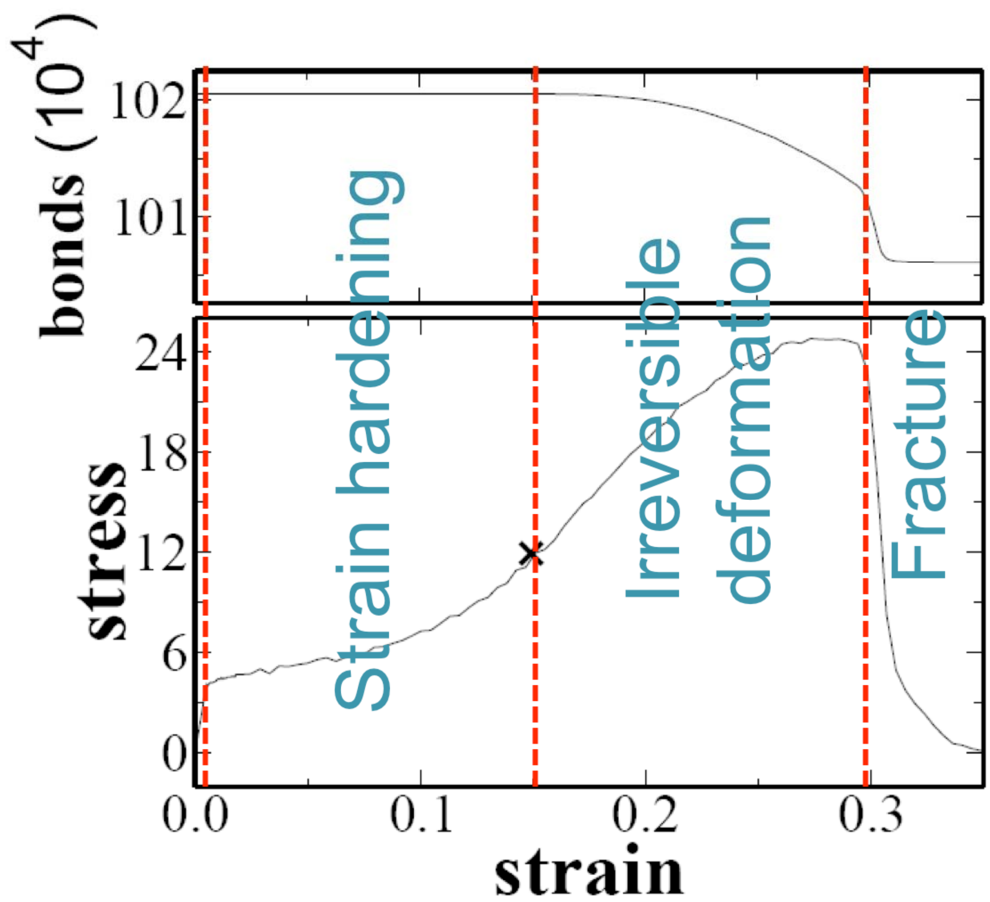
- •4 functional monomers
- •95% cure

Mukherji and Abrams, Phys. Rev. E, 79, 061802 (2009).



