Nanoscale mechanics of ultrathin polymer films using molecular dynamics

Brooklyn A. Noble

Nanotribology and Precision Engineering Laboratory
Department of Mechanical Engineering
University of Utah
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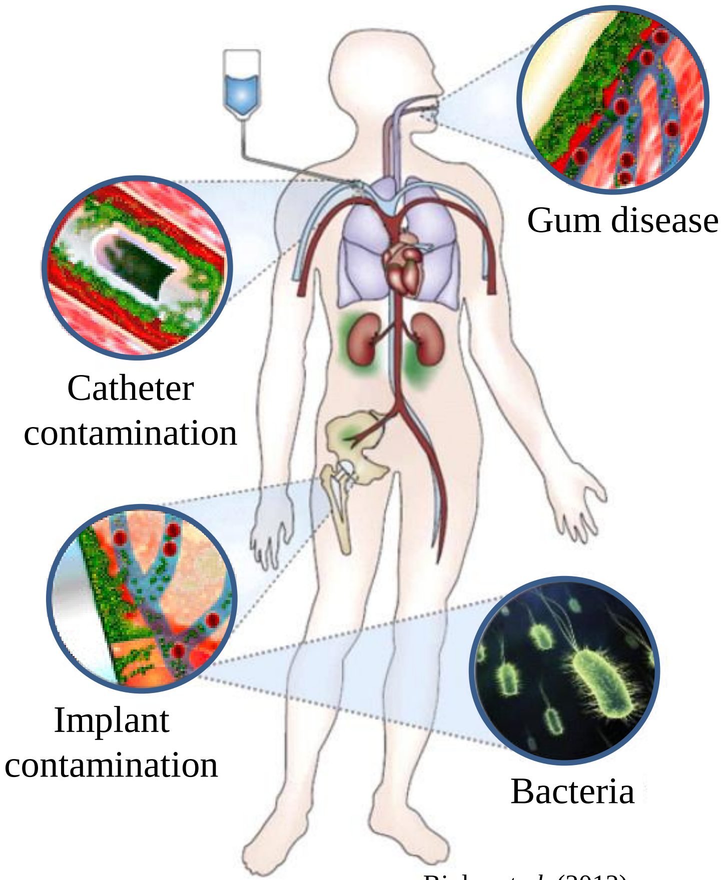
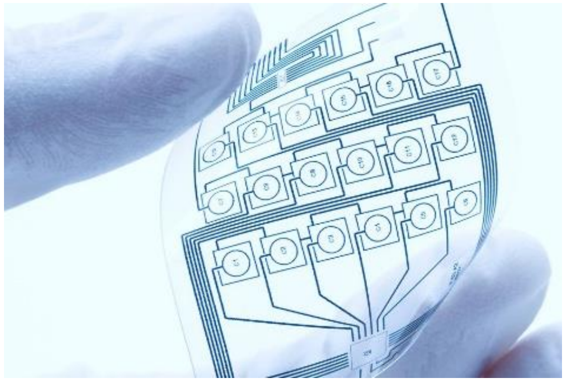
Ultrathin polymer film applications

Surface modification:
Antifouling surfaces



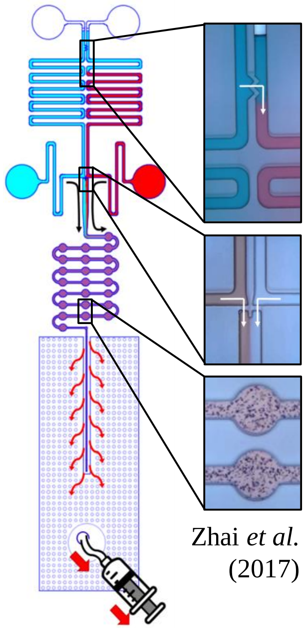
Bixler *et al.* (2012)

Micro/Nanofabrication:
Flexible electronics



Kovo (2015)

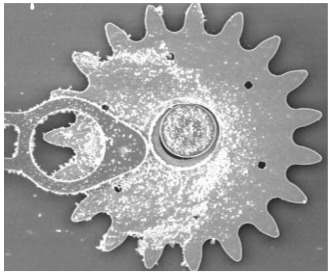
Micro/Nanofluidics:
Lab-on-a-chip



Zhai *et al.* (2017)

Thin film lubrication: HDDs and micromotors

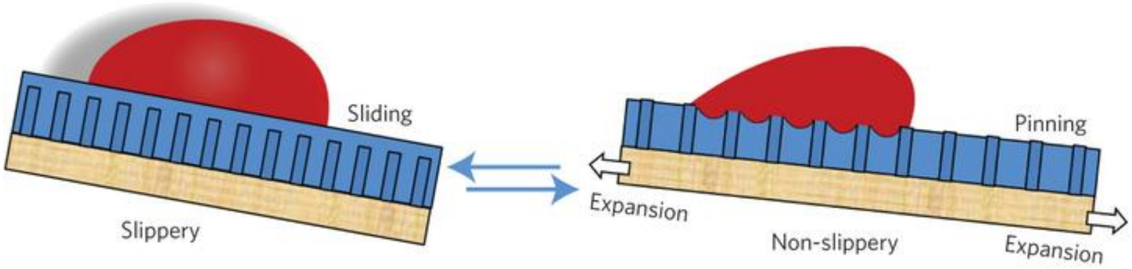
www.wdc.com

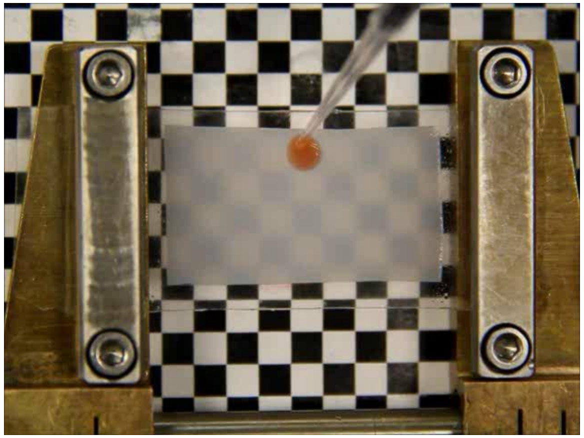


Tanner *et al.* (2000)

Nanoscale spreading

How a polymer-based liquid film interacts with and adsorbs onto a surface determines properties critical to performance:





Yao *et al.* (2013)

Research topics:

(1) Spreading morphology

(2) Spreading kinetics

(3) Spreading on nanotextured substrates

X. Yao *et al.* *Nature Materials* **12**, 6 (2013)

Overview

Spreading morphology

- Background and MD model
- Quantify thickness profile
  - Functional group layering
- Conclusions

Spreading kinetics

- Background and MD model
- Quantify droplet edge radius
  - Droplet pressure and molecular entanglement
- Conclusions

Spreading on nanotextured substrates

- Background and MD model
- Quantify anisotropic spreading
  - Substrate energy potentials
- Conclusions

Questions

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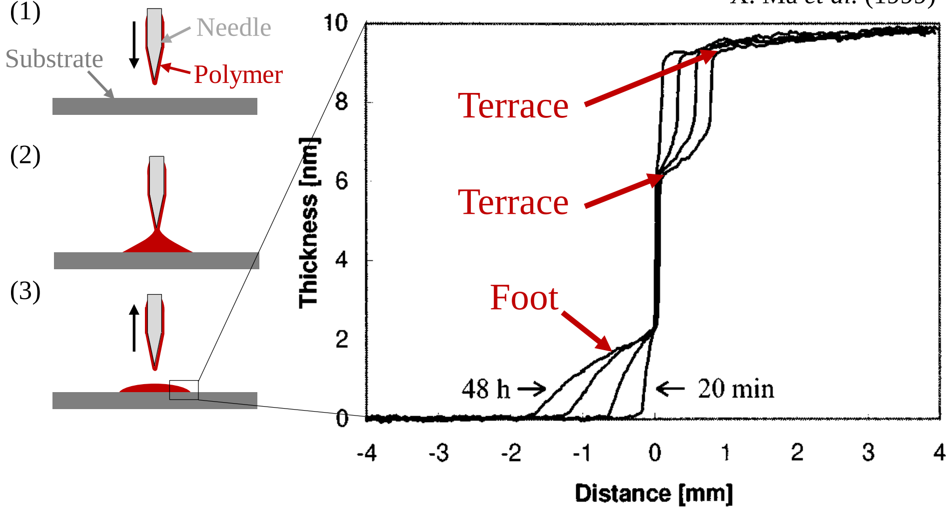
Questions

Spreading morphology background

Experiments

- Functional PFPE lubricants
- Observe a precursor film (foot) and a complex stepped (terraced) structure at:
  - 2.2 nm
  - 6.4 nm
  - 9.8 nm

X. Ma *et al.* (1999)

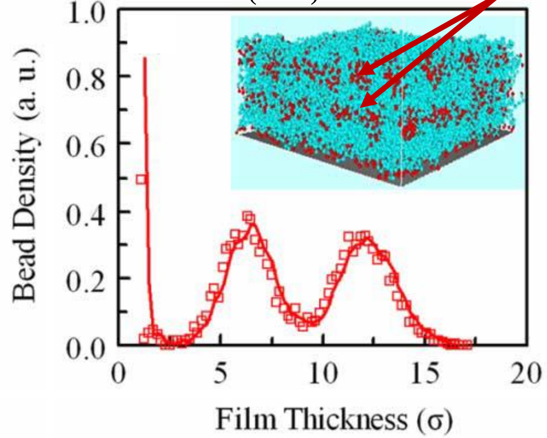


MD simulations

- Functional hydroxyl end groups conglomerate into molecular layers
- Functional hydroxyl end group density varies with distance from the surface
- Dependent on polymer length

Functional end group layers

Chen *et al.* (2007)



X. Ma, *et al*. *Phys. Rev. E* **59**, 722 (1999)
H. Chen, Q. Guo, and M. S. Jhon. *IEEE Trans. Magn.* **43**, 2247 (2007)

MD polymer model

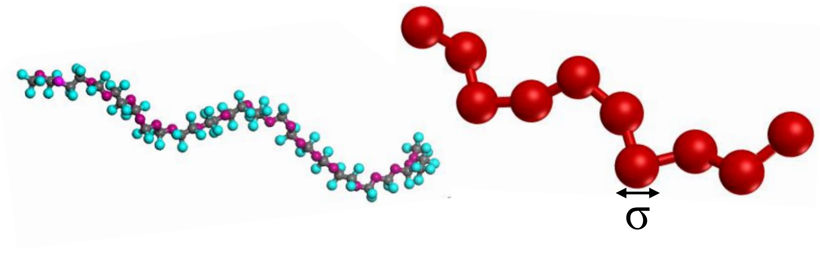
MD coarse-grained bead-spring (CGBS) model with *N* beads

