Semi-flexible dense polymer brushes in flow - simulation & theory

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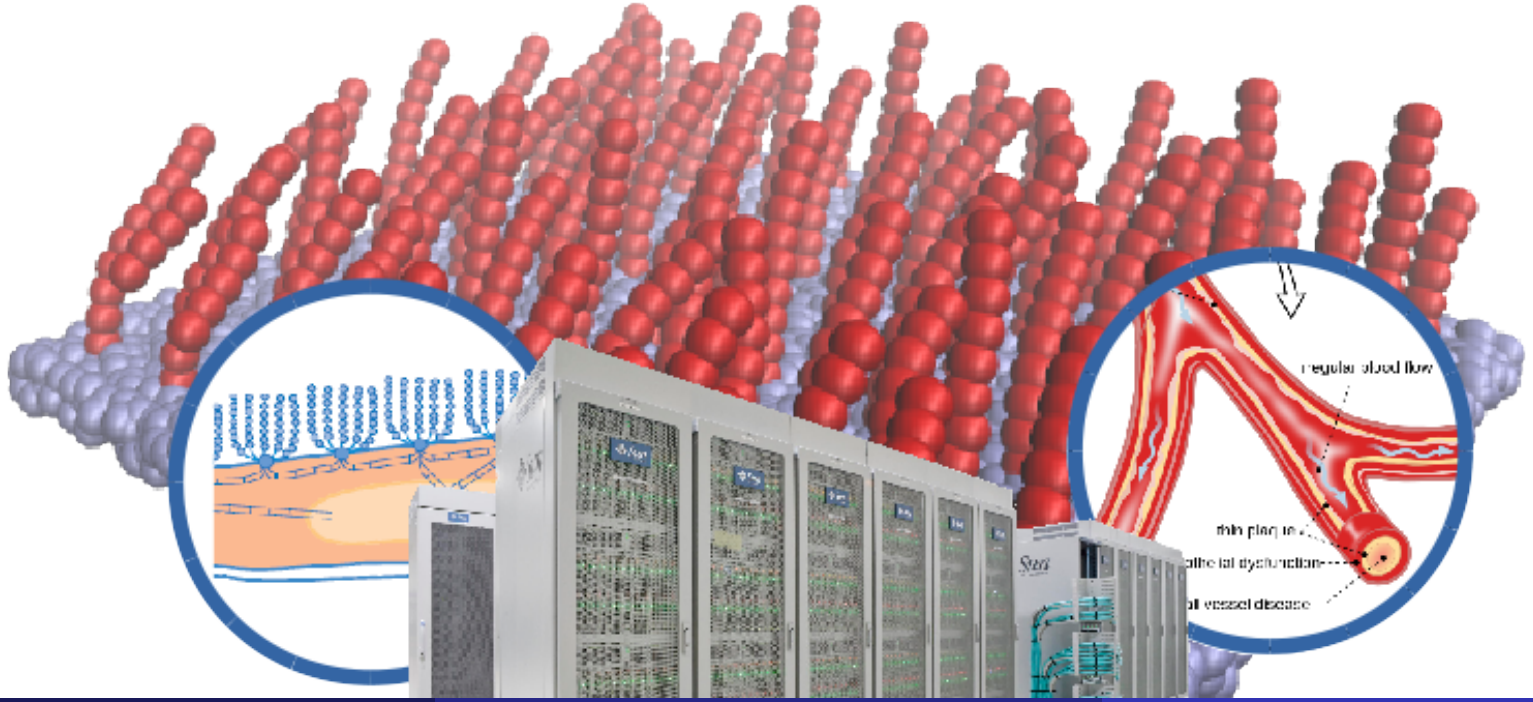
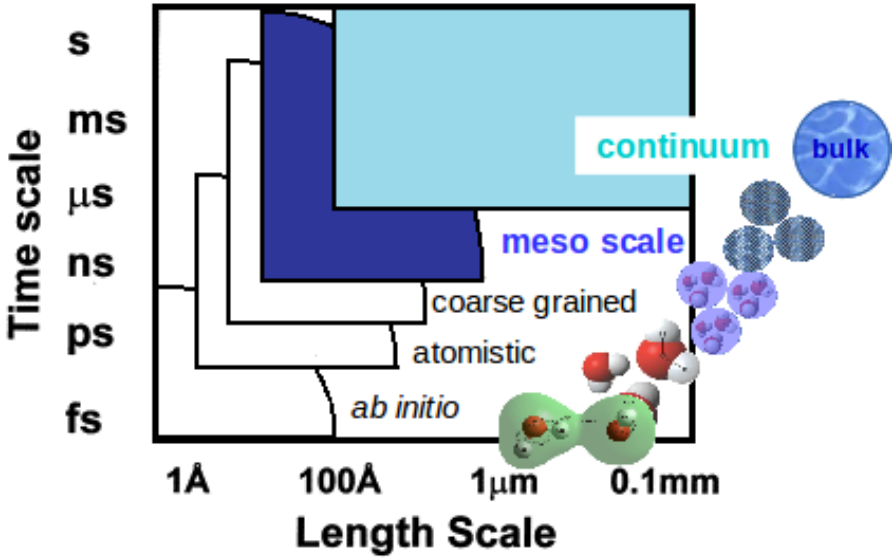
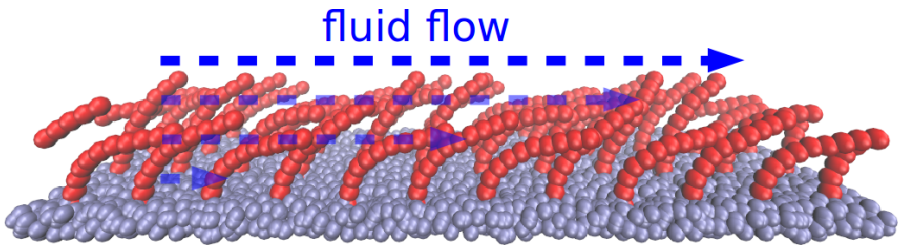


Introduction



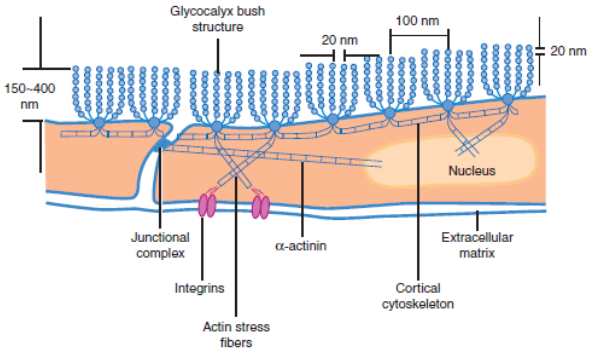


- theoretical & computational methods
- from meso scale to continuum
- hydrodynamic interactions

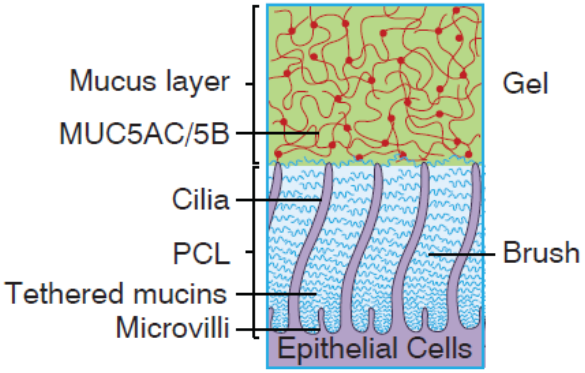
Motivation

Semi-flexible polymers at high density stiff anchored onto a surface:

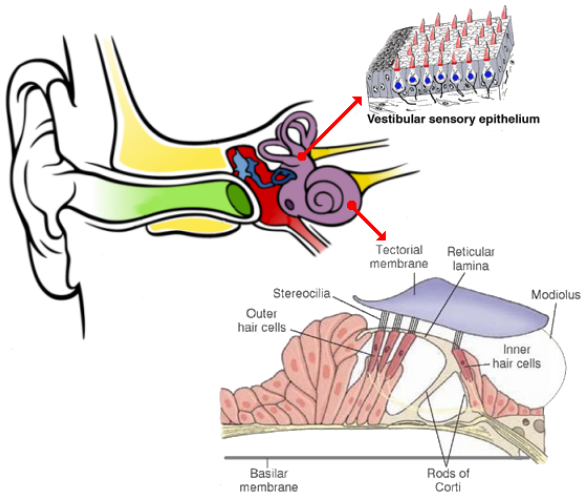
blood vessels



lung mucus layer



inner ear



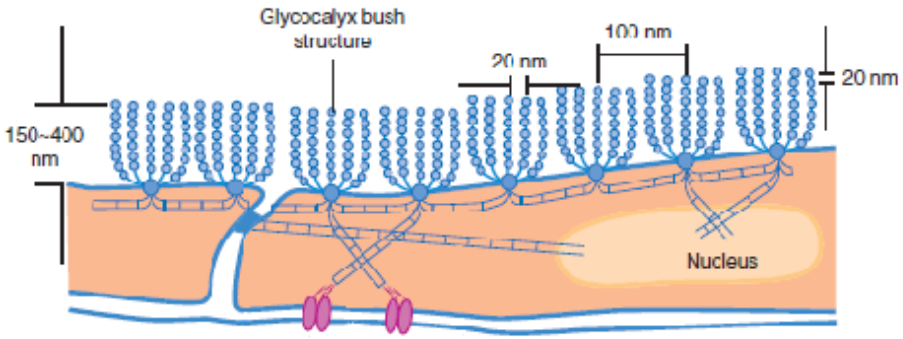
- glycocalyx brush structure on the endothelial surface layer[1] (EGL)
- periciliary layer of the lung airway[2]
- vestibular[3] & auditory[4] sensory epithelium

[1] S. Weinbaum et al., Annu. Rev. Biomed. Eng. **9**, 121–167 (2007).
[2] B. Button et al., Science **337**, 937–941 (2012).
[3] K. Legendre et al., J. Cell Sci. **121**, 3347–3356 (2008).
[4] J. Tolomeo and M. Holley, Biophys. J. **73**, 2241–2247 (1997).

