

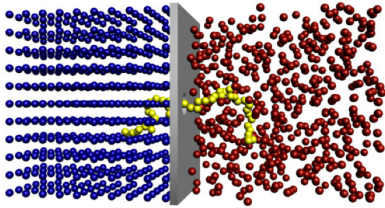
Ideal Retention Theory for μ FFF

Tyler Shendruk
Gary Slater

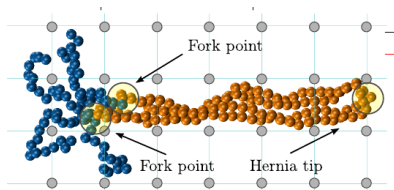
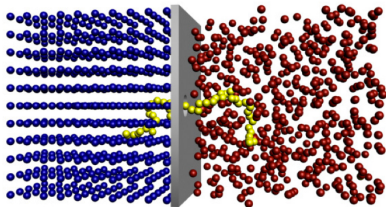
University of Ottawa

University of Manitoba, September 16 2011

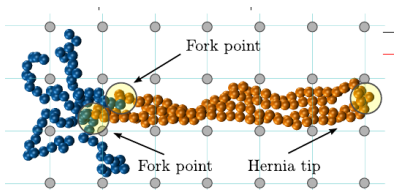
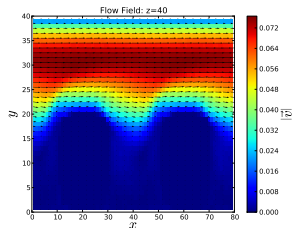
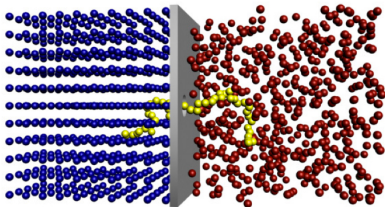
Polymer Physics at the University of Ottawa



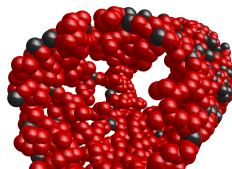
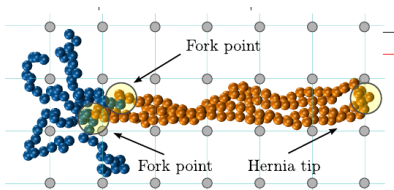
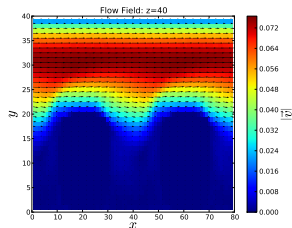
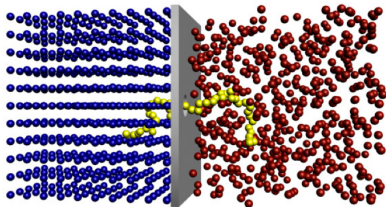
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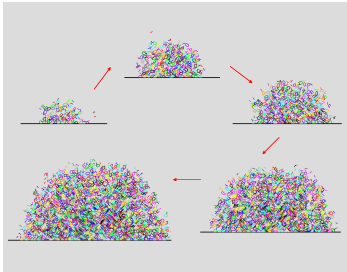