Perfluoropolyether (PFPE) polymers:

Z

$\mathbf{CF_3}\text{-[(OCF}_2\text{CF}_2)_p\text{-(OCF}_2)_q\text{]-O-}\mathbf{CF_3}$

($p/q \cong 2/3$)



- No functional end beads

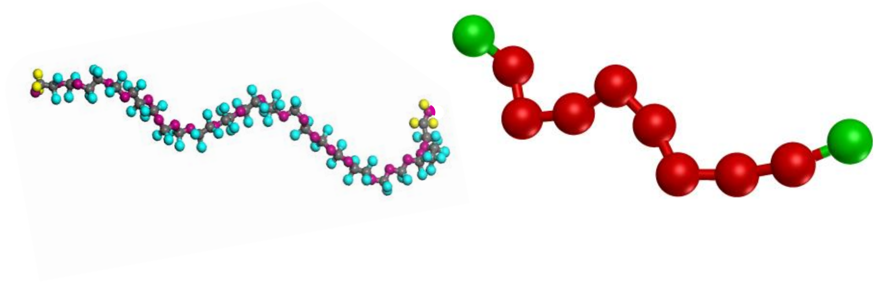
● F ● O ● Nonfunctional polymer

● C ● H ● Functional polymer

Zdol

$\mathbf{OHCH_2CF_2}\text{-[(OCF}_2\text{CF}_2)_p\text{-(OCF}_2)_q\text{]-O-}\mathbf{CF_2CH_2OH}$

($p/q \cong 2/3$)

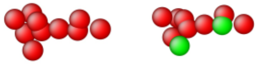


- Hydroxyl end groups simulated with terminating functional end beads
- Functional end beads attract to other functional beads

Spreading morphology MD model

- Polymer equilibrates between two walls
- Walls are removed and polymer spreads for 250 ns
- We quantify:
  - Polymer thickness profile
  - Location of end beads
  - Molecular orientation

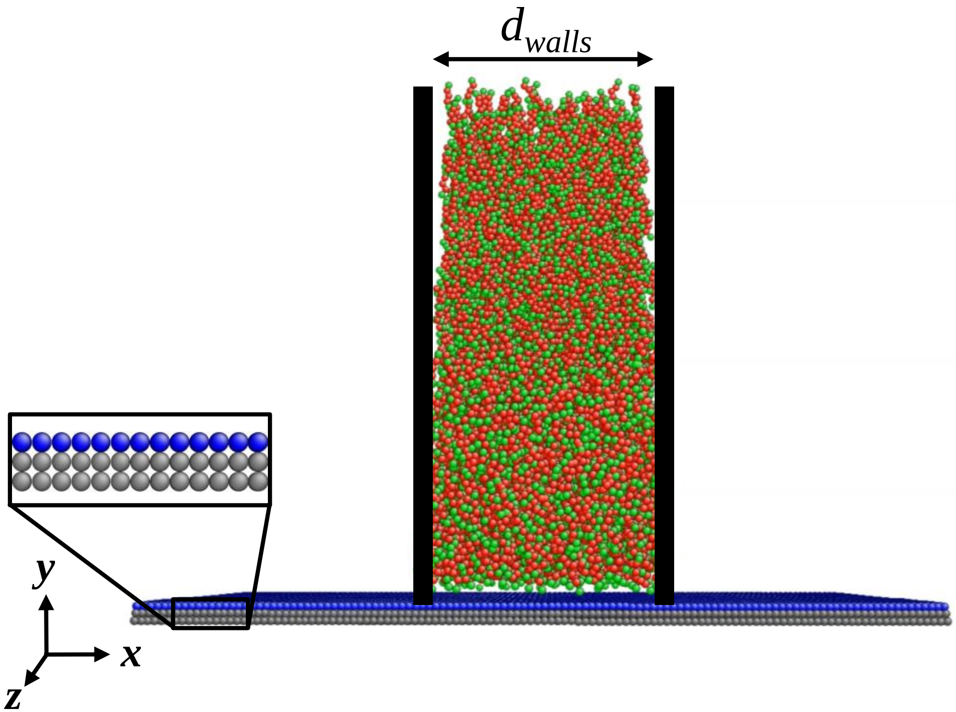
<u>Parameters</u>:
Z or Zdol polymer



$1 \leq N \leq 50$ beads/molecule
$0\% \leq S_f \leq 100\%$
$5{,}000 \leq Q \leq 40{,}000$ beads

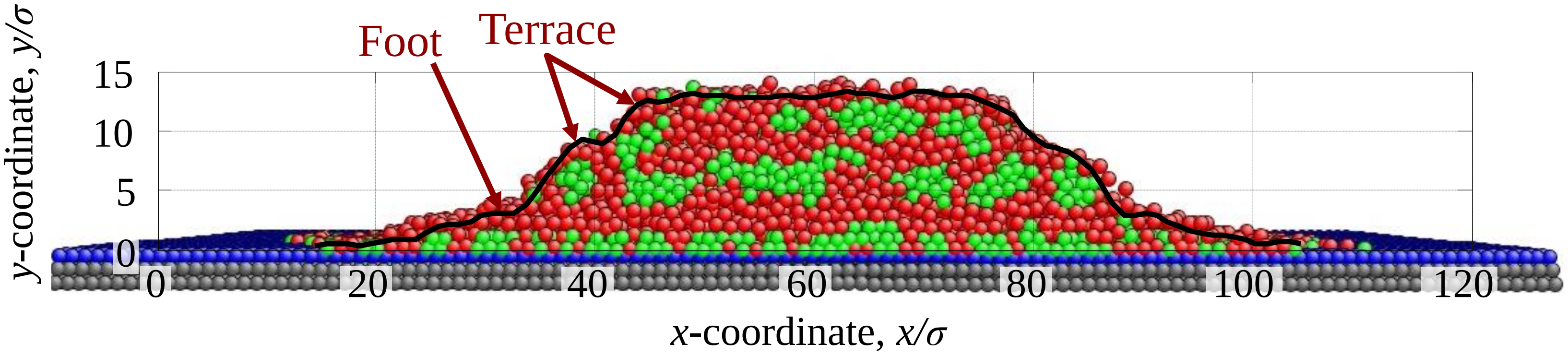
<u>Constants</u>:
d_{walls} = 28 nm
M_{bead} = 0.2 kg/mol
t = 250 ns, $\Delta\tau$ = 0.03 ps
T = 300 K

● Functional polymer
● Nonfunctional polymer
● Functional substrate
● Nonfunctional substrate



B. A. Noble, A. Ovcharenko, and B. Raeymaekers. *Polymer* **84**, 286-292 (2016)

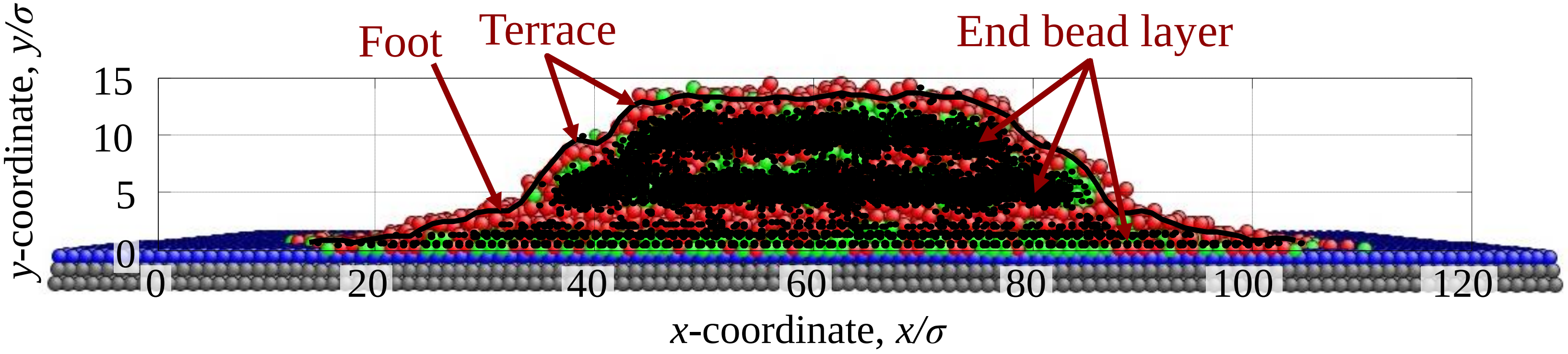
Quantify spreading morphology



- Observe foot and terrace formations in polymer thickness profile
- Foot formation at:
  - $y/\sigma = 3$
  - $y = 2.1$ nm
- Two terrace formations at:
  - $y/\sigma = 8.5$ and 13.5
  - $y = 6.0$ nm and 9.5 nm
- In good agreement with experimental observations where steps occur at:
  - $y = 2.2$ nm, 6.4 nm, and 9.8 nm

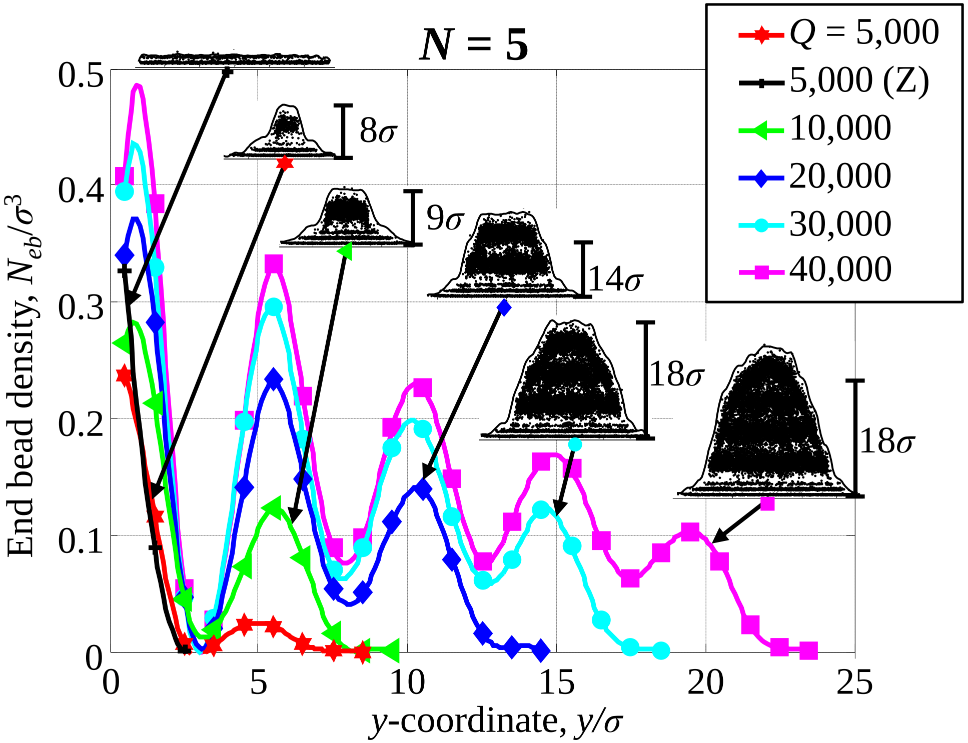
X. Ma, *et al*. *Phys. Rev. E* **59**, 722 (1999)
G. W. Tyndall, T. E. Karis, and M. S. Jhon. *Tribol. T*. **42**, 463 (1999)