Motivation

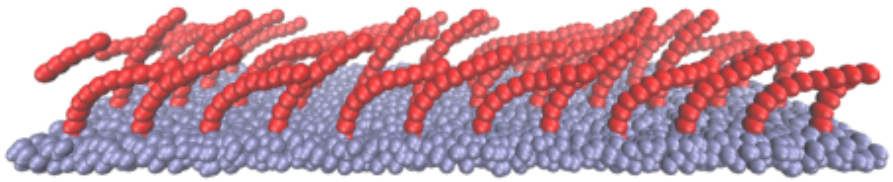
Modeling blood flow in vessels with explicit EGL:

EGL

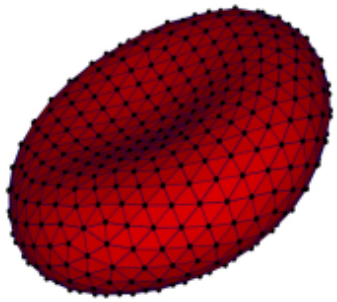


RBC

400 nm – 20 nm



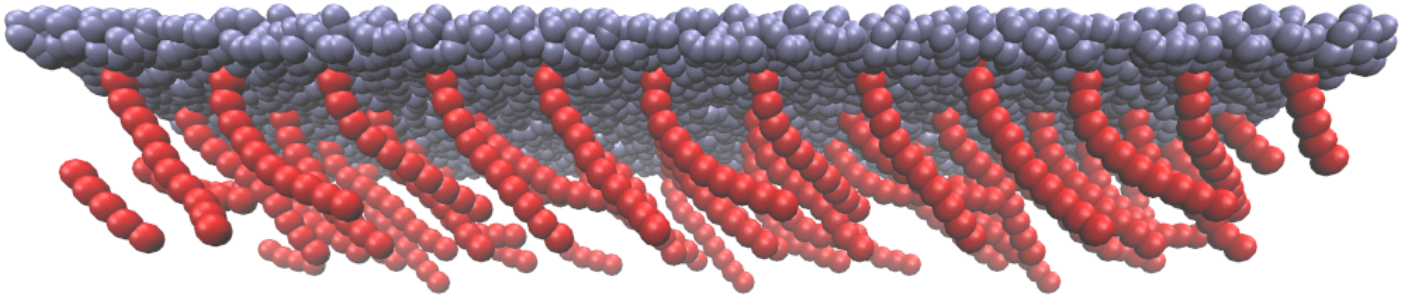
8 µm – 2 µm



scaling problem!

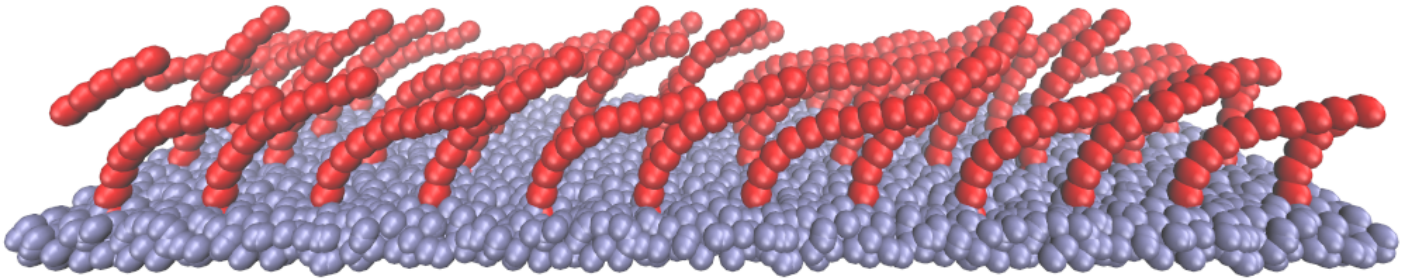
$\rightarrow$ implicit modeling or coarse graining

Motivation



Can we predict the properties (e.g. height) of a dense semi-flexible polymer brush in shear flow for a given set of parameters:

- *flexural rigidity* EI,
- *grafting density* σ and
- *shear rate* $\dot{\gamma}$ on top?



Already done?

There is a lot experimental, simulation & theoretical work done on full-flexible polymer brushes (PB), but only a few on semi-flexible PBs.

Semi-flexible polymer brushes in *equilibrium*:

- D. V. Kuznetsov and Z. Y. Chen, J. Chem. Phys. **109**, 7017–7027 (1998): scaling theory
- G. G. Kim and K. Char, Bull. Korean Chem. Soc. **20**, 1026–1030 (1999): continuous chain model
- C.-M. Chen and Y.-A. Fwu, Phys. Rev. E **63**, 011506 (2000): MC simulation

Semi-flexible polymer brushes in *flow*:

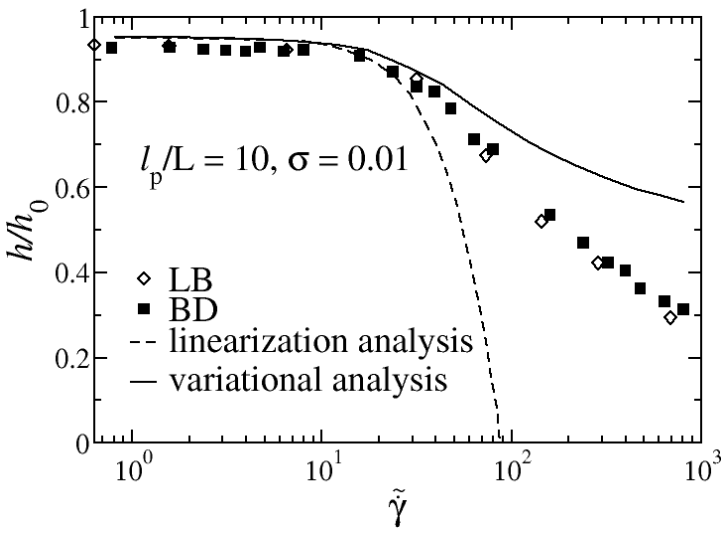
- Y. W. Kim et al., Macromolecules **42**, 3650–3655 (2009): theory & simulation

Already done?

Macromolecules **2009**, *42*, 3650−3655

Nonlinear Response of Grafted Semiflexible Polymers in Shear Flow

Yong Woon Kim,*,†,‡ V. Lobaskin,§ C. Gutsche,|| F. Kremer,|| Philip Pincus,‡ and Roland R. Netz§



$$EI\frac{d^2\theta}{ds^2} = -3\pi\eta\cos\theta(s)\int_s^L u(s)\,ds$$

with: $\frac{s^2 u}{dy^2} = 3\pi\sigma\frac{u(y)}{\cos\theta(y)}$

- no volume-exclusion interaction
- grafting density only influence velocity
- max. grafting density studied $\sigma = 0.03$
- model only works for small deformations

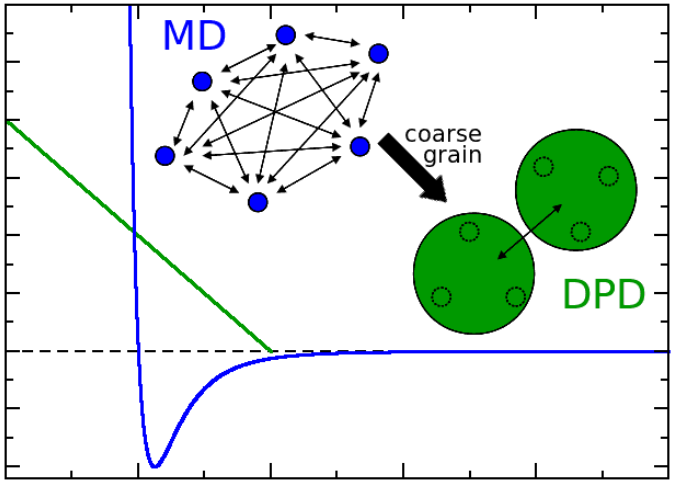
No, it is not done!

Simulations

Dissipative Particle Dynamics (DPD)

simulation method

Dissipative Particle Dynamics (DPD) was introduced by Hoogerbrugge and Koelman in 1992[5].



Particles in DPD represent clusters of molecules and interact through simple pair-wise forces: $\mathbf{F}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^{\mathrm{C}} + \mathbf{F}_{ij}^{\mathrm{R}} + \mathbf{F}_{ij}^{\mathrm{D}})$.

DPD system is thermally equilibrated through a thermostat defined by forces: $\mathbf{F}_{ij}^{\mathrm{R}}$ and $\mathbf{F}_{ij}^{\mathrm{D}}$.

The DPD scheme consists of the calculation of the position and velocities of interacting particles over time. The time evolution of positions and velocities are given by: $d\mathbf{r}_i = \mathbf{v}_i dt$ and $d\mathbf{v}_i = \mathbf{F}_i dt$.