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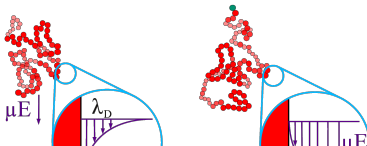
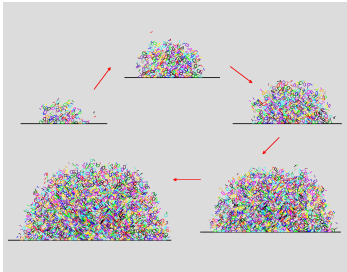
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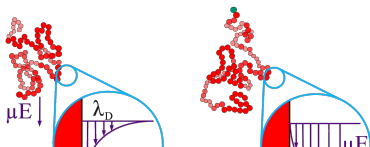
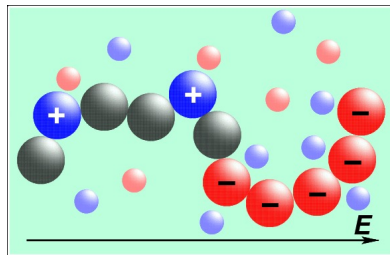
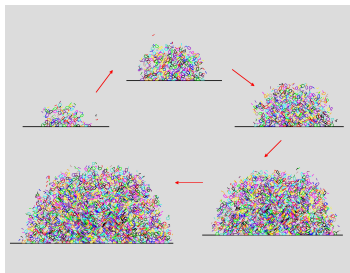
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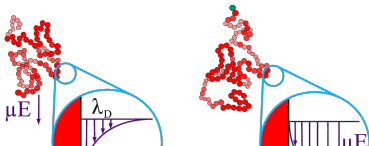
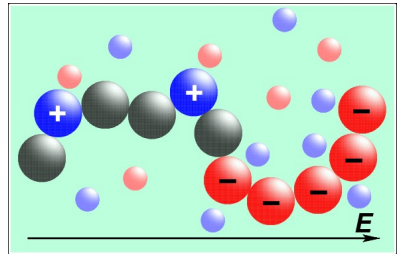
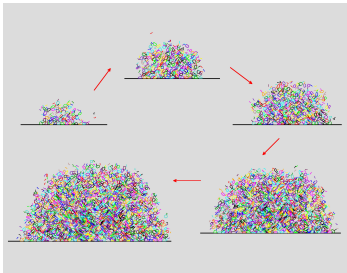
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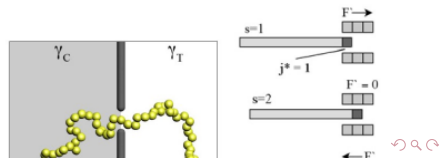
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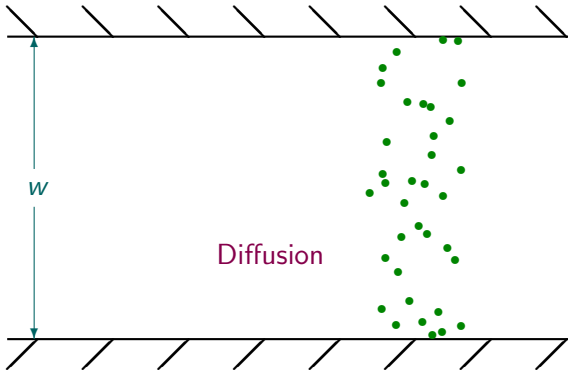