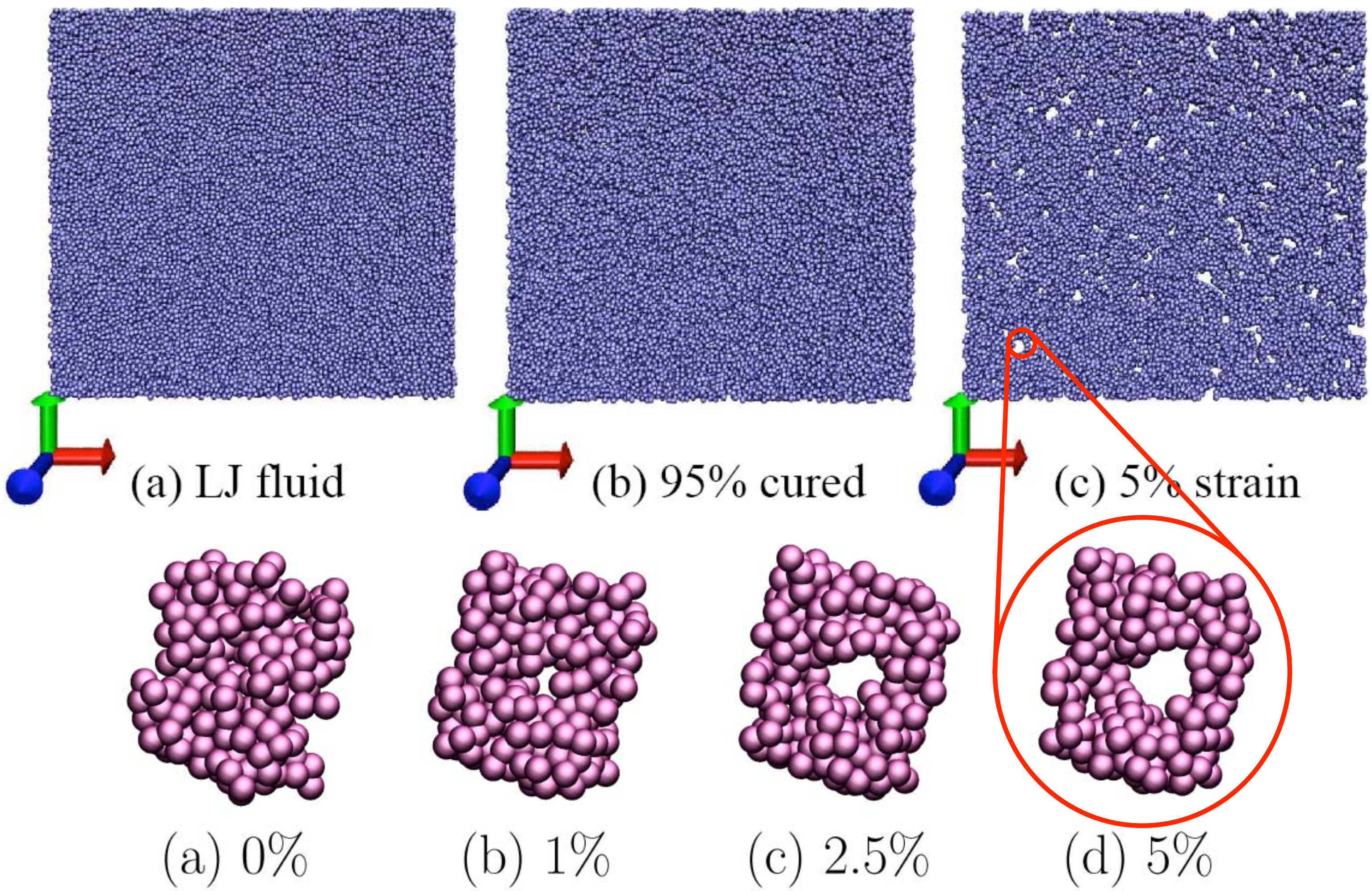
Stress-strain behavior





Mukherji and Abrams, Phys. Rev. E, 78, 050801(R) (2008).

Possible origin of strain hardening



Mukherji and Abrams, Phys. Rev. E, 78, 050801(R) (2008).

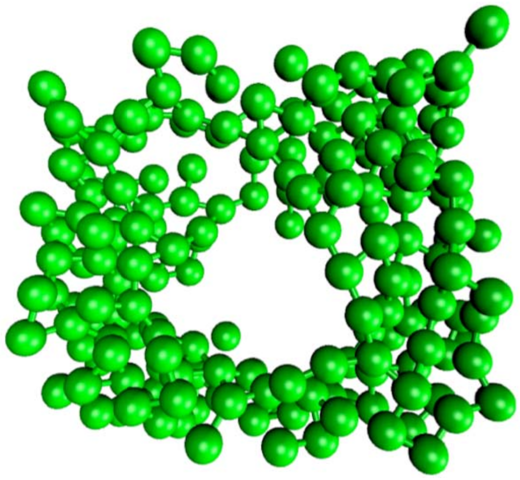
Why voids?

-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).