End bead layers



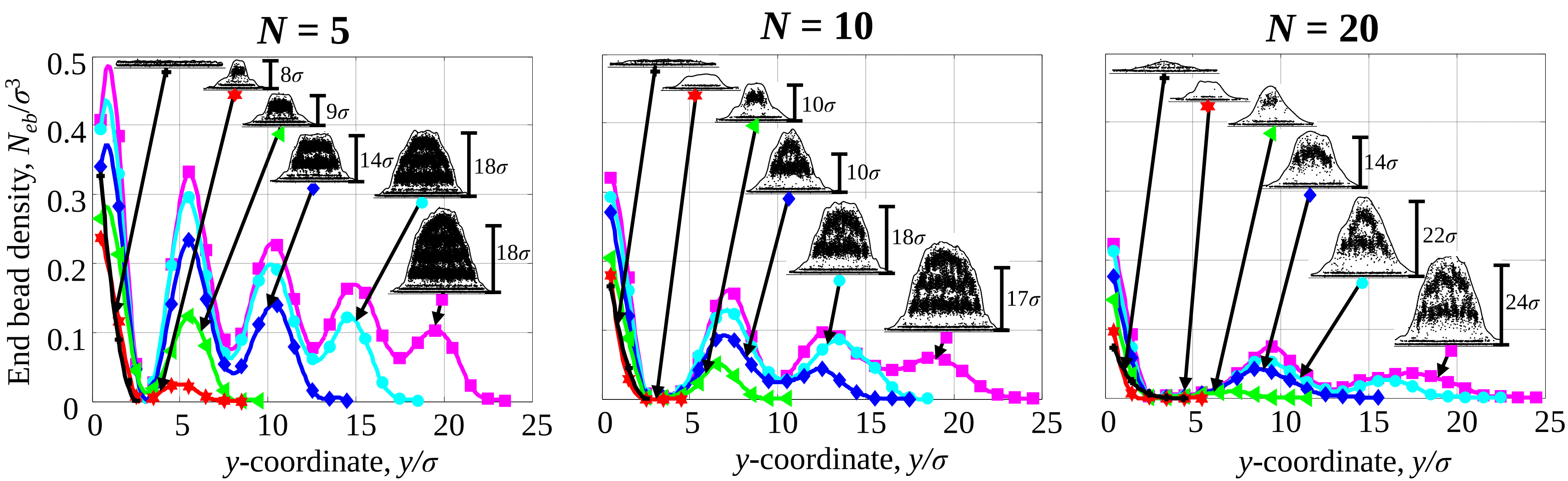
- Observe molecular layering indicated by three horizontal bands of conglomerated end beads
- These areas of high end bead density occur at:
  - $y/\sigma = 1$
  - $y/\sigma = 5.5$
  - $y/\sigma = 10.5$
- Terrace formations form around end bead layers

Effect of polymer quantity *Q*



- End bead density peaks occur for all polymer quantities of Zdol
- Peaks occur at approximately the same *y*-coordinate values
- Distance between peaks is constant and is approximately equal to the molecule length
- Initial peak is observed near the substrate for both Z and Zdol, corresponding to a foot formation

Spreading morphology conclusions



Main observations:

- The quantity and location of high end bead density layers correspond to the quantity and location of terraced formations
- Polymer quantity affects the number of layer and terrace formations
- Molecule length affects the location of layer and terrace formations

Overview

Spreading morphology

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  - Functional group layering
- Conclusions

Spreading kinetics

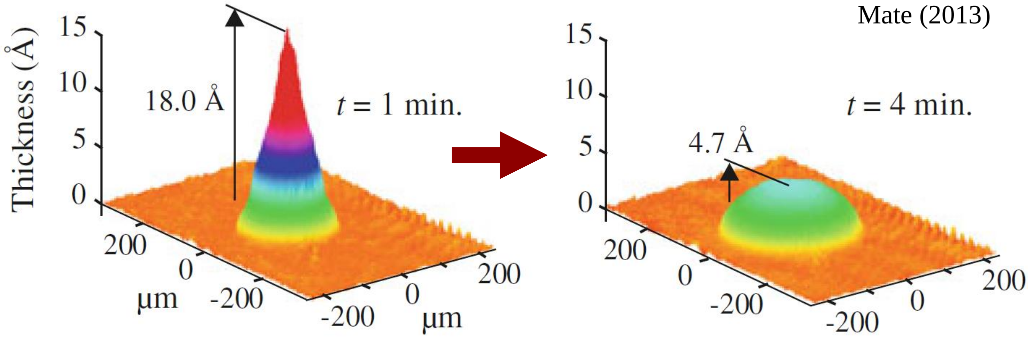
- Background and MD model
- Quantify droplet edge radius
  - Droplet pressure and molecular entanglement
- Conclusions

Spreading on nanotextured substrates

- Background and MD model
- Quantify anisotropic spreading
  - Substrate energy potentials
- Conclusions

Questions

Spreading kinetics background

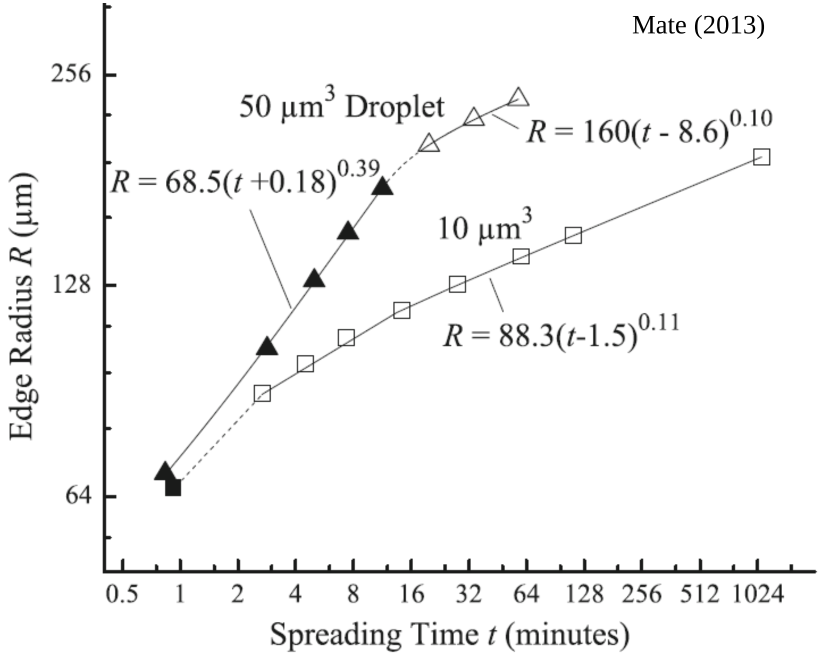


Mate (2013)

$$R \sim t^{\nu}$$

R = droplet radius
t = time
ν = spreading exponent

- Tanner’s law: $\nu = 1/10$
  - Droplet retains shape
  - Surface tension vs. viscous forces
- Diffusion theory: $\nu = 1/2$
  - Precursor film
  - Based on Brownian motion
- Microscale droplet: $\nu = 1/3$
  - Precursor film with intensified wall slip
  - Continuum flow driven by disjoining pressure
- Nonuniform ν



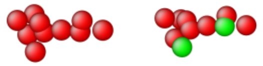
Mate (2013)

L. H. Tanner *J. Phys. D: Appl. Phys.* **12**, 1473 (1979)
F. Heslot *et al. J. Phys.: Condens.* Matter **1**, 5793 (1989)
Y. C. Liao *et al. Phys. Rev. Lett.* **111**, 136001 (2013)
C. M. Mate *Tribol. Lett.* **51**, 385 (2013)

Spreading kinetics MD model

- Polymer equilibrates within a cylindrical pipet
- Pipet is removed and polymer spreads for 250 ns
- We quantify:
  - Droplet edge radius
  - Central droplet pressure
  - Molecular entanglement

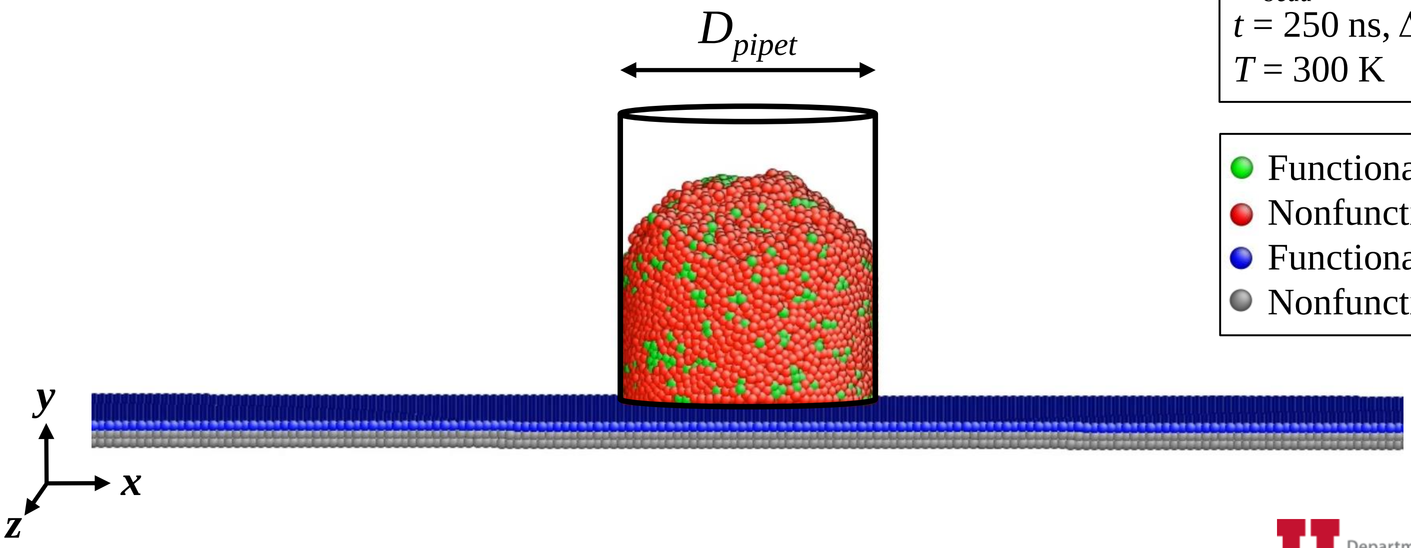
Parameters:
Z or Zdol polymer



$1 \le N \le 400$ beads/molecule
$0\% \le S_f \le 100\%$
$5{,}000 \le Q \le 40{,}000$ beads