[5] P. Hoogerbrugge and J. Koelman, Europhys. Lett. **19**, 155 (1992).

Smoothed Dissipative Particle Dynamics (SDPD)

simulation method

Español and Revenga combined in Smoothed Dissipative Particle Dynamics (SDPD)[6] best features of the Smoothed Particle Hydrodynamics (SPH)[7] and DPD methods.

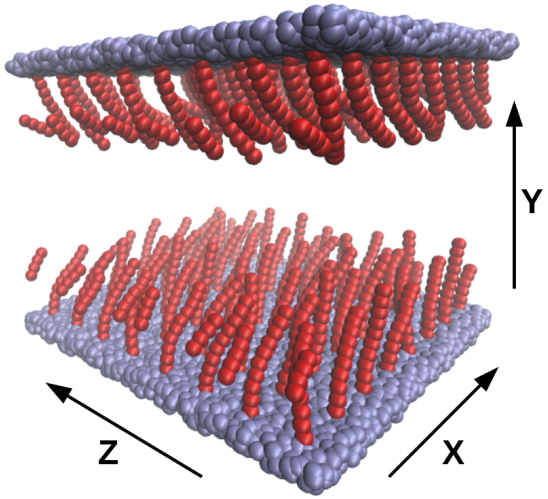
- SDPD allows to introduce an arbitrary equation of state:
  - e.g. control compressibility.
- SDPD particles has a well defined size and volume:
  - *consitent scaling* of thermal fluctuations of the fluid,
  - while dynamics of immersed objects is *scale-free*[8]
- In SDPD transport coefficients (viscosity, thermal conductivity) are a direct input.

[6] P. Español and M. Revenga, Phys. Rev. E **67**, 026705 (2003).
[7] R. Gingold and J. Monaghan, Mon. Not. R. Astron. Soc. **181**, 375 (1977).
[8] A. Vzquez-Quesada et al., J. Chem. Phys. **130**, 034901 (2009).

System

simulation model

The **SDPD ensemble**:



- slit like geometry (2D PBC)
- wall & fluid: SDPD particle
- reflection planes at walls
- Poiseuille flow in x direction: $f_{x,i} = (dP/dx)/\rho$
- polymers grafted on a tetragonal lattice with a_{lat}
- friction between fluid & polymer beads

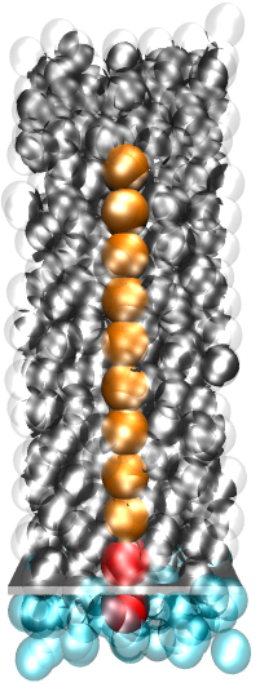
We characterize the system by:

- grafting density: $\sigma = (a_{\mathrm{lat}}/d)^{-2}$
- flexibility: $l_p/L = EI/(k_B TL)$
- rate: $\tilde{\dot{\gamma}} = L^3 \eta \dot{\gamma}/k_B T$

Polymer Beam

simulation model

The **Polymer beam** is represented by:



- $N = 10 + 1$ tangential bonded beads of diameter d
- 1st two beads fixed
- *extensible* worm-like chain model like
- friction interaction with fluid
- repulsive interaction between beads (WCA[a])
  $\rightarrow$ volume exclusion

[a] J. D. Weeks et al., J. Chem. Phys. **54**, 5237–5247 (1971).

Discretized elastic potential[9] for isotropic elastic cylinder of diameter d:

$$U(\{r_k\}) = \sum_{i=0}^{N-1} \left[\frac{k_b}{2d} \left[r_{i,i+1} - d \right]^2 + \frac{EI}{d} \left[1 - \cos \Delta\theta \right] \right]$$

with: $EI/k_b = d^2/16$

[9] X. Schlagberger and R. R. Netz, Europhys. Lett. **70**, 129 (2005).

Results

We have simulated systems with:

- grafting densities σ from 0.01 to 1,
- and beam elasticities l_p/L of 10 and 100
- at shear rates $\tilde{\dot{\gamma}}$ between 10^1 and 10^6.

The Reynolds number, referring to the maximum velocity the polymer brush is exposed at the tip and beam elasticity, varies between $R_e = \frac{\rho u d}{\eta} = \text{impuls}\frac{convection}{diffusion} = 10^{-6} - 10^{-1} \rightarrow$ Stokes regime[10].

Height of brush is calculated from the first moment of the polymer monomer density profile[11]:

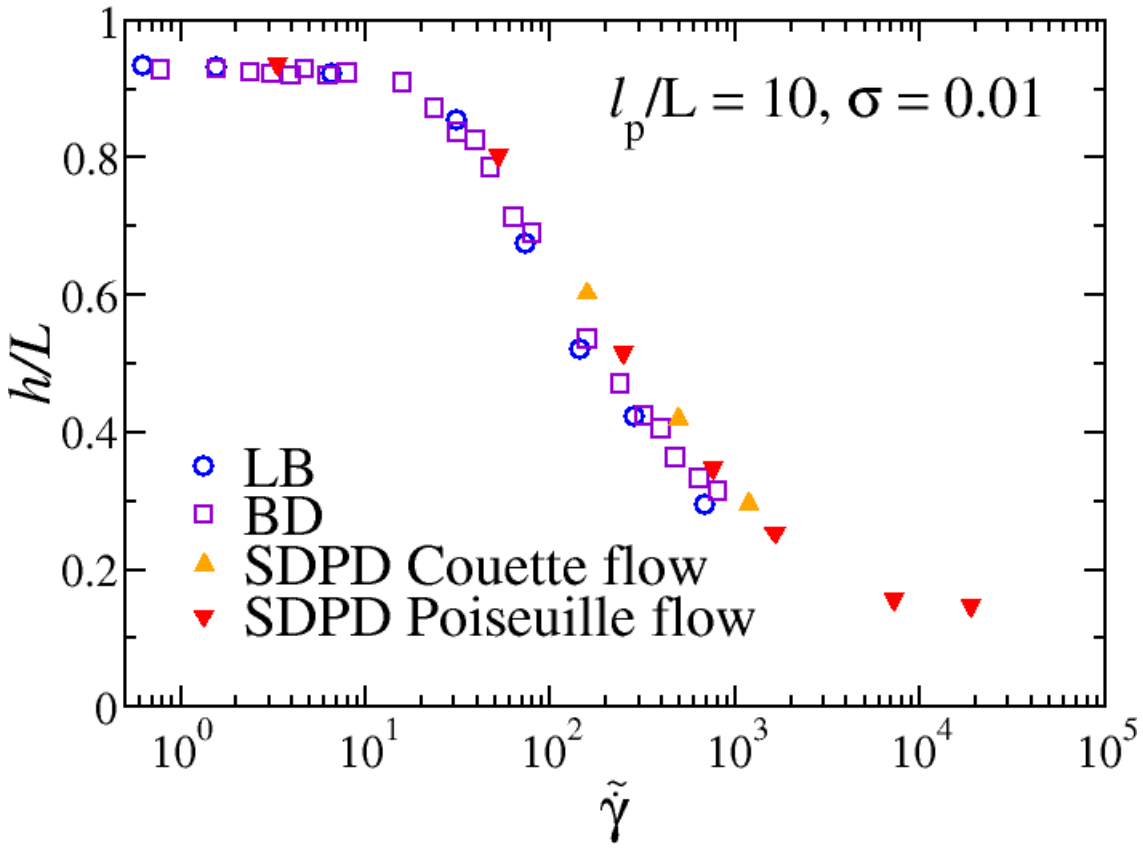
$$h = 2\frac{\int y\rho(y)dy}{\int \rho(y)dy}$$

[10] E. Guyon et al., *Physical hydrodynamics*, (Oxford University Press, 2001).
[11] M. Deng et al., J. Fluid Mech. **711**, 192–211 (2012).