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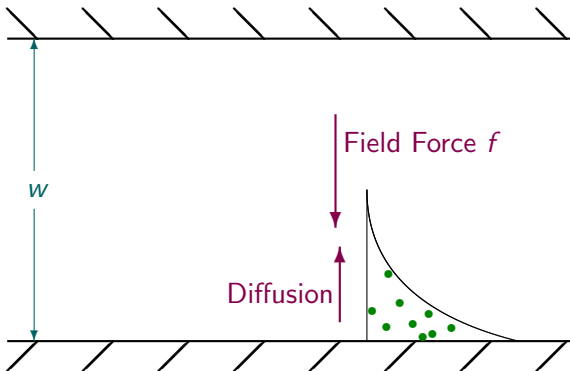


Ideal Retention Theory for μ FFF

Normal Mode



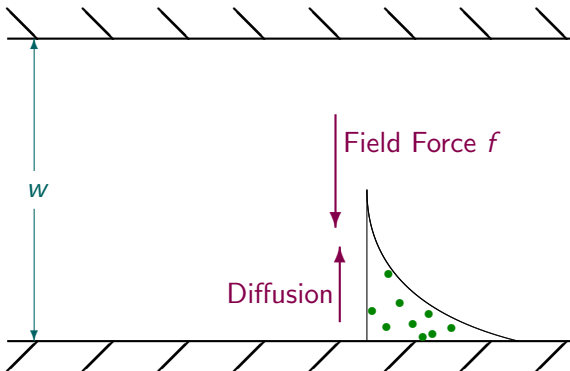
Normal Mode



Fractionation

$$\lambda \equiv \frac{k_B T}{fw}$$

Normal Mode

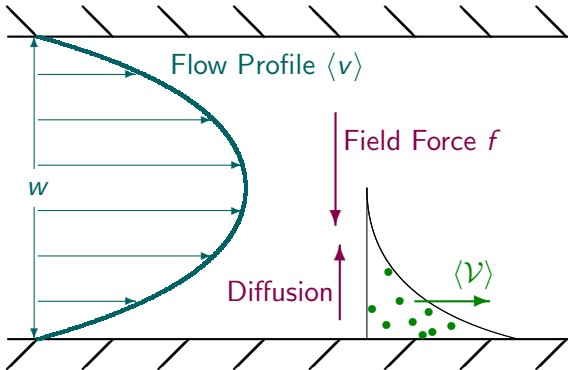


Fractionation

$$\lambda \equiv \frac{k_B T}{fw}$$

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

Normal Mode



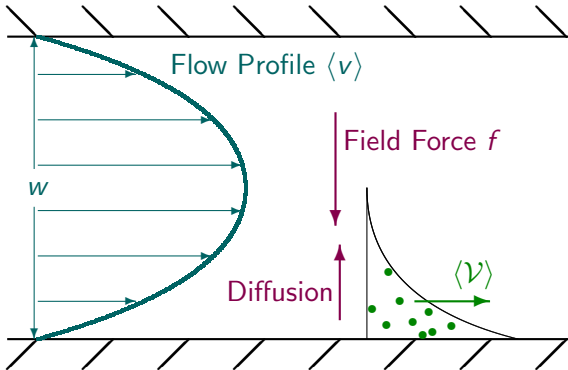
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$$\lambda \equiv \frac{k_B T}{fw}$$

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Normal Mode



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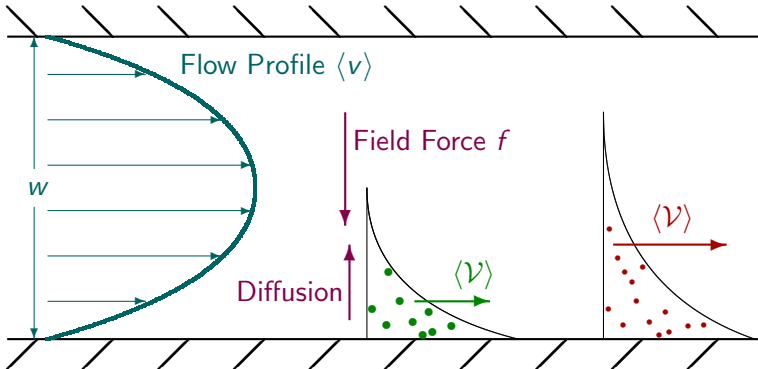
$$\lambda \equiv \frac{k_B T}{fw}$$

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

$$\langle \mathcal{V} \rangle = \frac{\langle cv \rangle}{\langle c \rangle}$$

$$R \equiv \frac{\langle \mathcal{V} \rangle}{\langle v \rangle}$$

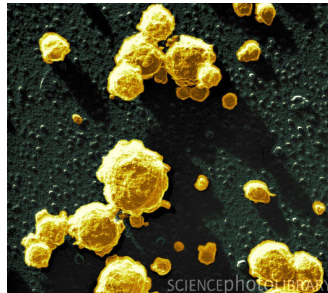
Normal Mode



Some Uses of FFF

Examples

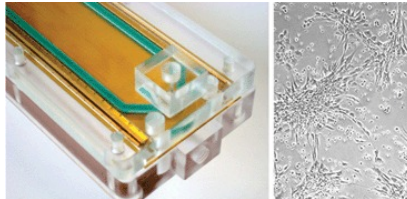
- Casein Micelles Langmuir 2010, 26(15), 12585-12591



Some Uses of FFF

Examples

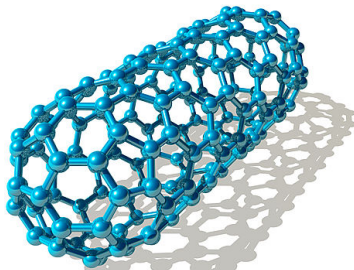
- Casein Micelles Langmuir 2010, 26(15), 12585-12591
- Stem Cells Lab Chip, 2008, 8, 1386-1393