Constants:
$D_{pipet} = 23$ nm
$M_{bead} = 0.2$ kg/mol
$t = 250$ ns, $\Delta\tau = 0.03$ ps
$T = 300$ K

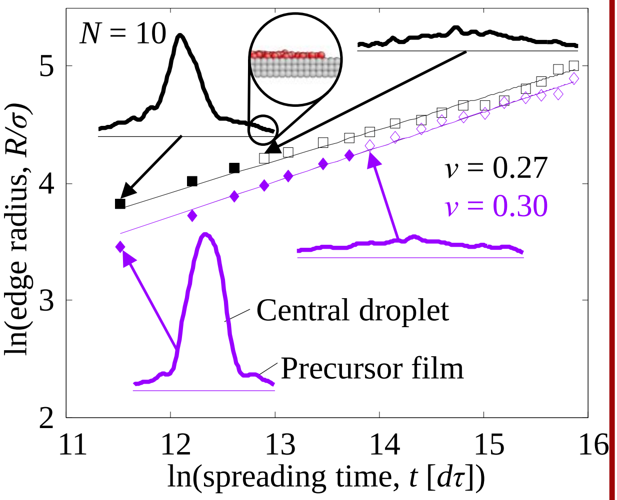
🟢 Functional polymer
🔴 Nonfunctional polymer
🔵 Functional substrate
⚫ Nonfunctional substrate



B. A. Noble, C. M. Mate, and B. Raeymaekers. *Langmuir* **33.14**, 3476-83 (2017)

Quantify spreading kinetics

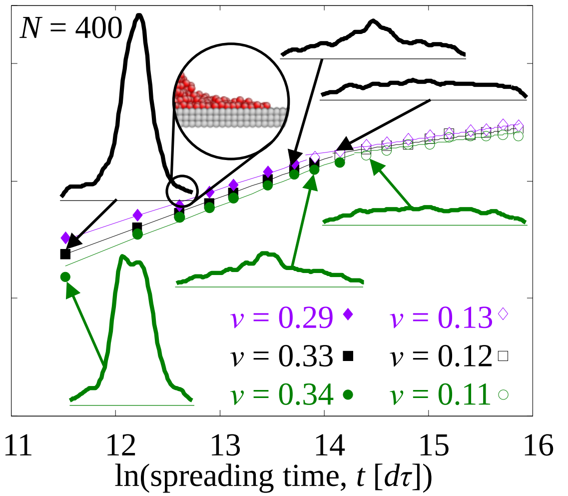
Pressure-driven flow



- ✓ Short molecules
- ✓ Functional or nonfunctional polymer
- ✓ Nonfunctional substrate

Z, $N = 10$, $Q = 10{,}000$

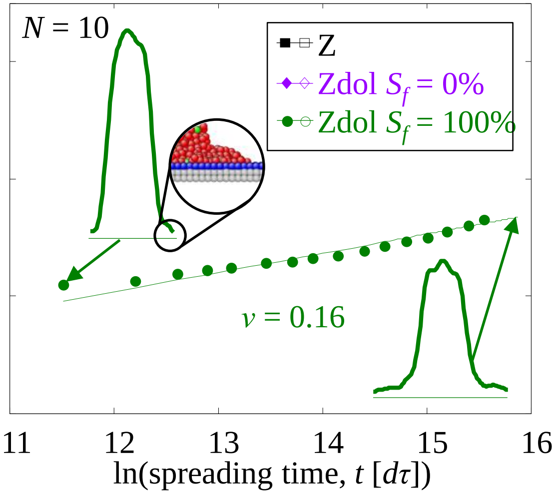
Pressure-driven entanglement inhibited flow



- ✓ Long molecules
- ✓ Functional or nonfunctional polymer
- ✓ Functional or nonfunctional substrate

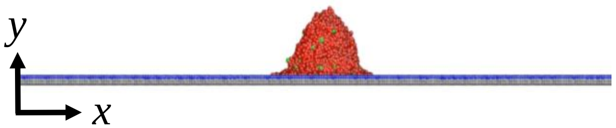
Z, $N = 400$, $Q = 10{,}000$

Pressure-driven chemically inhibited flow



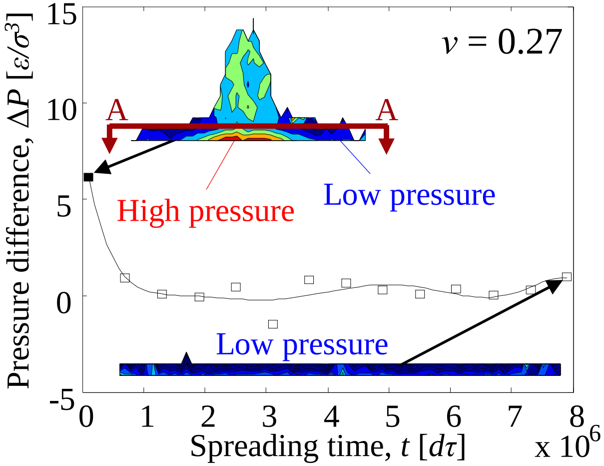
- ✓ Short molecules
- ✓ Functional polymer
- ✓ Functional substrate