Results

comparison of methods

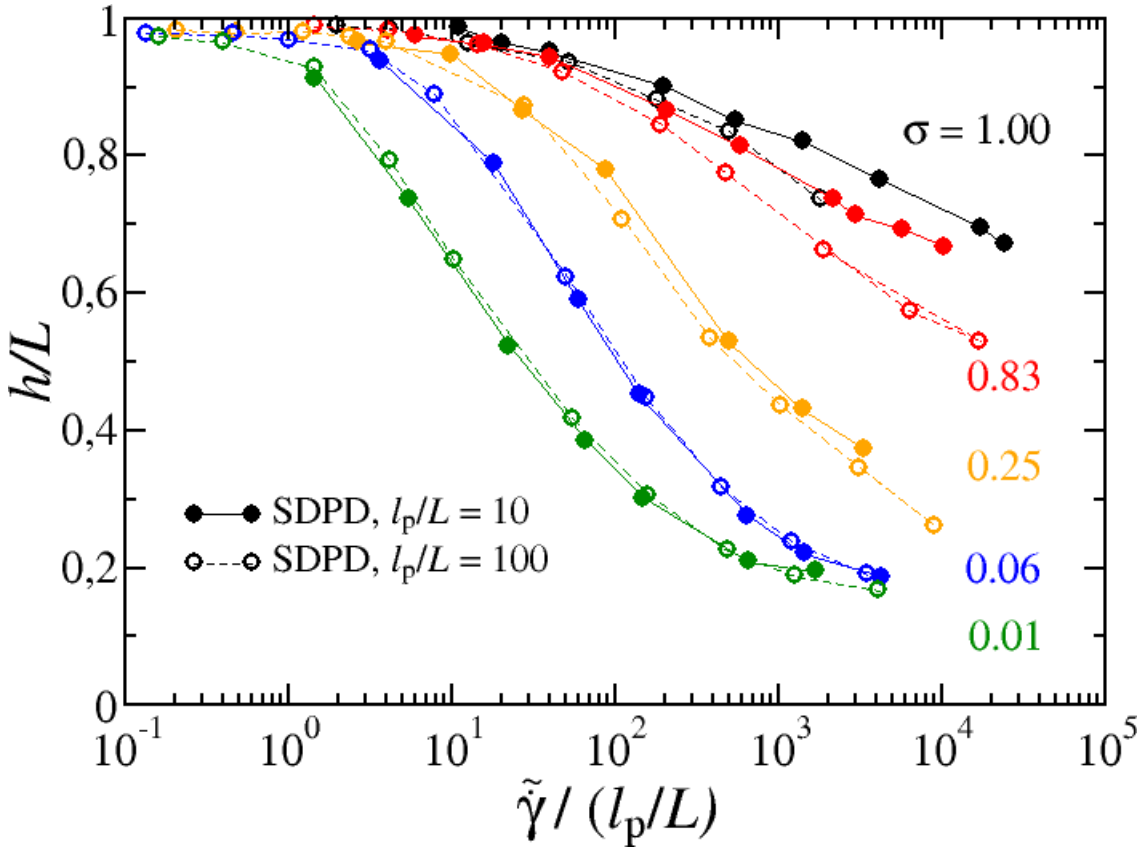
Comparison with LB and BD simulations from Y. W. Kim et al., Macromolecules **42**, 3650–3655 (2009):



Results

from SDPD simulations

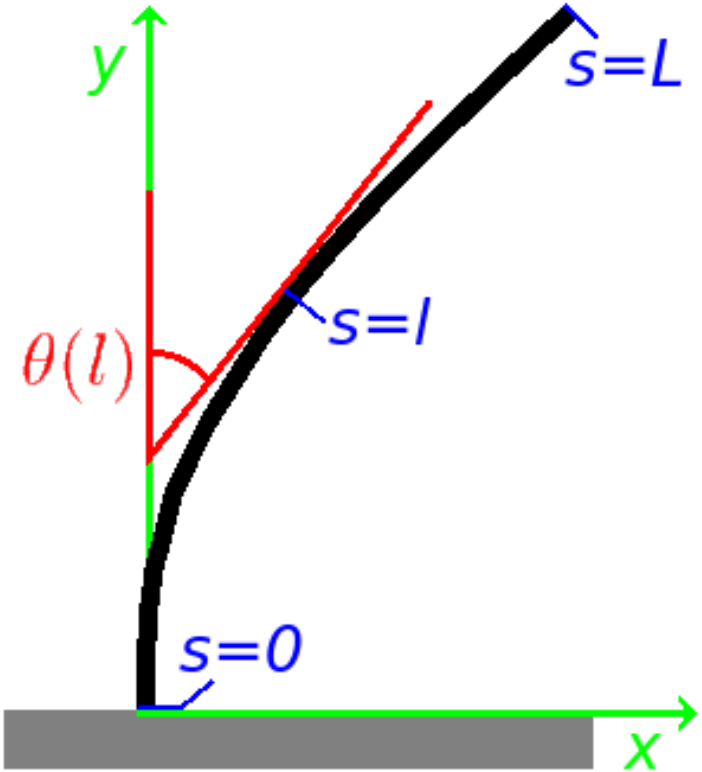
Polymer brush height as a function of shear rate on top of the brush:



Theory

Theoretical Model

The polymer beam is treated as a cantilever.



- Uniform behavior
- Quasi 2D: no perturbation in z
- Internal coordinates along contour line: $s, \theta(s)$

Euler-Bernoulli beam theory:

$$EI\frac{d\mathbf{r}(s)}{ds} \times \frac{d^3\mathbf{r}(s)}{ds^3} = \mathbf{F}(s) \times \frac{d\mathbf{r}(s)}{ds}$$

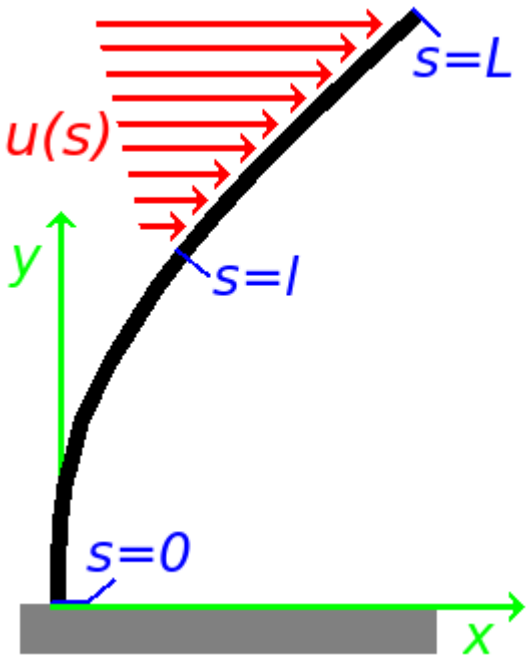
$$EI\frac{d^2\theta(s)}{ds^2} = F_y(s)\sin\theta(s) - F_x(s)\cos\theta(s)$$

- Hydrodynamic drag force: $\mathbf{F}^{\mathrm{d}}(s)$
- Volume exclusion force: $\mathbf{F}^{\mathrm{v}}(s)$

Boundary conditions:
$\theta(s)|_{s=0} = 0$ at the grafting surface, and $d\theta/ds|_{s=L} = 0$ at the free end.

Shear force on the beam

theoretical model



The effective shear force acting on the beam at position s:

$$\mathbf{F}^{\mathrm{d}}(s) = \int_s^L \mathbf{f}^{\mathrm{d}}(s')ds,$$

with the local force density due to hydrodynamic interaction for the x-component

$$f_x^{\mathrm{d}}(s) = f_\perp^{\mathrm{d}}(s)\cos\theta(s) + f_\parallel^{\mathrm{d}}(s)\sin\theta(s),$$

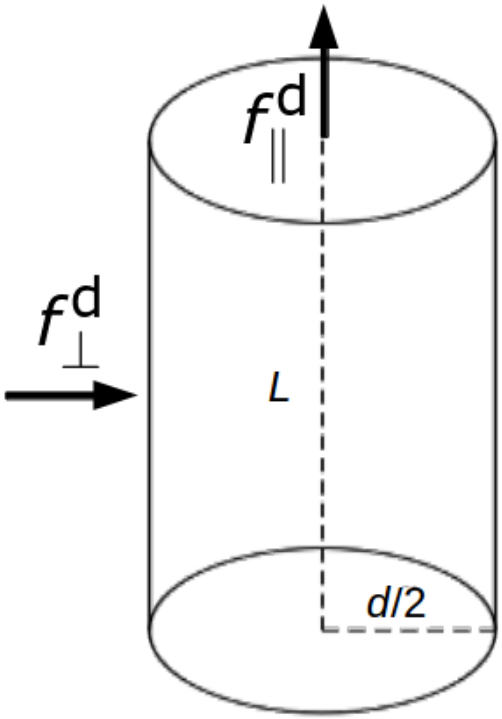
and the y-component

$$f_y^{\mathrm{d}}(s) = f_\perp^{\mathrm{d}}(s)\sin\theta(s) - f_\parallel^{\mathrm{d}}(s)\cos\theta(s)$$

Shear force on the beam

theoretical model

Shear force components:
$f_\perp^{\mathrm{d}}(s) = \zeta_\perp(s)\eta u_x(s)\cos\theta(s)$ and $f_\parallel^{\mathrm{d}}(s) = \zeta_\parallel(s)\eta u_x(s)\sin\theta(s)$



Friction coefficient from slender body theory[a], piecewise approximated as a cylinder[b]:

$$\zeta^\perp = \frac{8\pi}{\ln(L/d) - \frac{1}{2} + \ln(2)},$$
$$\zeta^\parallel = \frac{4\pi}{\ln(L/d) - \frac{3}{2} + \ln(2)}.$$

[a] R. G. Cox, J. Fluid Mech. **44**, 791–810 (1970).
[b] C. H. Wiggins et al., Biophys. J. **74**, 1043–1060 (1998).

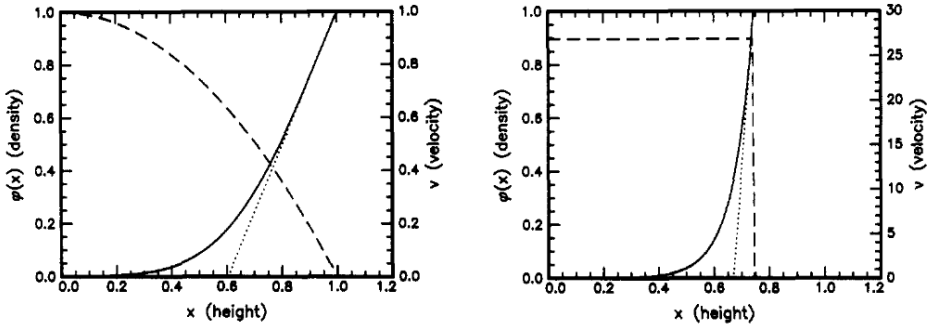
Local velocity $u_x(s)$ depend on the hydrodynamic penetration[c].