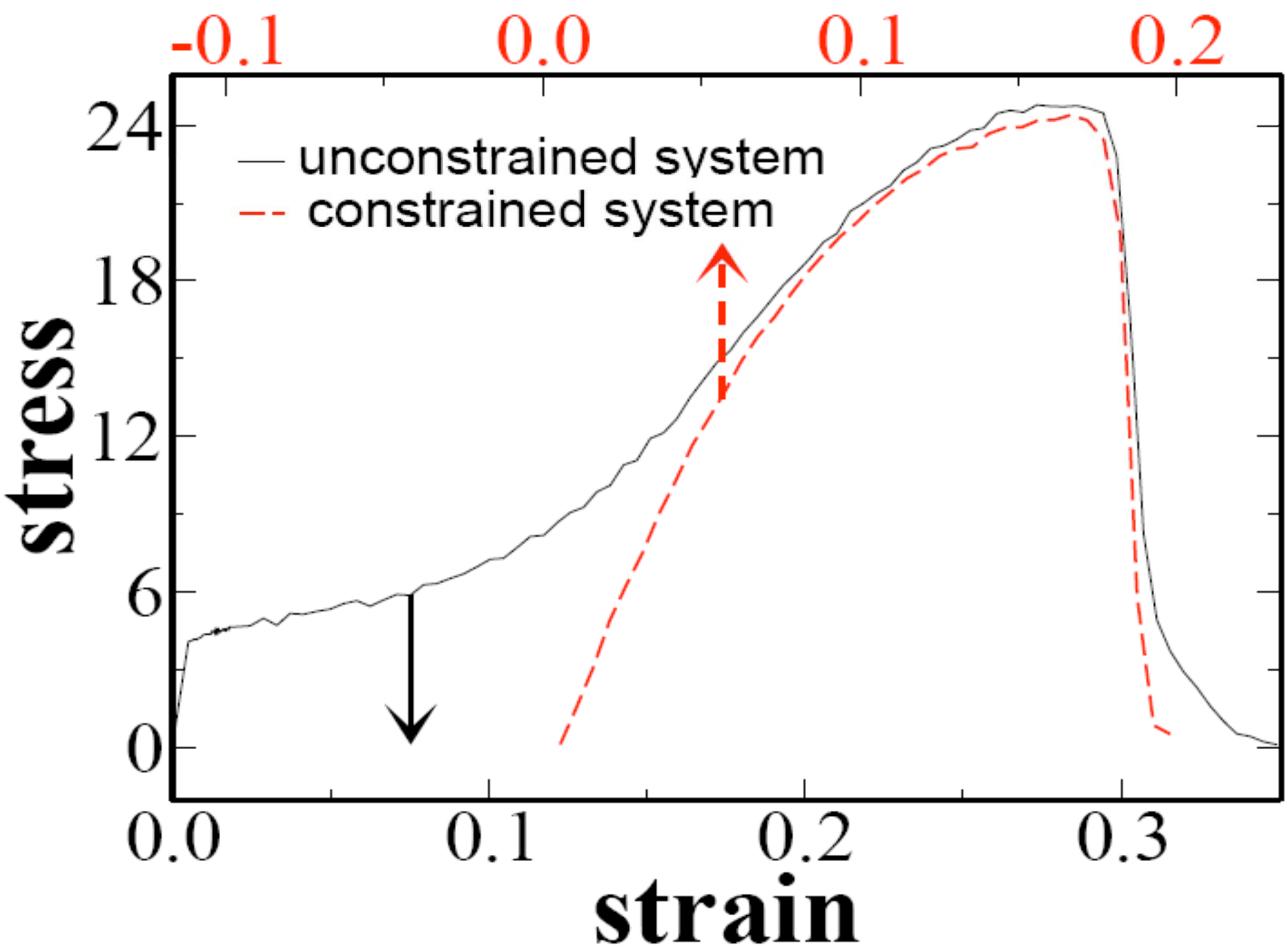


Mukherji and Abrams, Phys. Rev. E, 78, 050801(R) (2008).

What if we prevent void formation?

Im

V_{ϵ}



Mukherji and Abrams, Phys. Rev. E, 78, 050801(R) (2008).