Zdol, $N = 10$, $Q = 10{,}000$, $S_f = 100\%$



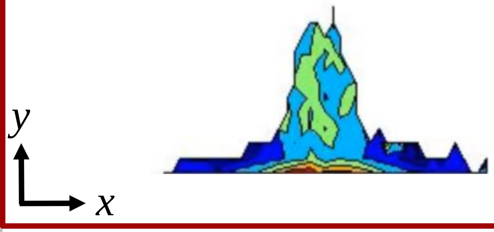
Droplet pressure

Pressure-driven flow

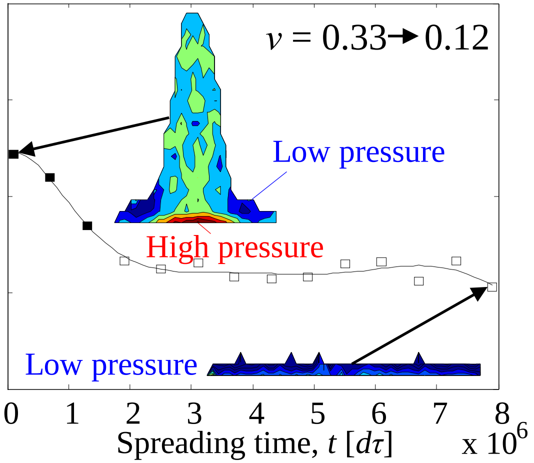


Pressure decreases immediately

Z, $N = 10$, $Q = 10{,}000$

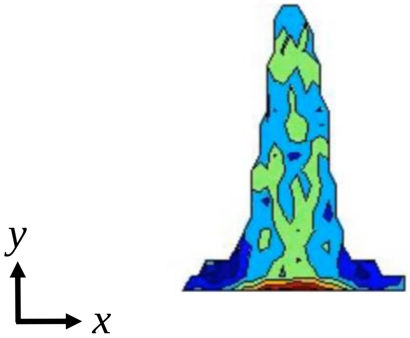


Pressure-driven entanglement inhibited flow

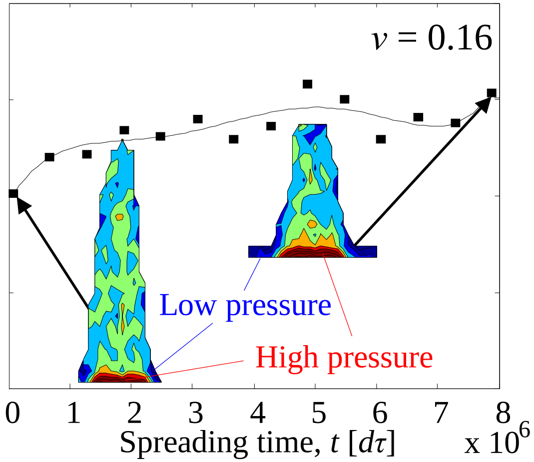


Pressure decreases when central droplet depletes

Z, $N = 400$, $Q = 10{,}000$

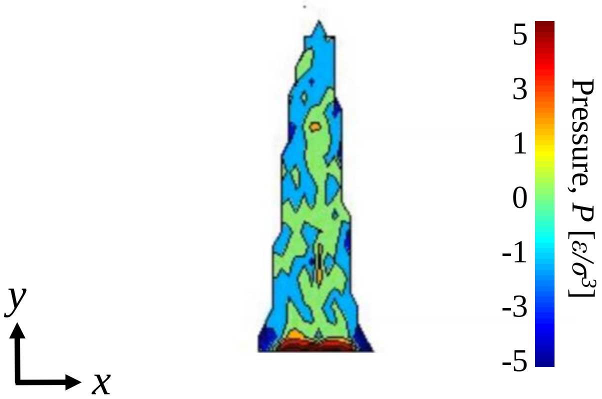


Pressure-driven chemically inhibited flow



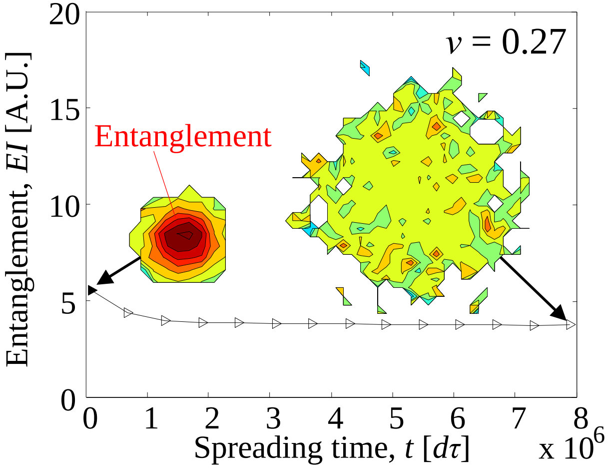
Pressure remains high

Zdol, $N = 10$, $Q = 10{,}000$, $S_f = 100\%$

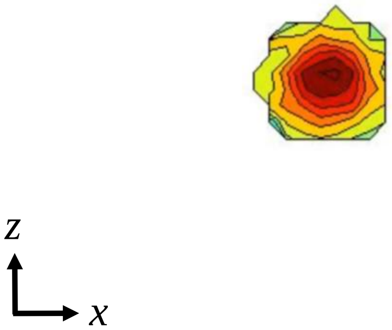


Molecular entanglement

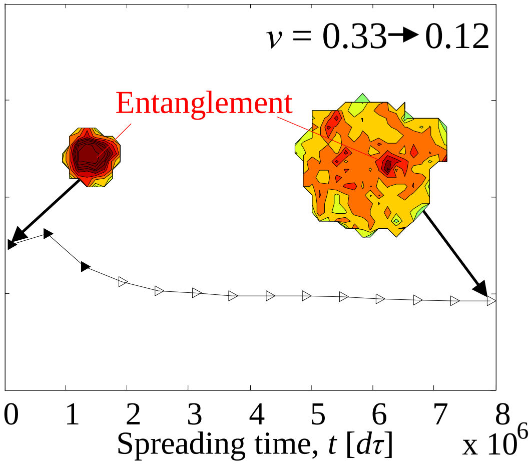
Pressure-driven flow



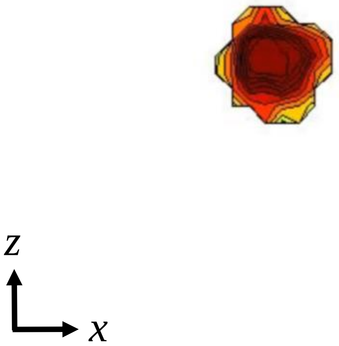
Z, $N = 10$, $Q = 10{,}000$



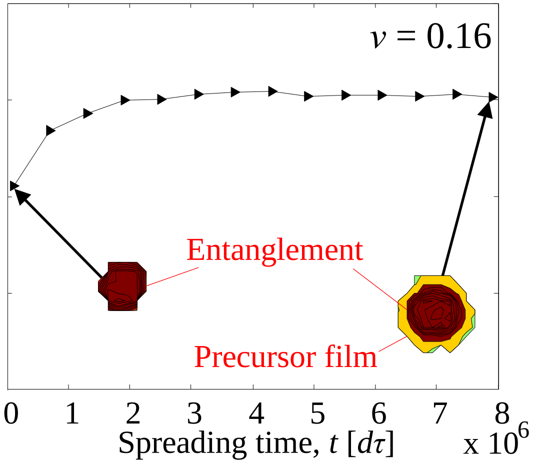
Pressure-driven entanglement inhibited flow



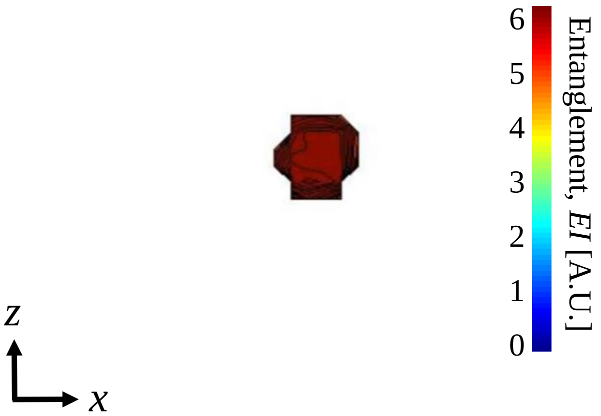
Z, $N = 400$, $Q = 10{,}000$



Pressure-driven chemically inhibited flow

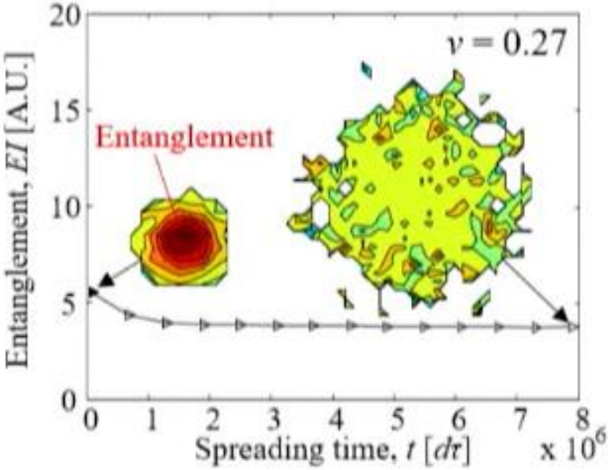


Zdol, $N = 10$, $Q = 10{,}000$, $S_f = 100\%$

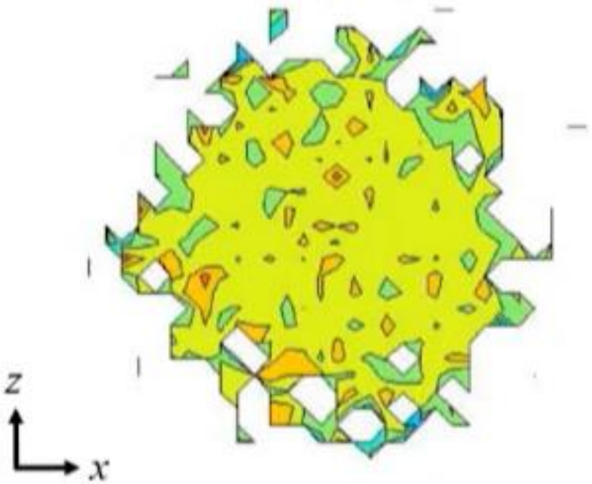


Molecular entanglement

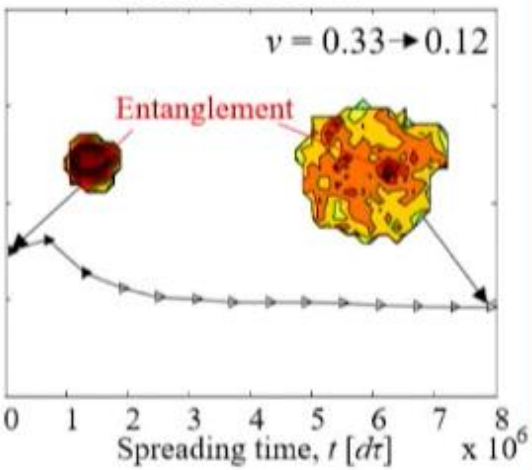
Pressure-driven flow



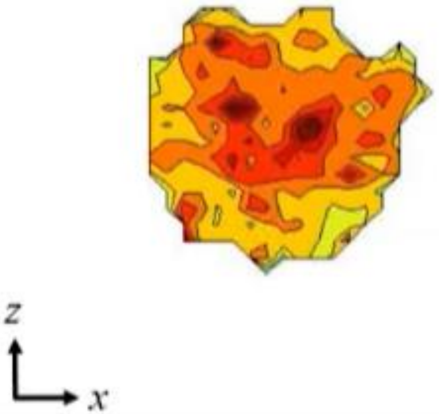
Z, N = 10, Q = 10,000



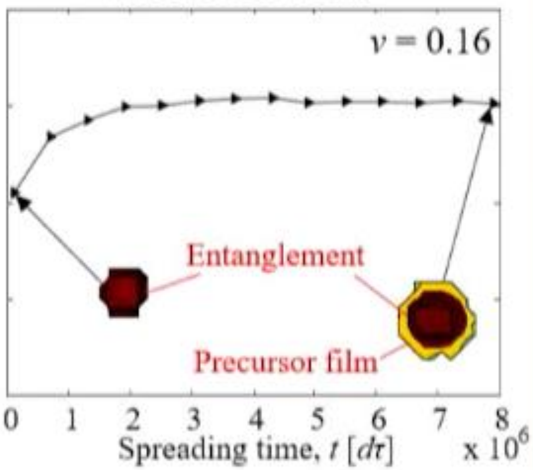
Pressure-driven entanglement inhibited flow



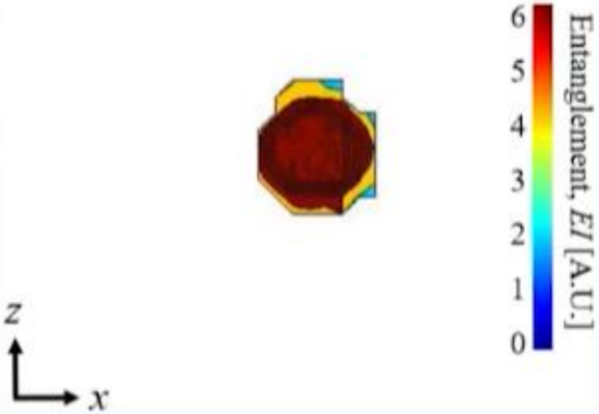
Z, N = 400, Q = 10,000



Pressure-driven chemically inhibited flow



Zdol, N = 10, Q = 10,000, S_f = 100%



Spreading kinetics conclusions

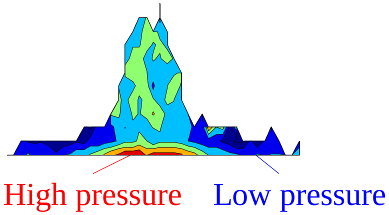
The leading edge of a liquid polymer droplet advances as a power law $R \sim t^{\nu}$ with:

(1) One regime according to microscale droplet theory: $\nu \approx 1/3 = 0.27\text{-}0.38$

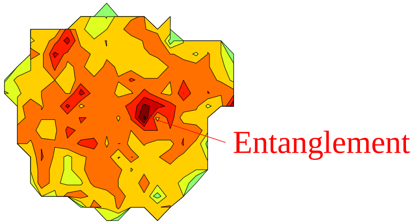
(2) Two successive regimes: $\nu \approx 1/3 = 0.27\text{-}0.35 \longrightarrow \nu \approx 1/10 = 0.10\text{-}0.16$

(3) One regime according to Tanner's theory: $\nu \approx 1/10 = 0.11\text{-}0.16$

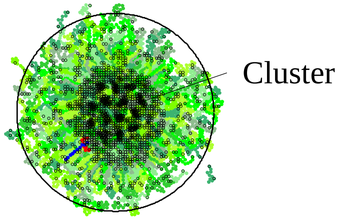
We attribute the transition to competing physical mechanisms:



- Pressure difference in the droplet
  - Vanishes if central droplet depletes



- Entanglement of molecules
  - Long molecules constrict around entangled regions



- Functional attraction
  - Functional molecules pin on a functional substrate

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Spreading on nanotextured substrates