[c] S. T. Milner, Macromolecules **24**, 3704–3705 (1991).

Velocity profile

theoretical model

Local velocity $u(s)$ depend on the hydrodynamic penetration into the brush[12]:



Like Kim *et al.*[13] we introduce an equation similar to the Brinkman equation[14] for flow in porous media but depending on local density:

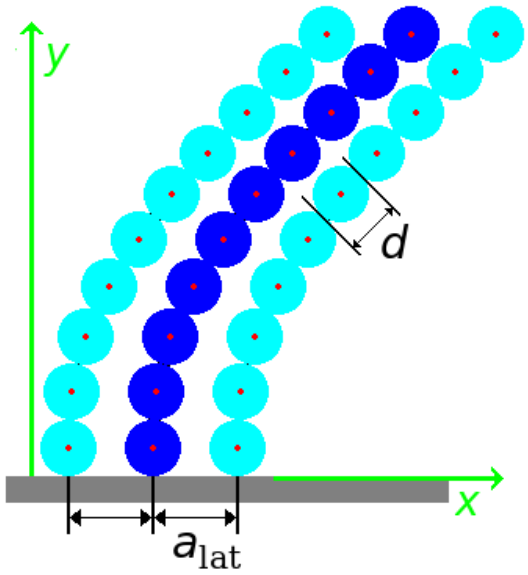
$$\frac{d^2u}{dy^2} = \zeta\sigma\frac{u(y)}{\cos\theta(y)} \rightarrow \frac{d^2u_x(s)}{ds^2} = \zeta(s)u_x(s)\frac{\sigma}{d^2}\cos\theta(s) - \frac{du_x(s)}{ds}\frac{d\theta(s)}{ds}\tan\theta(s),$$

with boundary conditions: $u(y)|_{y=0} = u(s)|_{s=0} = 0$, and $du/dy|_{y=L} = \dot{\gamma}_L$ resp. $du/ds|_{s=L} = \dot{\gamma}_L \sin\theta(L)$.

[12] S. T. Milner, Macromolecules **24**, 3704–3705 (1991).
[13] Y. W. Kim et al., Macromolecules **42**, 3650–3655 (2009).
[14] H. C. Brinkman, Appl. Sci. Res. A1 **A1**, 27 (1947).

Volume exclusion

theoretical model



- Discretise the beam: $N = \lfloor L/d \rfloor$ spheres
- Positions are given as a function of s:

  the f

  $x(s) = \int_0^s \sin\theta(s')ds' \wedge y(s) = \int_0^s \cos\theta(s')ds'$
- Assume a repulsive interaction:

  $$\mathbf{g}_{ij} = \begin{Bmatrix} r_{ij} \leqslant d: & \epsilon_g \frac{k_B T}{d} \left[(d/r_{ij})^\alpha - 1\right] \frac{\mathbf{r}_{ij}}{r_{ij}} \\ r_{ij} > d: & 0 \end{Bmatrix}$$

  with $\epsilon_g \gtrsim 50$ and $\alpha \geq 3$.
- Force density $\mathbf{f}_n^{\mathrm{v}}$ on a sphere $n \in [0 \ldots N-1]$ in a discretized beam:

  $\mathbf{f}_n^{\mathrm{v}} = \sum_j \frac{\mathbf{g}_{nj}}{d}$

$$\mathbf{F}^{\mathrm{v}}(s) = \mathbf{f}^{\mathrm{v}}_{\lfloor s/d \rfloor} \left(d \lceil s/d \rceil - s/d\right) + \sum_{n=\lceil s/d \rceil}^{N-1} \mathbf{f}_n^{\mathrm{v}} d$$

Theoretical Solution

Brinkman-like equation

$$\frac{d^2 u_x(s)}{ds^2} = \zeta(s) u_x(s) \frac{\sigma}{d^2} \cos\theta(s) - \frac{du_x(s)}{ds} \frac{d\theta(s)}{ds} \tan\theta(s)$$

Beam equation

$$EI \frac{d^2\theta(s)}{ds^2} = F_y(s) \sin\theta(s) - F_x(s) \cos\theta(s)$$

Solver scheme:

0. guess a configuration: $\theta_0(s)$ for $s \in [0, L]$
1. calculate volume exclusion force $\rightarrow \mathbf{F}^{\mathrm{v}}(s)$
2. solve *Brinkman-like* equation $\rightarrow u(s) \Rightarrow \mathbf{F}^{\mathrm{d}}(s)$
3. *Beam* equation & DuFort-Frankel scheme[15] $\rightarrow \theta_n(s)$
4. if $\int_0^L |\theta_n - \theta_{n-1}|\, ds > tol$: goto ① else : found final configuration ;)

[15] E. C. Du Fort and S. P. Frankel, Math. Comp. **7**, 135–152 (1953).

Results

SDPS vs theory

Comparison between SDPD simulation and our theoretical model:
brush height

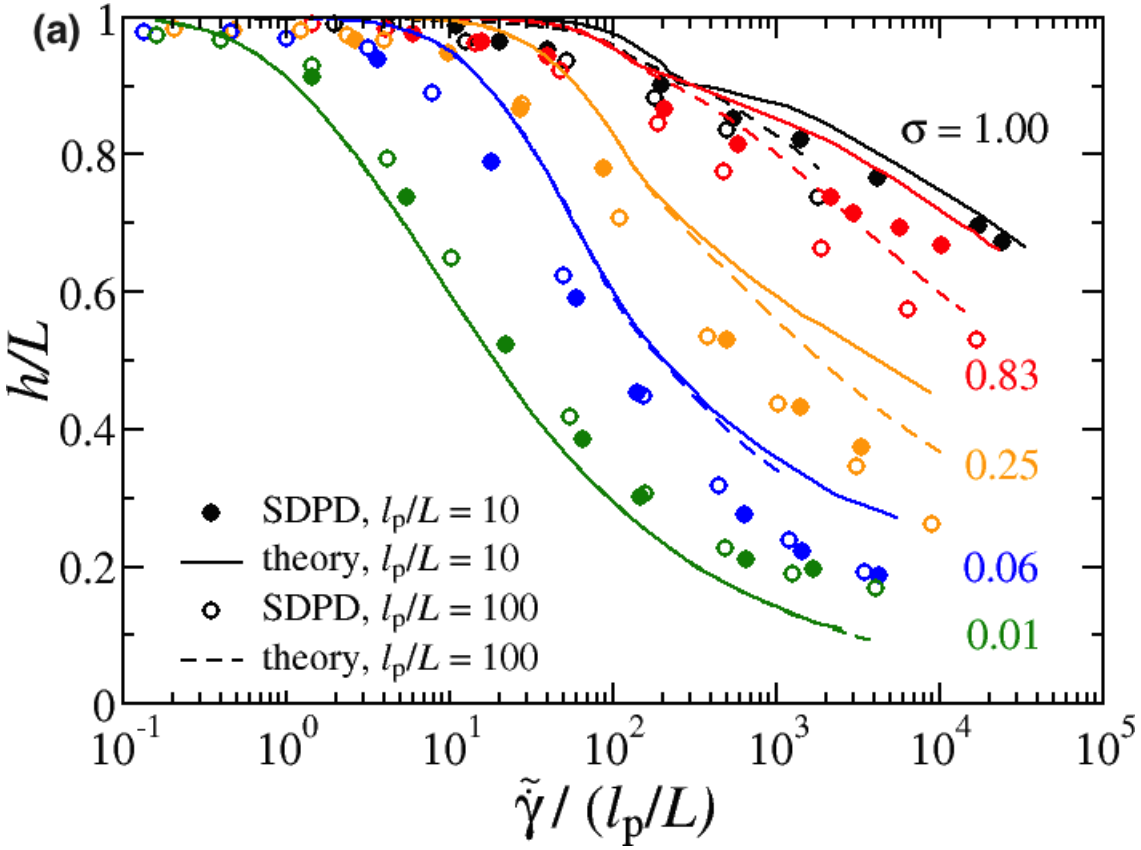
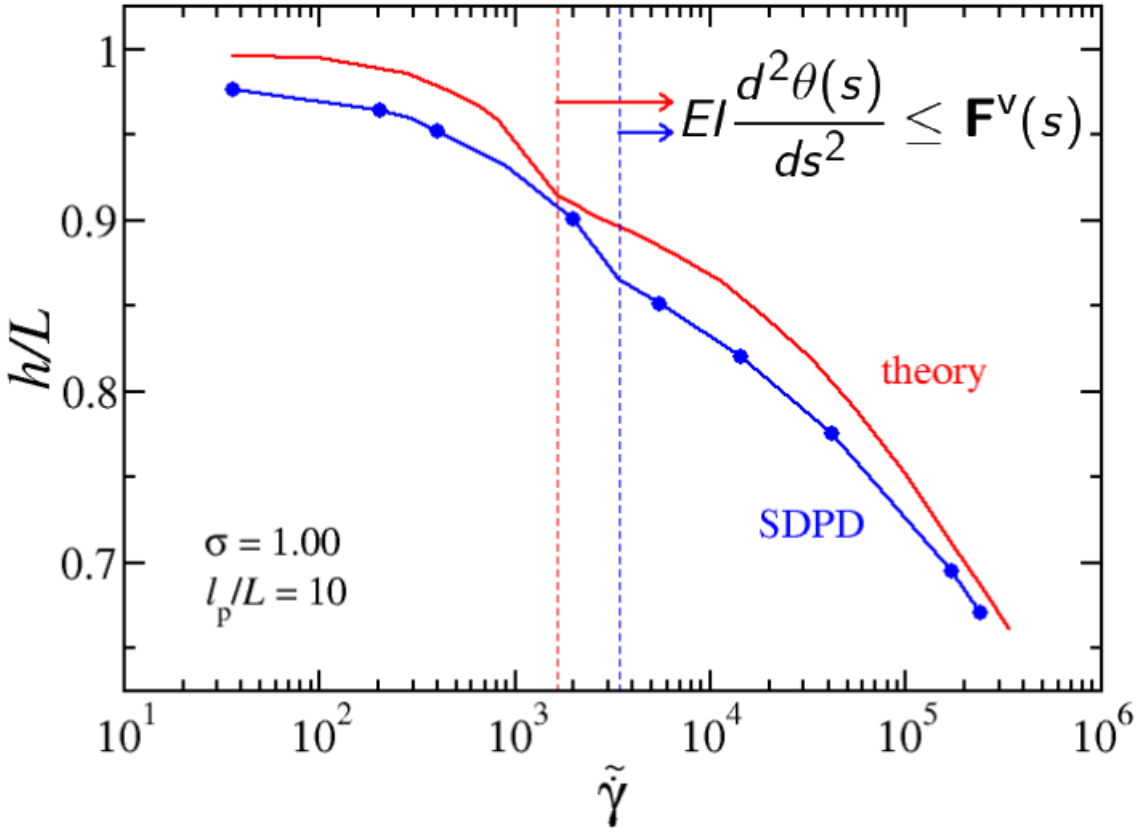