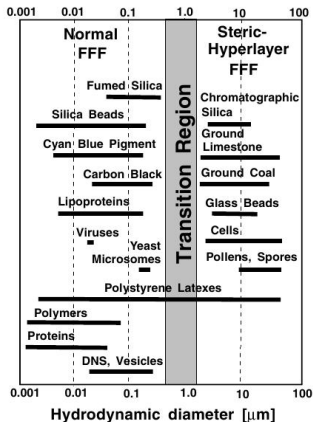
Some Uses of FFF

Examples

- Casein Micelles Langmuir 2010, 26(15), 12585-12591
- Stem Cells Lab Chip, 2008, 8, 1386-1393
- Nanotubes Anal. Chem., 2008, 80 (7), 2514-2523



Some Uses of FFF



Adv. Poly. Sci., 2000, 157, 67-187

Steric Mode

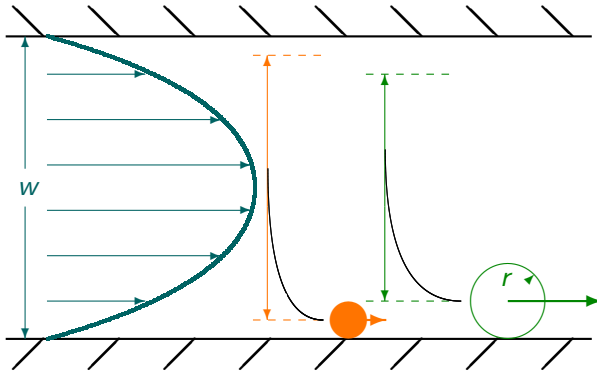


Figure: Schematic of steric-mode FFF.

Steric Mode

Retention Ratio

The new boundaries on the integrals give

$$R = \frac{\langle cv \rangle}{\langle c \rangle \langle v \rangle}$$

$$= 6\lambda (1 - 2\tilde{r}) \mathcal{L} \left(\frac{1 - 2\tilde{r}}{2\lambda} \right) + \mathcal{F}_p$$

where

Steric Mode

Retention Ratio

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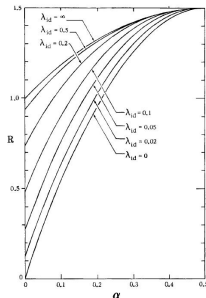
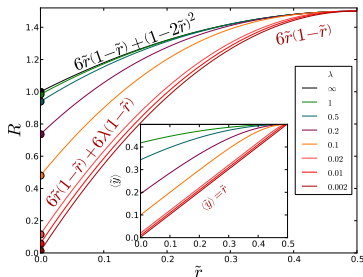
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where

Steric Mode

Even if the force is held constant for all particles sizes there is still separation because steric effects move larger particles closer to the centre than smaller particles.



Scaling

Before

Had variation of R as function of $\tilde{r}$ for fixed λ *i.e.* fixed force f .

Scaling

Before

Had variation of R as function of $\tilde{r}$ for fixed λ i.e. fixed force f .

Closer to Reality

Force will change with particle size. For instance, in sedimentation the weight goes as the volume of the particle or $\lambda \propto r^{-3}$. To be general, let force scale as α such that the retention parameter is

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

where μ is the “strength” / coefficient of the force.

Scaling

FFF-Method	f	α	Λ
Sedimentation	$\frac{4\pi}{3} g \Delta \rho r^3$	3	$\frac{3}{4\pi} \frac{k_B T}{g \Delta \rho w^4}$
Flow	$6\pi\eta \frac{w \dot{V}_c}{V_0} r$	1	$\frac{k_B T}{6\pi\eta w^3} \frac{V_0}{\dot{V}_c}$
Thermal	$6\pi\eta \frac{D_T \Delta T}{w} r$	1	$\frac{k_B T}{6\pi w \eta D_T \Delta T}$
Magnetic	$\frac{\Delta \mu H}{6} \frac{dH}{dy} r^3$	3	$\frac{6 k_B T}{w^4 \Delta \mu H} \left(\frac{dH}{dy} \right)^{-1}$
Electrical	$6\pi\eta \mu_e E r$	1	$\frac{k_B T}{6\pi\eta \mu_e E w}$

Retention Ratio

Retention Ratio as an Explicit Function of Size

$$R(\tilde{r}, \Lambda) = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L}\left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda}\right) + \mathcal{F}_p(\tilde{r})$$

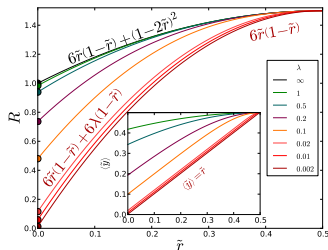


Figure: Fixed λ (equivalent to $\alpha = 0$).

