Coating microchannels to improve Field-Flow Fractionation

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Normal-mode Field Flow Fractionation

Figure: Schematic of normal-mode FFF.
Normal-mode Field Flow Fractionation

Figure: Schematic of normal-mode FFF.

Fractionation

\[ \lambda \equiv \frac{k_B T}{f_W} \]
Normal-mode Field Flow Fractionation

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\[ c(\tilde{y}) = c_0 e^{-\tilde{y}/\lambda} \]

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Normal-mode Field Flow Fractionation

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\langle \mathcal{V} \rangle = \frac{\langle cv \rangle}{\langle c \rangle}
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Normal-mode Field Flow Fractionation

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Fractionation

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\[ R \equiv \frac{\langle \mathcal{V} \rangle}{\langle \mathcal{V} \rangle} \]
Steric-mode Field Flow Fractionation

Figure: Schematic of steric-mode FFF.
Steric-mode Field Flow Fractionation

Figure: Schematic of steric-mode FFF.

Excluded Region

\[ c(\tilde{y}) = \begin{cases} 
  c_0 e^{- (\tilde{y} - \tilde{r}) / \lambda} & \text{for } \tilde{r} < \tilde{y} < 1 - \tilde{r} \\
  0 & \text{otherwise.}
\end{cases} \]
Selective-mode Field Flow Fractionation

Figure: Schematic of selective-mode FFF.
Selective-mode Field Flow Fractionation

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Polymer Brush
- Free energy cost
- Hydrodynamic thickness
Selective-mode Field Flow Fractionation

Figure: Schematic of selective-mode FFF.

Polymer Brush
- Free energy cost
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Brush Model
- Alexander Brush
  - step-function model
Flow Profile

Brush Model

- Alexander Brush
  - porous: blob
  - size sets
  - permeability

Brinkman Equation

\[ \eta \nabla^2 \mathbf{v} + \frac{\eta}{\xi^2} \mathbf{v} = \nabla p \]
Flow Profile

Brush Model
- **Alexander Brush**
  - porous: blob size sets permeability
- **Brinkman Equation**
  \[ \eta \nabla^2 v + \frac{\eta}{\xi^2} v = \nabla p \]

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Modes of Approach

Compression Mode

\[ F_{\text{cmp}} = F_{\text{int}} + F_{\text{el}} \approx F_0 \left[ \left( \frac{H}{h} \right)^{\frac{1}{3\nu-1}} + \left( \frac{h}{H} \right)^{\frac{4\nu-1}{3\nu-1}} \right] \]

where \( F_0 = H/\xi \).

Figure: Two modes of approach.
Modes of Approach

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Insertion Mode

Generally,

\[ F_{\text{ins}} = \Pi(\phi)V + \gamma(\phi)A \]
Modes of Approach

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When \( r > \xi \)

\[ \frac{F_{\text{ins}}}{k_B T} \sim \left( \frac{r}{\xi} \right)^3 \left[ 1 + \frac{\xi}{r} \right] \]
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Figure: The piece-wise free energy cost creates abrupt changes in $c(\tilde{y}, \tilde{r})$ such that the concentration plumets when $r < \xi$. For $\lambda = k_B T / f w = 0.05$, $\tilde{H} = 0.1$ and $\tilde{\xi} = 0.05$. 
Retention Ratio, \( R = \langle \mathcal{V} \rangle / \langle v \rangle \)

FFF is nonmonotonic
Retention Ratio, \( R = \frac{\langle V \rangle}{\langle v \rangle} \)

- FFF is nonmonotonic
Retention Ratio, $R = \langle \mathcal{V} \rangle / \langle \mathcal{v} \rangle$

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- Brush makes $R : \tilde{r} \to 1 : 1$ over larger range

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Retention Ratio, $R = \langle \mathcal{V} \rangle / \langle v \rangle$

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- Dense brush increases resolution
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- Dense brush increases resolution
- At this size, retention is independent of field

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Multi-Particle Collision Dynamics

MPC-MD Hybrid

Ideal for $\text{Pé} \approx 1$

Graph showing the relationship between $1/R$ and $D$ with error bars and a trend line.
Multi-Particle Collision Dynamics

MPC-MD Hybrid
Ideal for \( \text{Pe} \approx 1 \)

\[ D \sim \frac{1}{R} \]

\[ \text{Coating microchannels to improve Field-Flow Fractionation} \]
Multi-Particle Collision Dynamics

MPC-MD Hybrid
Ideal for \( \text{Pé} \approx 1 \)

\( D \) vs. \( 1/R \)

\( \sigma = 0.20 \)
\( \sigma = 0.40 \)

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Conclusions

Selective Steric-mode Field Flow Fractionation

- Polymer brush alters FFF by
  - screening flow within the brush
  - enacting free energy cost to enter
- Polymer brush leads to
  - increased monotonic range
  - increased resolution
  - significantly increased resolution of solutes smaller than blobs
- Simple model to be corroborated by MPC-MD simulations
Thank you to the U. of O. Polymer Physics Group members

- Mykyta Chubynsky
- Yugou Tau
- Henk DeHaan
- David Sean
- Owen Hickey
Steric-mode FFF

Figure: Retention ratios for fixed retention parameters, $\lambda$.