Figure : Relative brush height vs shear rate normalized by polymer elasticity

Results

SDPS vs theory

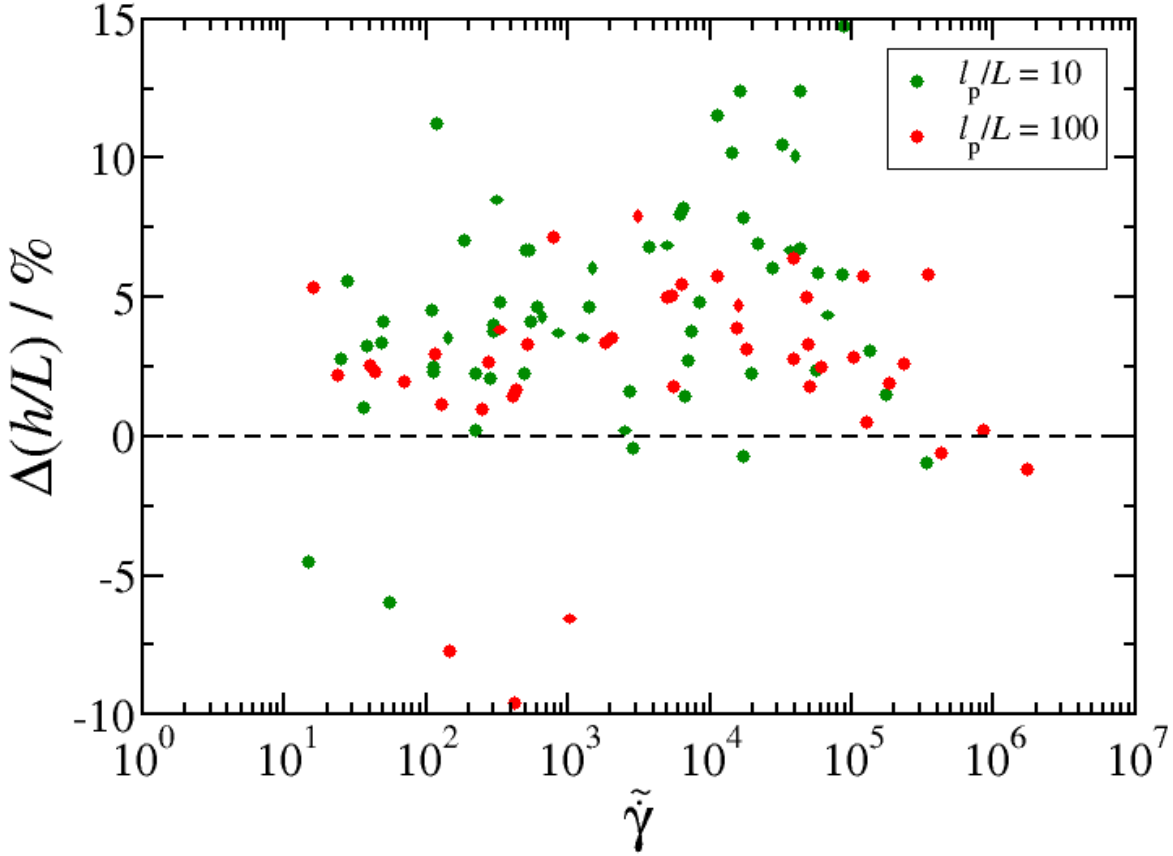
Comparison between SDPD simulation and our theoretical model:
brush height



overestimation of volume-exclusion term $\mathbf{F}^{\mathrm{v}}$ $\leftarrow$ neglected perturbation in z

Results

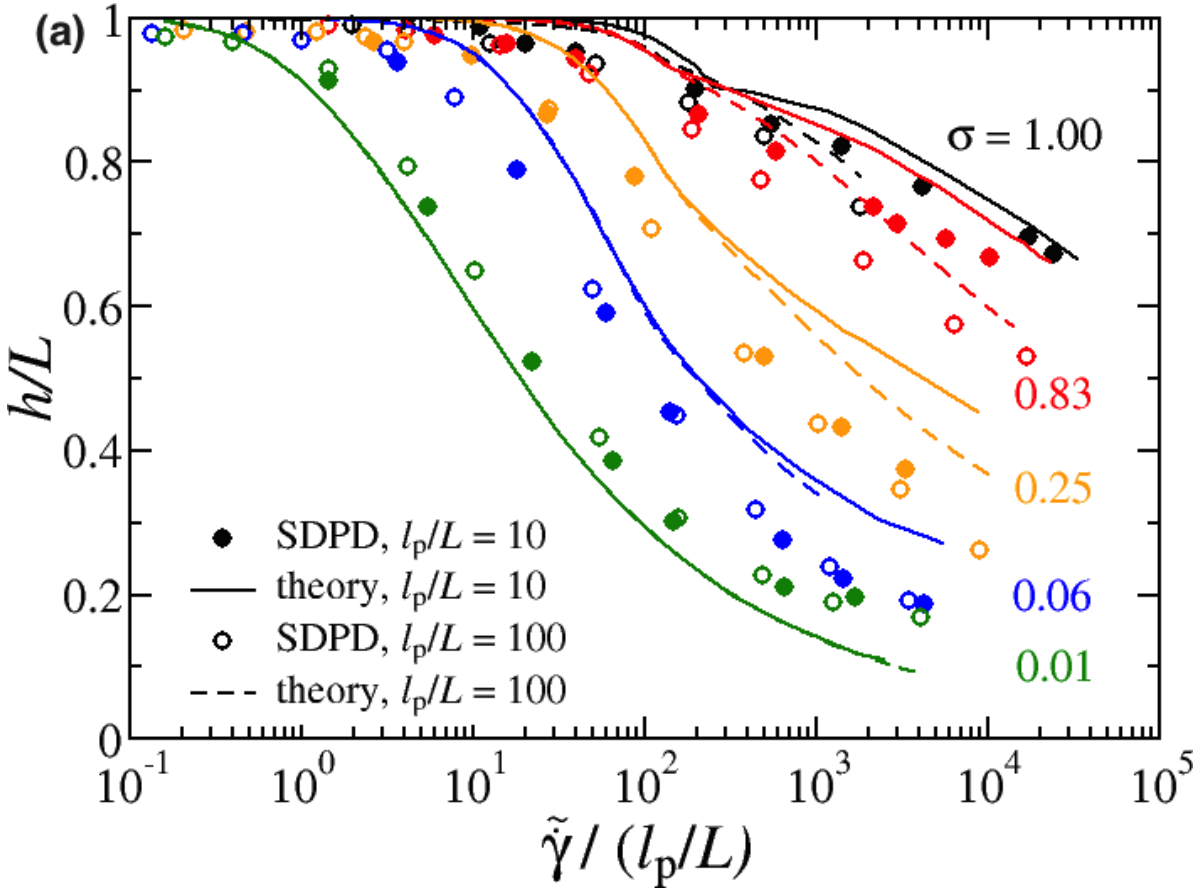
error analysis

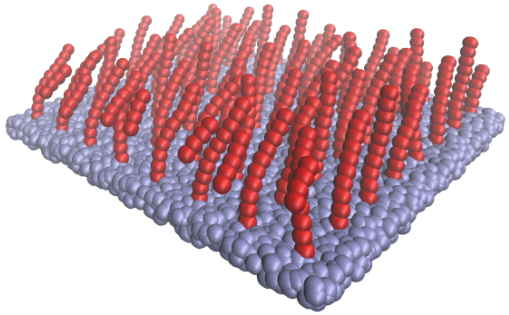


N	106
RMS	14.6 %
AAD	9.5 %
Bias	8.3 %

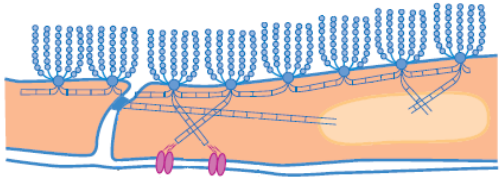
Figure : Relative deviation of brush height vs shear rate.