- Background and MD model
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  - Substrate energy potentials
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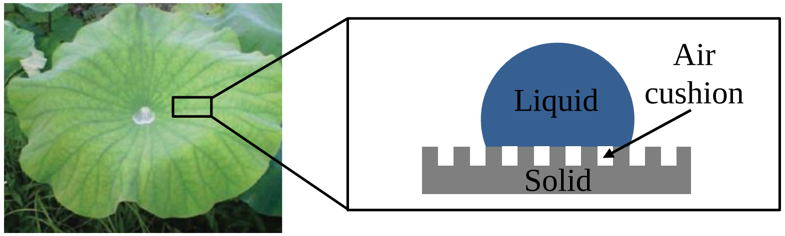
Questions

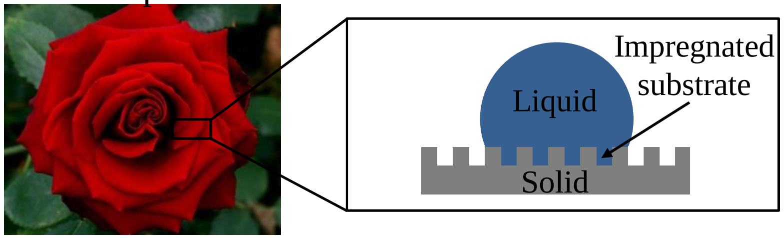
Nanotextured substrates background

Nature's textured substrates

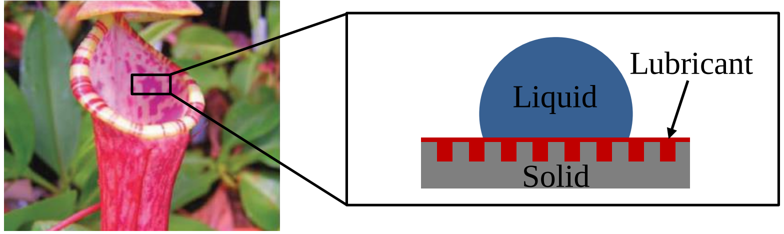
Lotus leaf



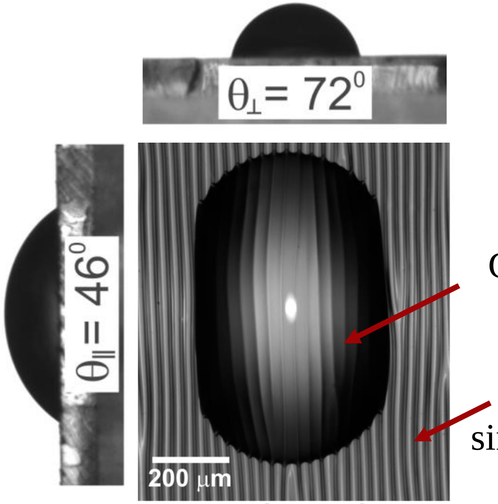
Rose petal



Pitcher plant



Engineered textured substrates



Glycerin droplet

PDMS with sinusoidal grooves

Khare *et al.* (2009)

- Droplet spreads mostly along grooves
- Perpendicular contact line experiences the presence of energy barriers imposed by the texture
- Anisotropic spreading is affected by the texture size and polymer molecular weight

M. Cao *et al. ACS Appl. Mater. Interfaces* **8.6**, 3615-23 (2015)
X. Dai *et al. ACS Nano* **9.9**, 9260-7 (2015)
L. Feng *et al. Langmuir* **24**, 4114-9 (2008)
K. Khare *et al. Langmuir* **25**, 12794-9 (2009)

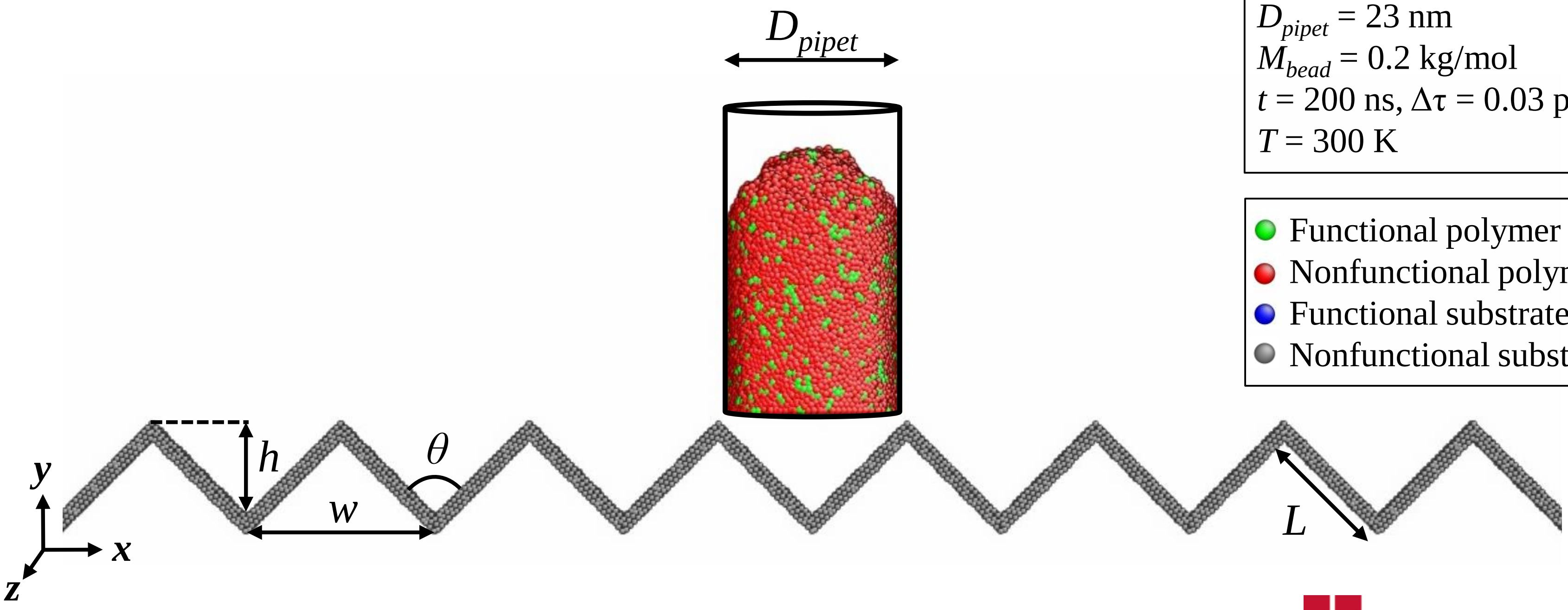
Nanotextured MD model

- Polymer equilibrates within a cylindrical pipet
- Pipet is removed and polymer spreads for 200 ns
- We quantify:
  - Polymer spreading parallel and perpendicular to the texture
  - Potential energy created by each substrate

Parameters:
$15 \leq L \leq 250\sigma$
Substrate texture shape

Constants:
Zdol polymer
N = 10 beads/molecule
S_f = 0%
Q = 40,000 beads
D_{pipet} = 23 nm
M_{bead} = 0.2 kg/mol
t = 200 ns, $\Delta\tau$ = 0.03 ps
T = 300 K

● Functional polymer
● Nonfunctional polymer
● Functional substrate
● Nonfunctional substrate



B. A. Noble and B. Raeymaekers. *Nanotechnology* **30.9**, 095701 (2019)
B. A. Noble and B. Raeymaekers. *Langmuir* (2019)

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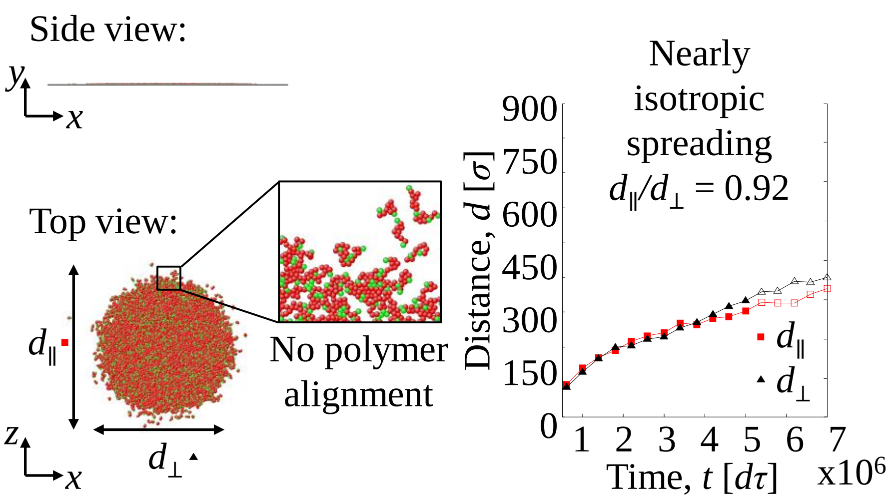
B. A. Noble and B. Raeymaekers. *Langmuir* (2019)

Anisotropic spreading in a single groove

Polymer spreading parallel $d_{\parallel}$ and perpendicular $d_{\perp}$ to the groove as a function of texture geometry

Flat substrate

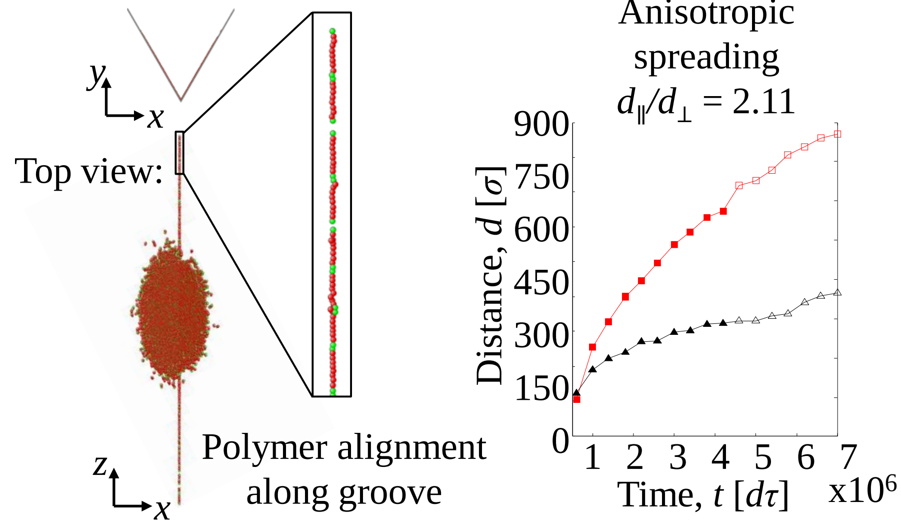


Nearly isotropic spreading
$d_{\parallel}/d_{\perp}$ = 0.92

No polymer alignment

60° groove

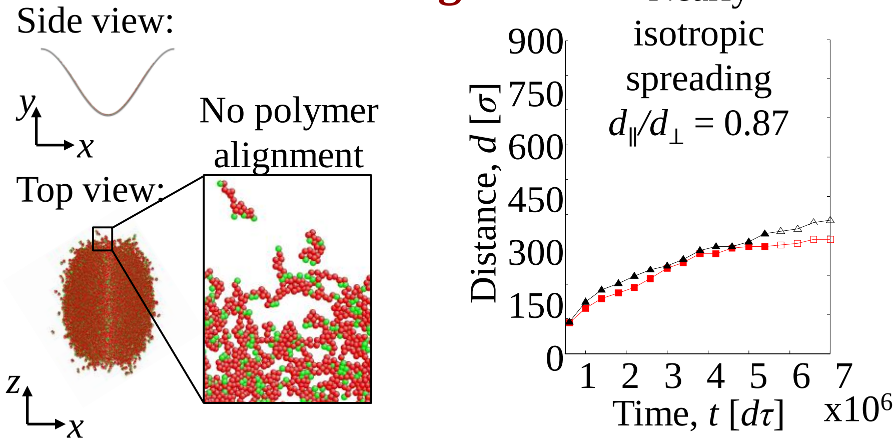
Side view:



Anisotropic spreading
$d_{\parallel}/d_{\perp}$ = 2.11

Polymer alignment along groove

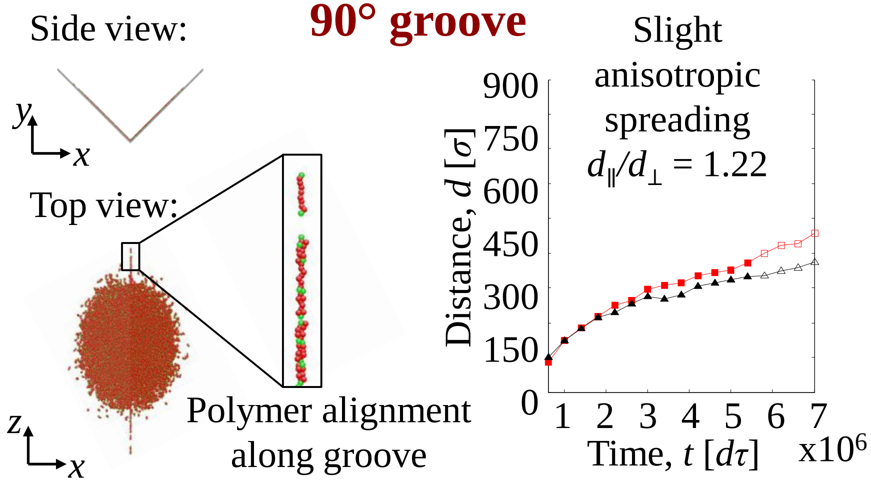
Wave groove



Nearly isotropic spreading
$d_{\parallel}/d_{\perp}$ = 0.87

No polymer alignment

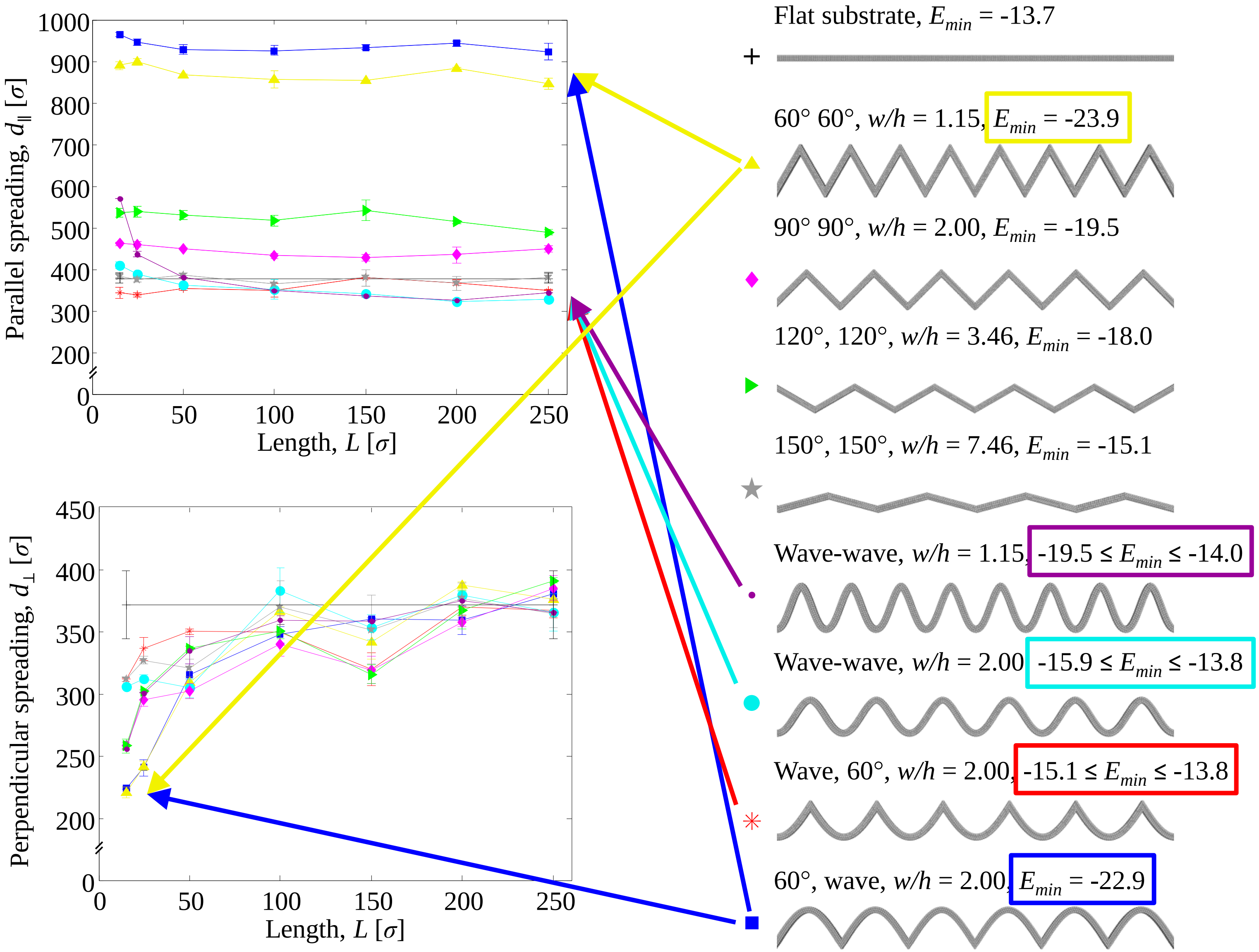
90° groove



Slight anisotropic spreading
$d_{\parallel}/d_{\perp}$ = 1.22

Polymer alignment along groove

Anisotropic spreading on multiple features



Flat substrate, E_{min} = -13.7
+

60° 60°, w/h = 1.15, E_{min} = -23.9
▲

90° 90°, w/h = 2.00, E_{min} = -19.5
◆

120°, 120°, w/h = 3.46, E_{min} = -18.0
▶

150°, 150°, w/h = 7.46, E_{min} = -15.1
★

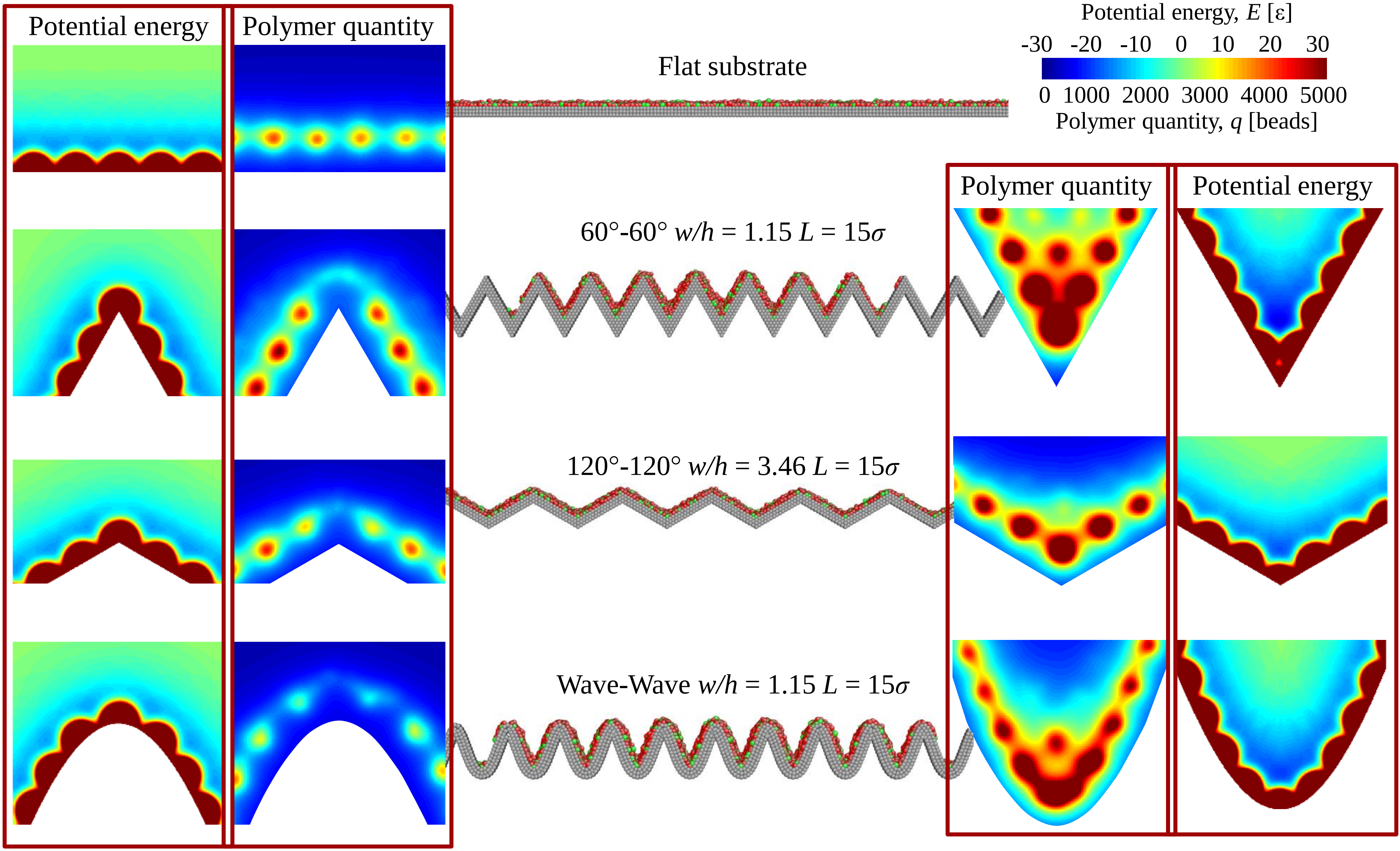
Wave-wave, w/h = 1.15, -19.5 ≤ E_{min} ≤ -14.0
•

