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

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Introduction

- theoretical & computational methods
- from meso scale to continuum
- hydrodynamic interactions
Semi-flexible polymers at high density stiff anchored onto a surface:

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

Motivation

Modeling blood flow in vessels with explicit EGL:

EGL

RBC

400 nm – 20 nm

8 μm – 2 μm

scaling problem!
→ implicit modeling or coarse graining
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* $\sigma$ 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*:


Semi-flexible polymer brushes in *flow*:

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) was introduced by Hoogerbrugge and Koelman in 1992\textsuperscript{5}.

Particles in DPD represent clusters of molecules and interact through simple pair-wise forces: \( F_i = \sum_{j \neq i} (F^C_{ij} + F^R_{ij} + F^D_{ij}) \).

DPD system is thermally equilibrated through a thermostat defined by forces: \( F^R_{ij} \) and \( F^D_{ij} \).

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: \( dr_i = v_i dt \) and \( dv_i = F_i dt \).

Español and Revenga combined in Smoothed Dissipative Particle Dynamics (SDPD)\textsuperscript{6} best features of the Smoothed Particle Hydrodynamics (SPH)\textsuperscript{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:
  - \textit{consistent scaling} of thermal fluctuations of the fluid,
  - while dynamics of immersed objects is \textit{scale-free}\textsuperscript{8}
- In SDPD transport coefficients (viscosity, thermal conductivity) are a direct input.

The **SDPD ensemble**:

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

We characterize the system by:

- grafting density: $\sigma = (a_{\text{lat}}/d)^{-2}$
- flexibility: $l_p/L = EI/(k_B T L)$
- rate: $\dot{\gamma} = L^3 \eta \dot{\gamma}/k_B T$
The **Polymer beam** is represented by:

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

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

with: \( EI/k_b = d^2/16 \)


We have simulated systems with:

- grafting densities $\sigma$ from 0.01 to 1,
- and beam elasticities $l_p/L$ of 10 and 100
- at shear rates $\tilde{\gamma}$ 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

$$R_e = \frac{\rho u d}{\eta} = \text{impuls} \left( \frac{\text{convection}}{\text{diffusion}} \right) = 10^{-6} - 10^{-1} \rightarrow \text{Stokes regime}^{10}.$$  

Height of brush is calculated from the first moment of the polymer monomer density profile$^{11}$:

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

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Results
comparison of methods


\[
l_p / L = 10, \sigma = 0.01
\]

\[
\frac{h}{L}
\]

\[
\tilde{\gamma}
\]

- LB
- BD
- SDPD Couette flow
- SDPD Poiseuille flow
Results from SDPD simulations

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

![Graph showing polymer brush height as a function of shear rate.](image)
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:**

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

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

- Hydrodynamic drag force: $F^d(s)$
- Volume exclusion force: $F^v(s)$

Boundary conditions:
- $\theta(s)|_{s=0} = 0$ at the grafting surface, and $d\theta/ds|_{s=L} = 0$ at the free end.
The effective shear force acting on the beam at position $s$:

$$F^d(s) = \int_s^L f^d(s') ds,$$

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

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

and the $y$-component

$$f_y^d(s) = f_{\perp}^d(s) \sin \theta(s) - f_{\parallel}^d(s) \cos \theta(s).$$
Shear force components:
\[ f_{\perp}^d(s) = \zeta_{\perp}(s) \eta u_x(s) \cos \theta(s) \quad \text{and} \quad f_{\parallel}^d(s) = \zeta_{\parallel}(s) \eta u_x(s) \sin \theta(s) \]

Friction coefficient from slender body theory\(^a\), piecewise approximated as a cylinder\(^b\):
\[
\begin{align*}
\zeta_{\perp} &= \frac{8\pi}{\ln(L/d)-\frac{1}{2}+\ln(2)}, \\
\zeta_{\parallel} &= \frac{4\pi}{\ln(L/d)-\frac{3}{2}+\ln(2)}.
\end{align*}
\]

Local velocity \(u_x(s)\) depend on the hydrodynamic penetration\(^c\).

---

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:

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

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

---

Discretise the beam: \( N = \lceil L/d \rceil \) spheres

Positions are given as a function of \( s \):

\[
x(s) = \int_0^s \sin \theta(s') \, ds' \quad \text{and} \quad y(s) = \int_0^s \cos \theta(s') \, ds'
\]

Assume a repulsive interaction:

\[
g_{ij} = \begin{cases} r_{ij} \leq d : & \epsilon_g \frac{k_B T}{d} \left[ (d/r_{ij})^\alpha - 1 \right] \frac{r_{ij}}{r_{ij}} \\ r_{ij} > d : & 0 \end{cases}
\]

with \( \epsilon_g \gtrsim 50 \) and \( \alpha \geq 3 \).

Force density \( f^\nu_n \) on a sphere \( n \in [0...N-1] \) in a discretized beam:

\[
f^\nu_n = \sum_j \frac{g_{nj}}{d}
\]

\[
F^\nu(s) = f^\nu_{\lfloor s/d \rfloor} \left( d \left\lfloor s/d \right\rfloor - s/d \right) + \sum_{n=\lfloor s/d \rfloor}^{N-1} f^\nu_n \, d
\]
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 \( \rightarrow F^v(s) \)
2. solve Brinkman-like equation \( \rightarrow u(s) \Rightarrow F^d(s) \)
3. Beam equation & DuFort-Frankel scheme\(^\text{15}\) \( \rightarrow \theta_n(s) \)
4. if \( \int_0^L |\theta_n - \theta_{n-1}| \, ds > tol \) : goto ① else : found final configuration ;)

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

\[ \text{overestimation of volume-exclusion term } F^v \leftarrow \text{neglected perturbation in } z \]
Results

error analysis

Figure: Relative deviation of brush height vs shear rate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>106</td>
</tr>
<tr>
<td>RMS</td>
<td>14.6%</td>
</tr>
<tr>
<td>AAD</td>
<td>9.5%</td>
</tr>
<tr>
<td>Bias</td>
<td>8.3%</td>
</tr>
</tbody>
</table>
Prediction of the response to shear flow of dense polymer brushes.
Comparison between SDPD simulation and our theoretical model: velocity profile

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

theoretical model

Prediction of flow rates in channels or tubes.
Comparison between SDPD simulation and our theoretical model:

Relative apparent viscosity

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

Prediction of app. viscosity as input for continuous methods.

\[ \frac{\eta_{app}}{\eta_0} = f(\tilde{\gamma}/(l_p/L)) \]

- SDPD, \( l_p/L = 10 \)
- theory, \( l_p/L = 10 \)
- SDPD, \( l_p/L = 100 \)
- theory, \( l_p/L = 100 \)

microfluidic devices
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: $(\Delta h)_{\text{max}} \approx d$.
- 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!

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?