Retention Ratio

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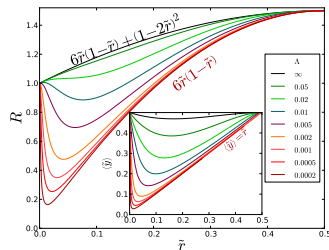
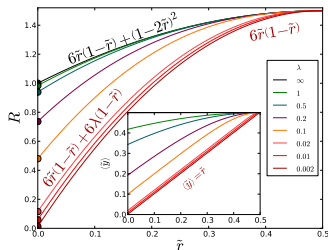


Figure: Fixed Λ (equivalent to $\alpha = 0$).

Figure: $\alpha = 1$.

Nonmonotonic

Moral of the Story:

Non-monotonic is bad

- One elution time, two particle sizes.

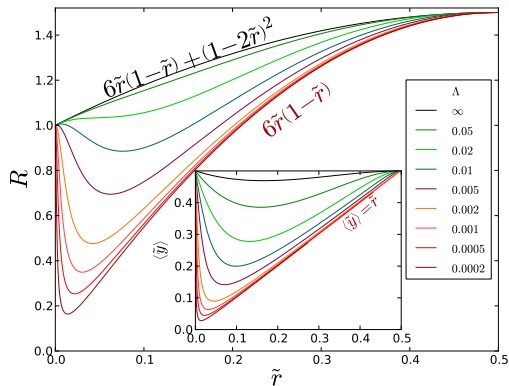


Figure: $\Lambda_c = 1.90 \times 10^{-2}$ for $\alpha = 1$.

Nonmonotonic

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But why is it nonmonotonic?

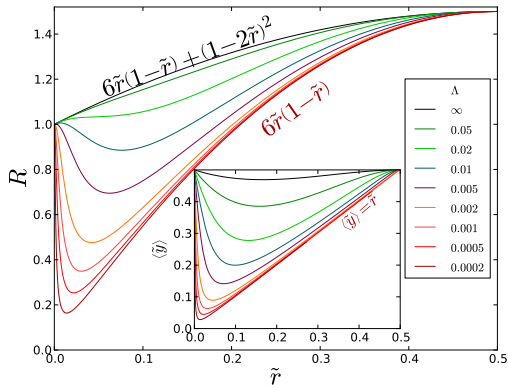


Figure: $\Lambda_c = 1.90 \times 10^{-2}$ for $\alpha = 1$.

Elution Order

Statements:

Recall $R = \langle \mathcal{V} \rangle / \langle v \rangle = t_0/t_R$

normal-mode smaller particles elute before larger particles because the force increases with size.

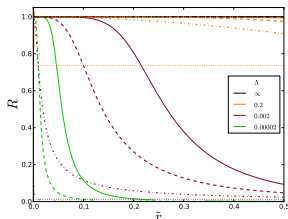


Figure: Normal $\alpha = 1, 2, 3$

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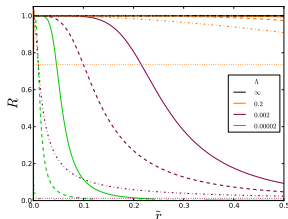


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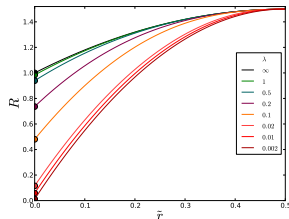


Figure: Steric Mode, fixed λ

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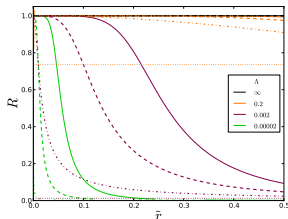


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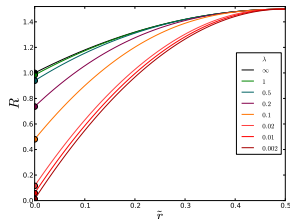


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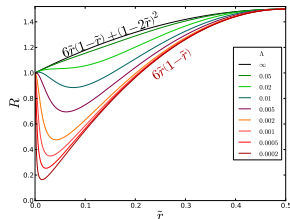


Figure: Steric Mode, $\alpha = 1$

Normal-Steric Transition

Order

Normal Mode when $R' < 0$ smaller particles elute before larger.