Wave-wave, w/h = 2.00 -15.9 ≤ E_{min} ≤ -13.8
●

Wave, 60°, w/h = 2.00, -15.1 ≤ E_{min} ≤ -13.8
✳

60°, wave, w/h = 2.00, E_{min} = -22.9
■

Substrate potential energy



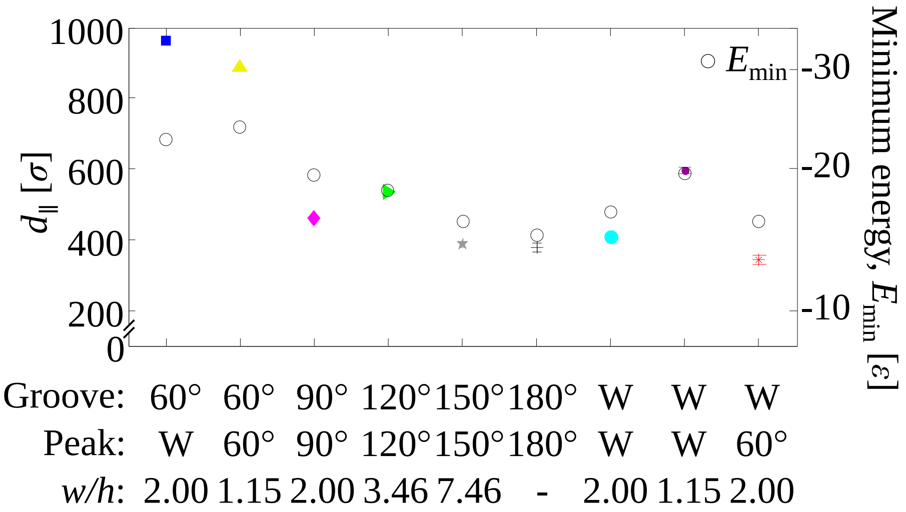
Flat substrate

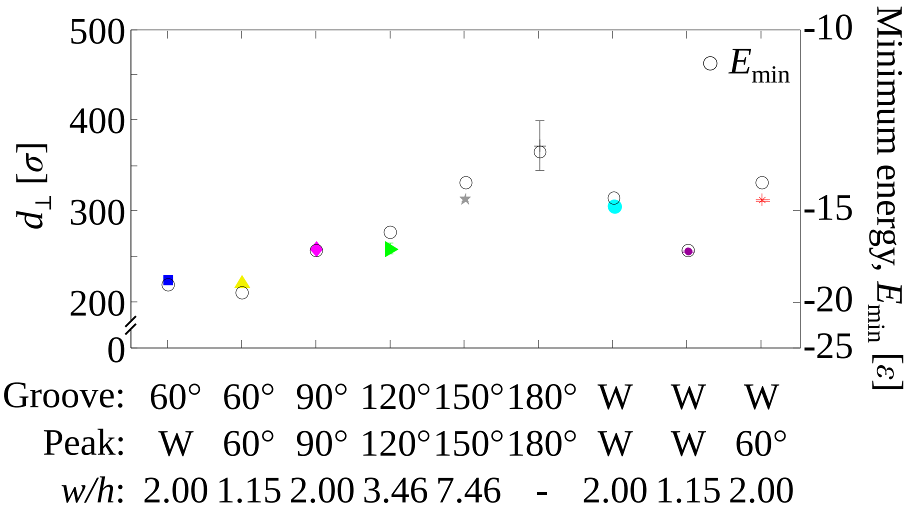
60°-60° w/h = 1.15 L = 15σ

120°-120° w/h = 3.46 L = 15σ

Wave-Wave w/h = 1.15 L = 15σ

Nanotextured substrates conclusions





Main observations:

- Texture groove shape is the primary factor that modifies polymer spreading on unidirectionally nanotextured surfaces
- Texture groove shape determines the minimum potential energy of a substrate
- At the texture groove, the energy potentials of several surfaces combine, which increases polymer attraction and drives spreading along the texture groove.

Achievements

- Journal publications:
  - **Noble, B. A.** and B. Raeymaekers. “ Polymer spreading on unidirectionally nanotextured surfaces using Molecular Dynamics." *Langmuir* Article ASAP (2019).
  - **Noble, B. A.** and B. Raeymaekers. “Polymer spreading on substrates with nanoscale grooves using molecular dynamics." *Nanotechnology* 30.9 (2019): 095701.
  - **Noble, B. A.**, C. M. Mate, and B. Raeymaekers. "Spreading kinetics of ultrathin liquid films using molecular dynamics." *Langmuir* 33.14 (2017): 3476-3483.
  - **Noble, B. A.**, A. Ovcharenko, and B. Raeymaekers. "Terraced spreading of nanometer-thin lubricant using molecular dynamics." *Polymer* 84 (2016): 286-292.
  - **Noble, B. A.**, A. Ovcharenko, and B. Raeymaekers. "Quantifying lubricant droplet spreading on a flat substrate using molecular dynamics." *Applied Physics Letters* 105.15 (2014): 151601.

- Conference presentations:
  - **Noble, B. A.** and B. Raeymaekers. “Spreading of ultrathin polymer films on nanotextured substrates using Molecular Dynamics.” STLE Annual Meeting. Minneapolis, MN, 21 May 2018.
  - **Noble, B. A.** and B. Raeymaekers. “Spreading Kinetics of Ultrathin Liquid Films Using Molecular Dynamics.” STLE Annual Meeting. Atlanta, GA, 24 May 2017.
  - **Noble, B. A.** and B. Raeymaekers. “Terraced spreading of nanometer-thin lubricant using molecular dynamics.” STLE Tribology Frontiers Conference. Denver, CO, 26 Oct. 2015.
  - **Noble, B. A.** and B. Raeymaekers. “Quantifying lubricant droplet spreading on a flat substrate using molecular dynamics.,” STLE Annual Meeting. Dallas, TX, 20 May 2015.

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U.S. DEPARTMENT OF
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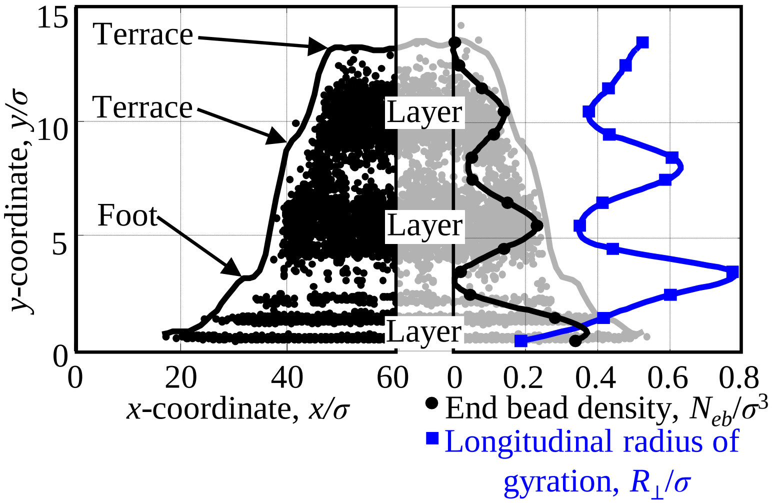
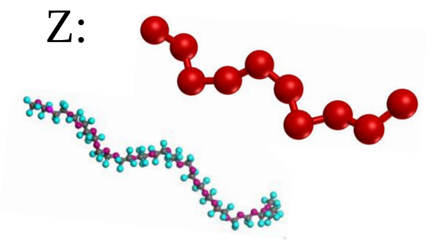
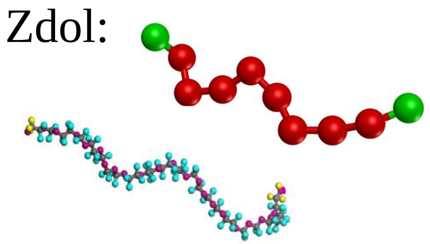
STEWARDSHIP SCIENCE GRADUATE FELLOWSHIP

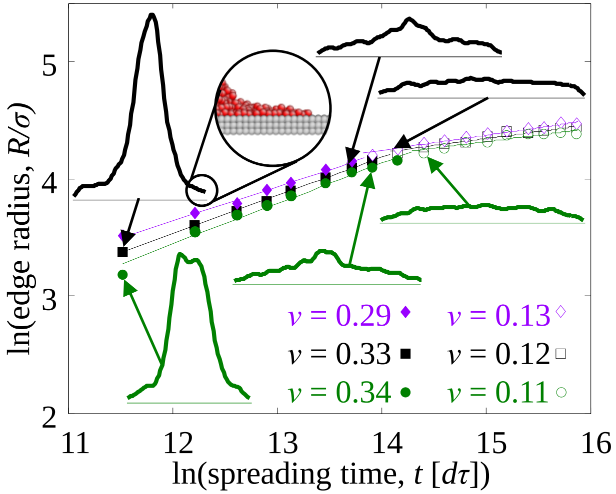
KRELL
institute

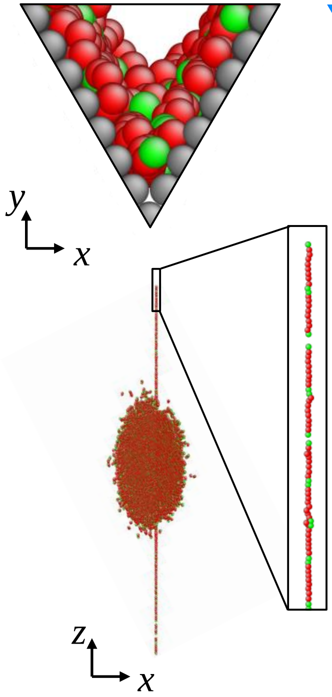
Questions

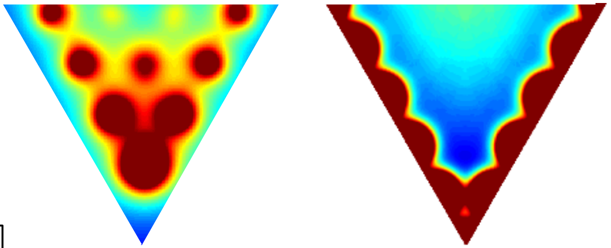












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