Prediction of the response to shear flow of *dense polymer brushes*.





EGL, $\sigma \approx 1$



Results

SDPS vs theory

Comparison between SDPD simulation and our theoretical model:
velocity profile

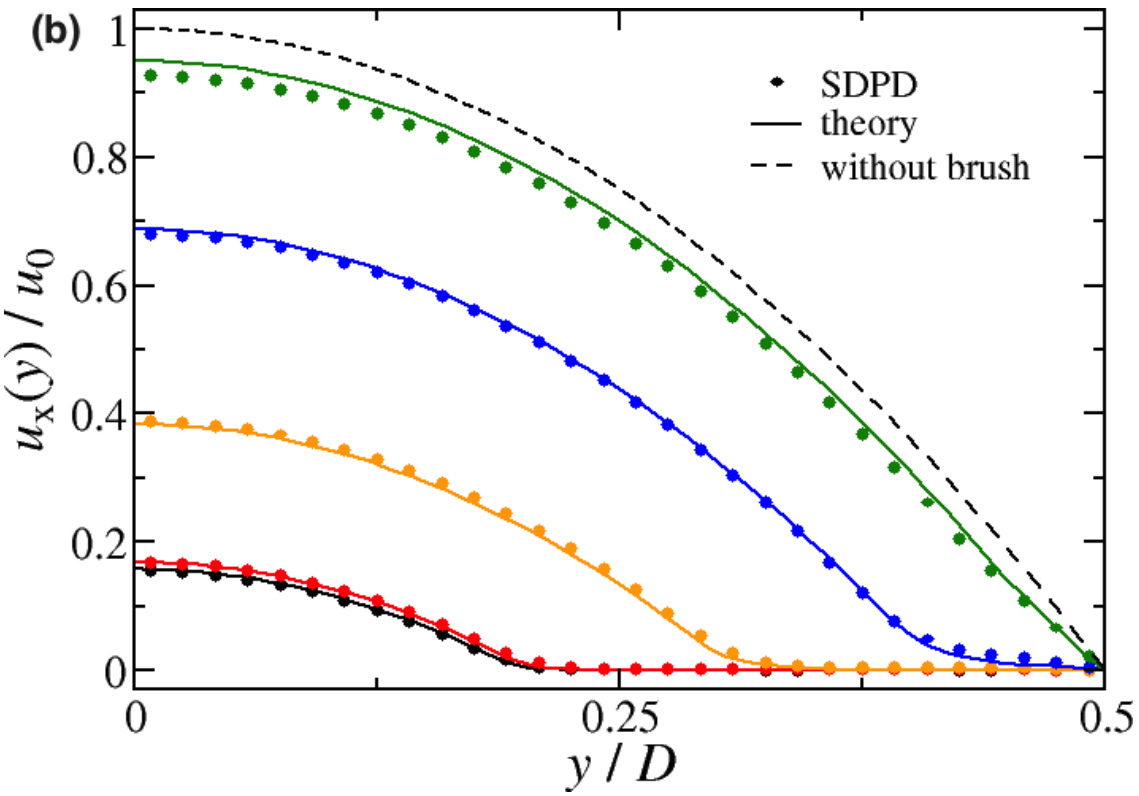
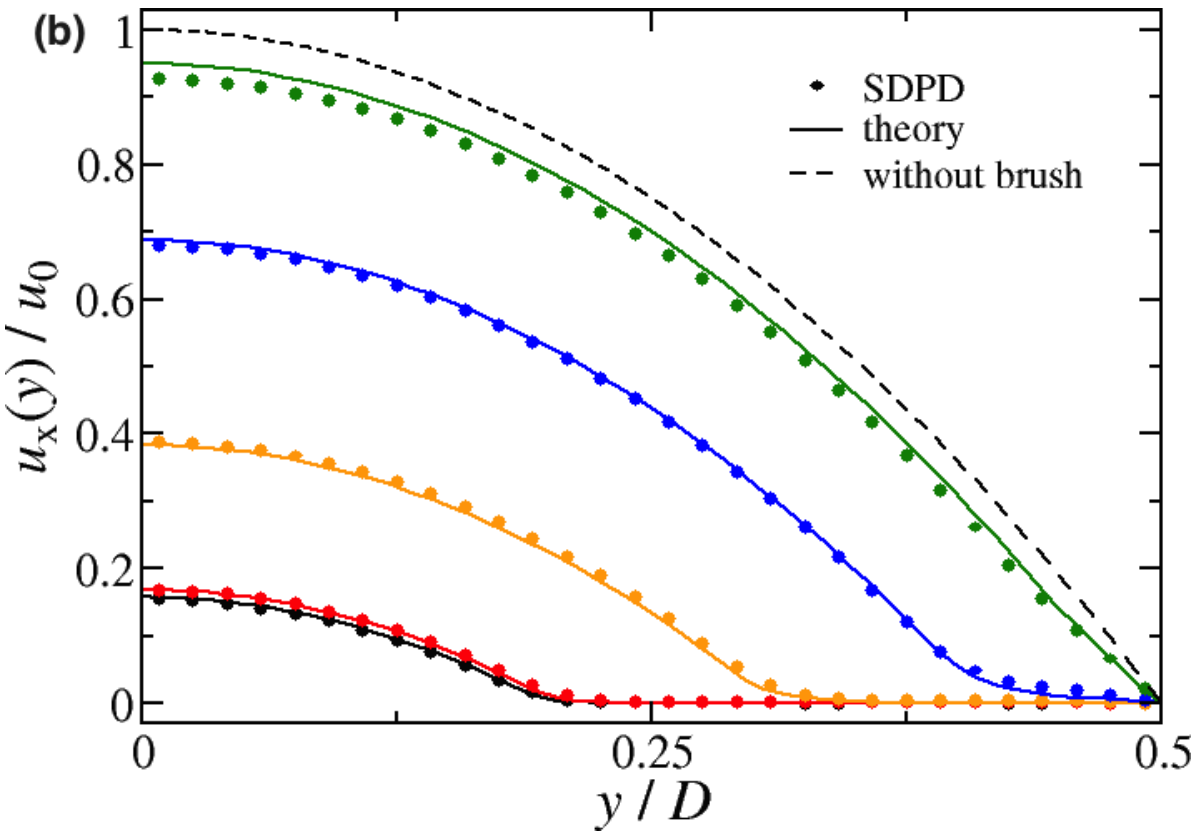
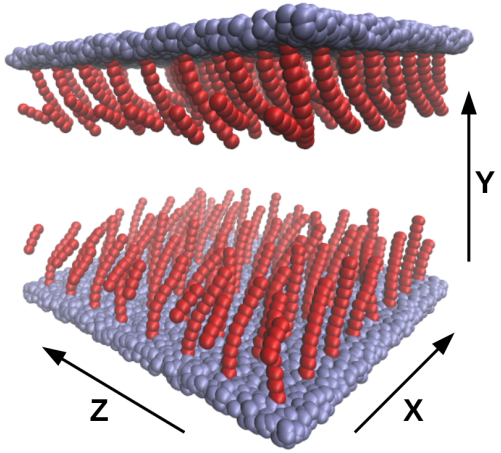


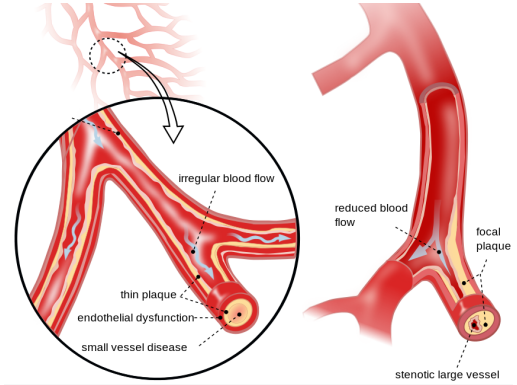
Figure : normalized velocity profiles, $\partial P/\partial x = \text{const.}$

Prediction of flow rates in channels or tubes.





micro-vascular flow



Results

SDPS vs theory

Comparison between SDPD simulation and our theoretical model:

Relative apparent viscosity

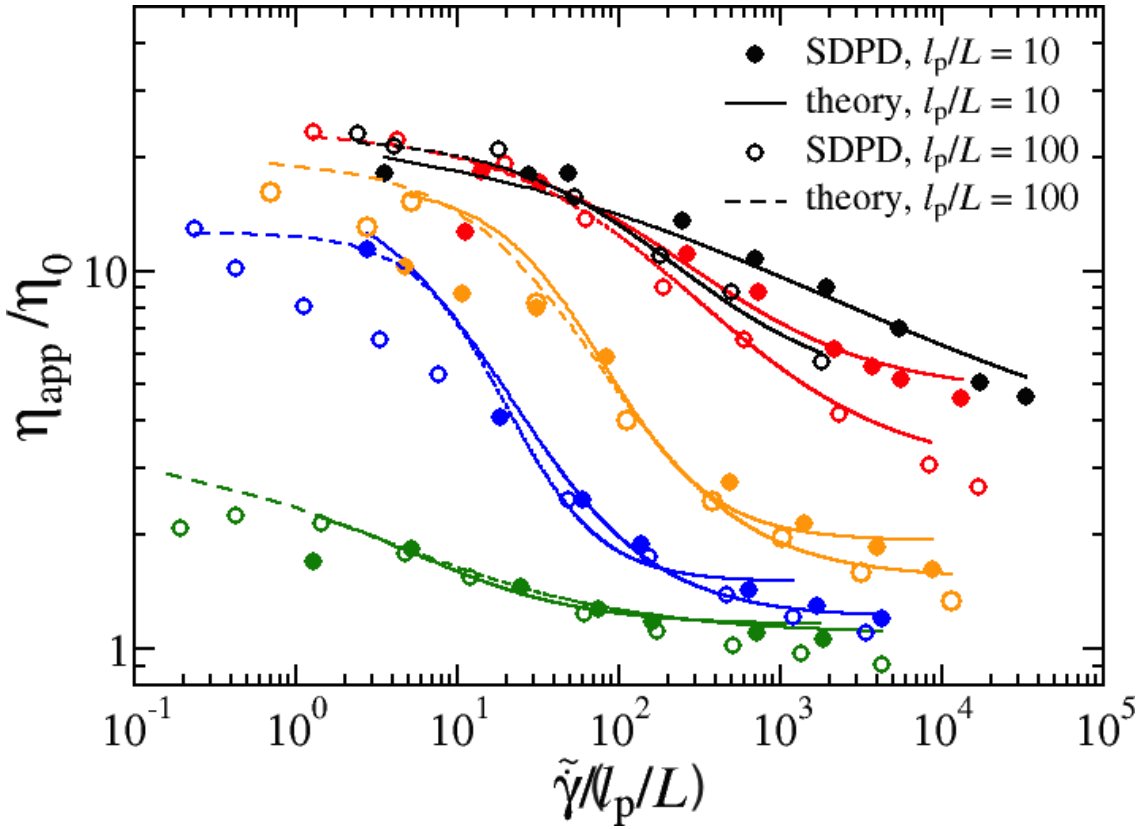
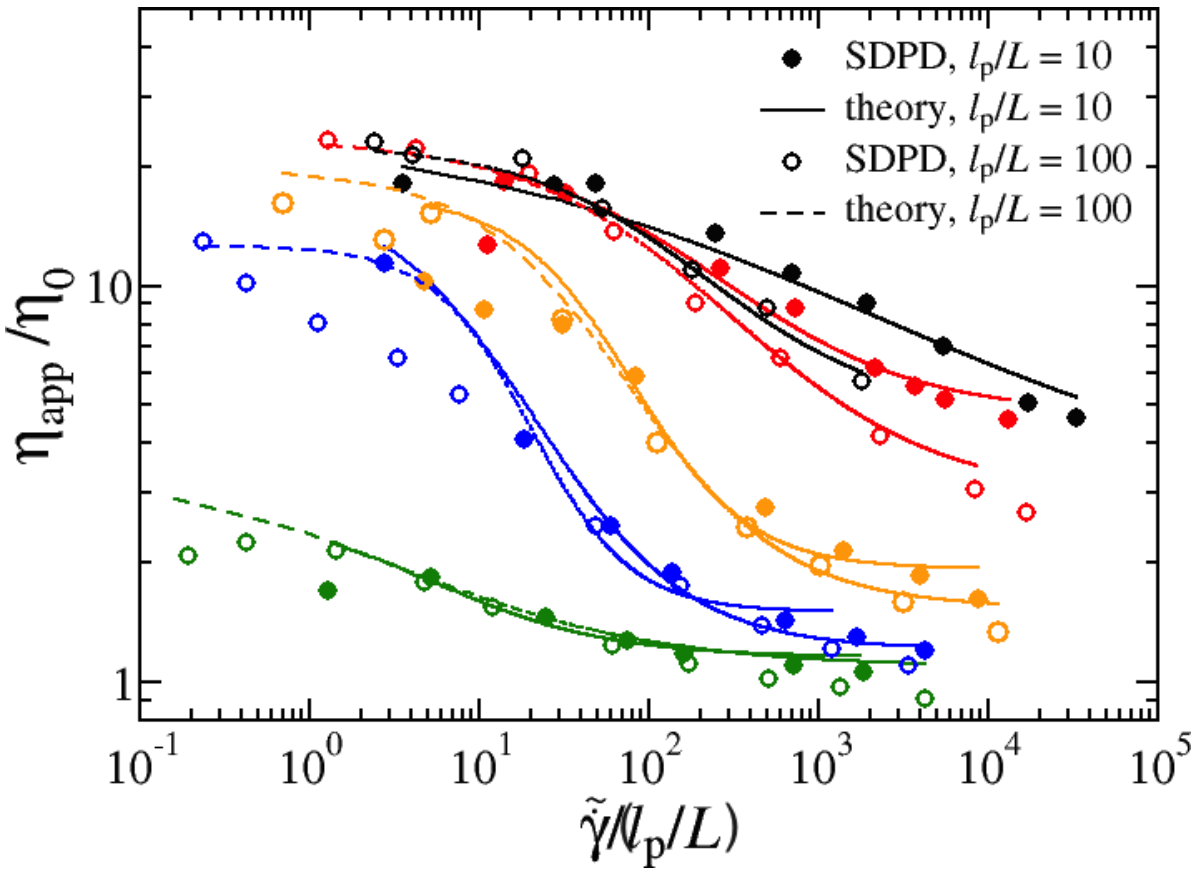
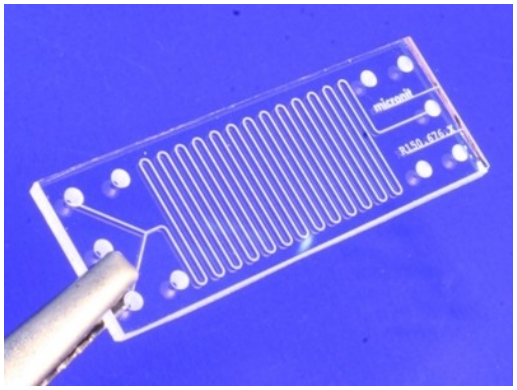


Figure : Relative apparent viscosity vs shear rate scaled by elasticity.

Prediction of app. viscosity as input for continuous methods.



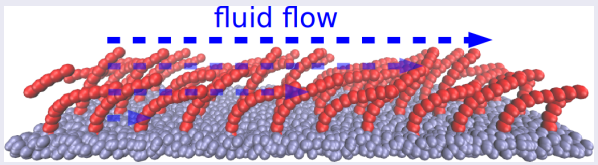


microfluidic devices

Conclusion

- Simulations of polymer brushes with
  - densities varying between 0.01 (no interaction between polymers) and 1 (maximum density of SC packing),
  - with elasticities in range of 2 orders of magnitude and
  - under top shear loads in range of 6 orders of magnitude.
- Simulations $h(\sigma, EI, \dot{\gamma})$ in good agreement with previous studies.
- We propose the first theoretical model describing dense semi-flexible polymer brushes in a wide parameter range:
  - Good agreement with simulations: $(\Delta h)_{\max} \approx d$.
  - Model reproduces all features shown in simulation.
  - Systematic overestimation of height due to reduced dimensionality.

Now we can predict the interaction of a dense semi-flexible polymer brush with shear flow!

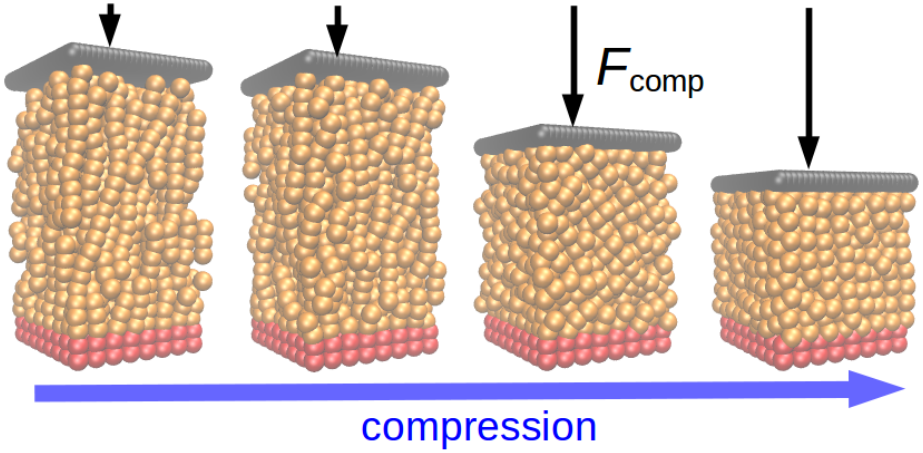


F. Römer and D. A. Fedosov, Europhysics Letters **109**, 68001 (2015)

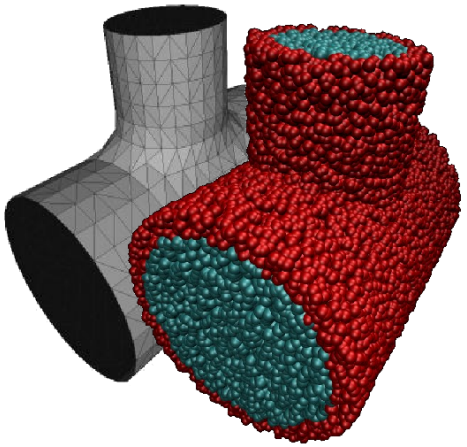
Outlook

Direct mechanical stress or deformation of the brush.

→ simulation of brush compression:
preliminary results in good agreement with theoretical model



⇒ add viscoelasticity to vessel walls:
model mechanical transduction of forces due to e.g. EGL–RBC interactions



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THANK YOU FOR YOUR ATTENTION! ANY QUESTIONS?