Experiment

IR spectra

Wavenumber (cm^{-1})

Solvent evaporation and Tg

Toughness

Voids: SEM pictures

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Kirkwood-Buff Theory of Solutions

Thermodynamic properties from structural details
(Grand-canonical ensemble)

$$G_{ij}(r) = 4\pi \int_0^\infty \left\{ g_{ij}(r) - 1 \right\} r^2 dr$$

for $r \rightarrow \infty$

$$G_{ij}(r) = V \left[\frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{\langle N_j \rangle} \right]$$

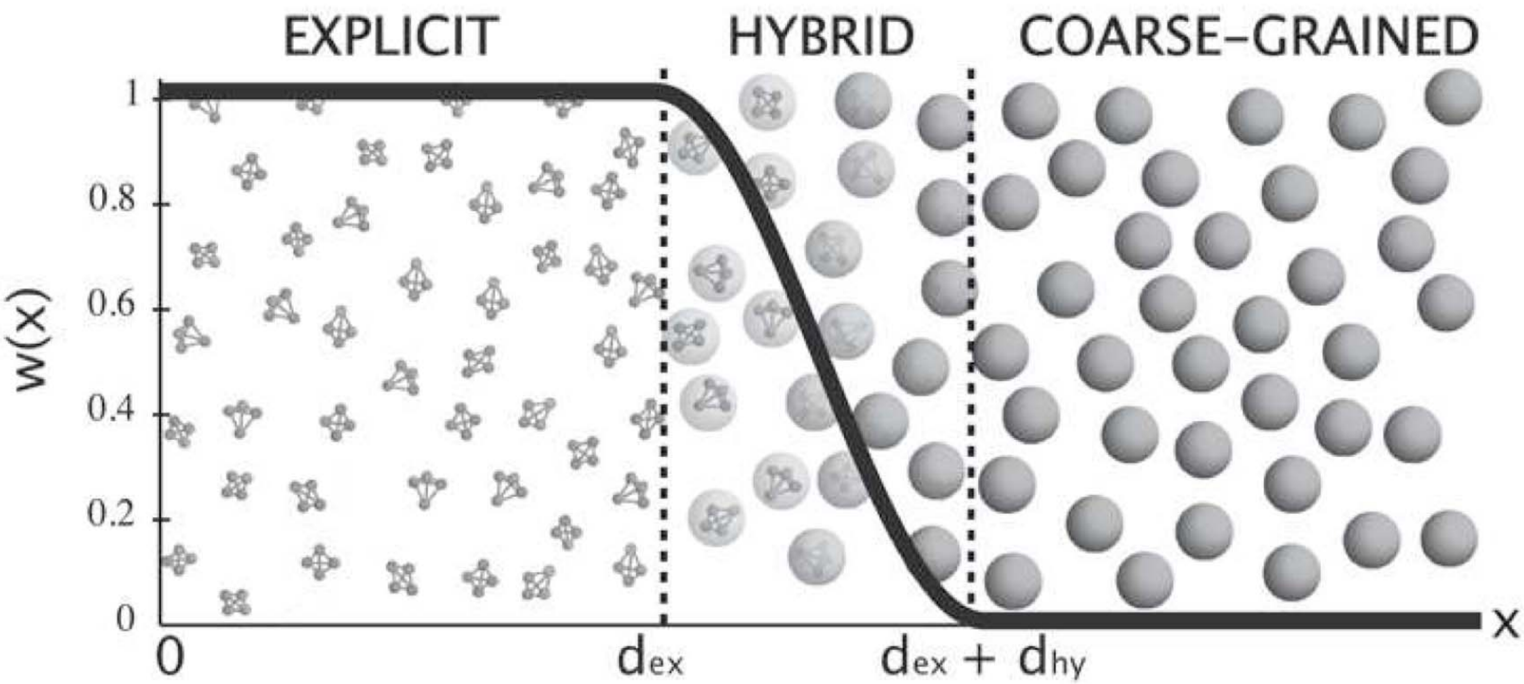
Strong aggregation

Problems with closed boundary simulations NVT (Methanol + Water)

Effective Grand-canonical MD scheme

AdResS Scheme

Adaptive Resolution Molecular Dynamics Scheme



$$\vec{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\vec{F}^{\mathrm{atom}}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\vec{F}^{\mathrm{cg}}_{\alpha\beta}$$

Praprotnik, Delle Site, and Kremer, J. Chem. Phys., 123, 224106 (2005).

Liquid mixture: AdResS Scheme

Mukherji, van der Vegt, Delle Site, and Kremer (to be submitted).

Take home message

- 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

Acknowledgement!

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