Figure: Retention ratios when force varies with particle size $\lambda = \Lambda \tilde{r}^{-\alpha}$.

$$\lambda = \frac{k_B T}{f_w} = \frac{k_B T}{\mu \tilde{r}^{\alpha} w} = \Lambda \tilde{r}^{-\alpha}$$
Snug-mode FFF

Figure: Schematic of snug-mode FFF.
Snug-mode FFF

Figure: Retention ratios for fixed retention parameters, $\lambda$.

Figure: Retention ratios when force varies with particle size $\lambda = \Lambda \tilde{r}^{-\alpha}$.

Figure: Retention ratios when velocity profile average over surface area.
Snug-mode FFF

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Flow Profile

Brinkman equation:

\[ \eta \nabla^2 v + \frac{\eta}{\xi^2} \nabla v = \nabla p \]

where \( \xi \) is the hydrodynamic penetration depth which acts as the typical pore size and corresponds to the correlation length of the chains.

- **Alexander Brush - step function density**

  \[ \xi = \frac{b}{\phi \nu/(3\nu-1)} \]


- **Parabolic Brush - density falls linearly at extremity**

  \[ \xi = \frac{b}{\phi} \]

Free Energy Coefficients

\[ \frac{\Delta F}{k_B T} \sim \begin{cases} 
F_0 \left[ \left( \frac{H}{h} \right)^{1/(3\nu-1)} \left( \frac{h}{H} \right)^{(1-4\nu)/(1-3\nu)} - 1 \right] & r \gg H \\
\left( \frac{r}{\xi} \right)^3 & H \gg r \gg \xi \\
\left( \frac{r}{\xi} \right)^3 \left[ 1 + \frac{\xi}{r} \right] & r \geq \xi \\
\left( \frac{r}{\xi} \right)^{3-1/\nu} & \xi > r > \xi_T \\
\frac{r}{\xi_{id}} & \xi_T > r > b 
\end{cases} \]
Free Energy Coefficients

\[ \frac{\Delta F}{k_B T} \sim \begin{cases} F_0 \left[ \left( \frac{H}{h} \right)^{1/(3\nu-1)} + \left( \frac{h}{H} \right)^{(1-4\nu)/(1-3\nu)} - 1 \right] & r \geq H \\ \left( \frac{r}{\xi} \right)^{3} \left[ 1 + \frac{\xi}{r} \right] & \xi \leq r \leq H \\ \left( \frac{r}{\xi} \right)^{3-1/\nu} & r \leq \xi \end{cases} \]
Free Energy Coefficients

\[
\frac{\Delta F}{k_B T} = \begin{cases} 
    a_1 F_0 \left[ \left( \frac{H}{h} \right)^{1/(3\nu-1)} + \left( \frac{h}{H} \right)^{(1-4\nu)/(1-3\nu)} - 1 \right] & r \geq H \\
    a_2 \left( \frac{r}{\xi} \right)^3 \left[ 1 + \frac{\xi}{r} \right] & \xi \leq r \leq H \\
    a_3 \left( \frac{r}{\xi} \right)^{3-1/\nu} & r \leq \xi 
\end{cases}
\]
Free Energy Coefficients

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\frac{\Delta F}{k_B T} = \begin{cases} 
    a_1 F_0 \left[ \left( \frac{H}{h} \right)^{1/(3\nu - 1)} + \left( \frac{h}{H} \right)^{(1-4\nu)/(1-3\nu)} - 1 \right] & r \geq H \\
    a_2 \left( \frac{r}{\xi} \right)^3 \left[ 1 + \frac{\xi}{r} \right] & \xi \leq r \leq H \\
    a_3 \left( \frac{r}{\xi} \right)^{3-1/\nu} & r \leq \xi 
\end{cases}
\]

Recalling \( F_0 = H/\xi \). At \( r = H \), \( F_1 = F_2 \) such that

\[
a_1 = a_2 \left( \frac{H}{\xi} \right)^2 \left[ 1 + \frac{\xi}{H} \right]
\]

At \( r = \xi \), \( F_2 = F_3 \) and we see

\[
a_3 = 2a_2
\]

We choose \( a_2 = 1 \).