Steric Mode when $R' > 0$ larger particles elute earlier than smaller.

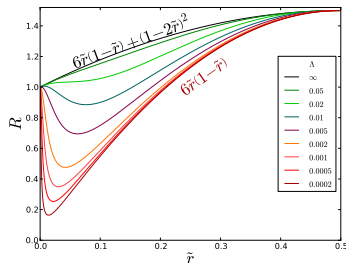


Figure: $\alpha = 1$

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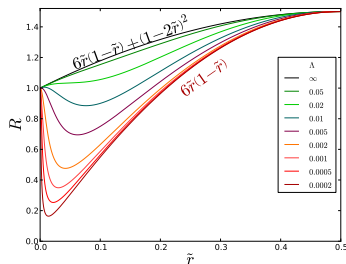


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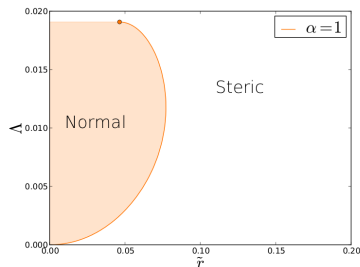


Figure: Trace the minimum of the retention ratio.

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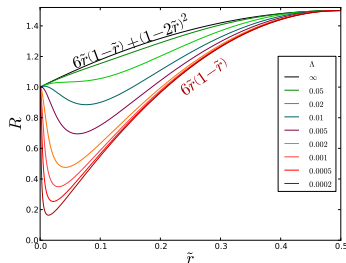


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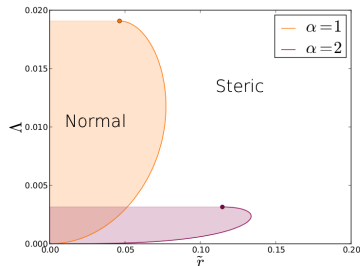


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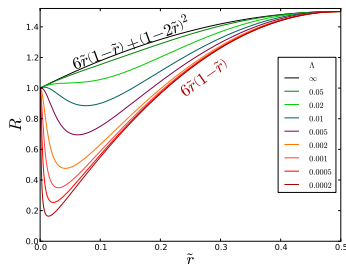


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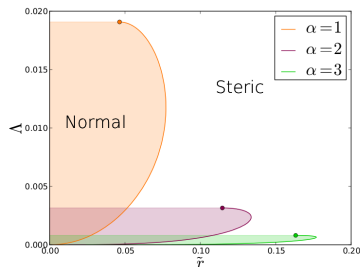


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Hydrodynamic Chromatography-mode

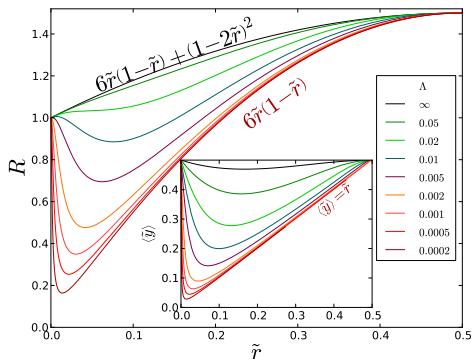


Figure: For $\alpha = 1$ and mid-range Λ , R shows a steric-mode-like elution order at **tiny** $\tilde{r}$.

Hydrodynamic Chromatography-mode

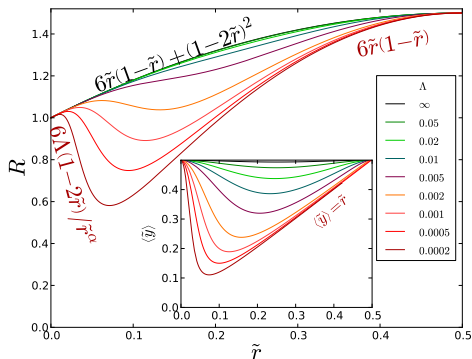
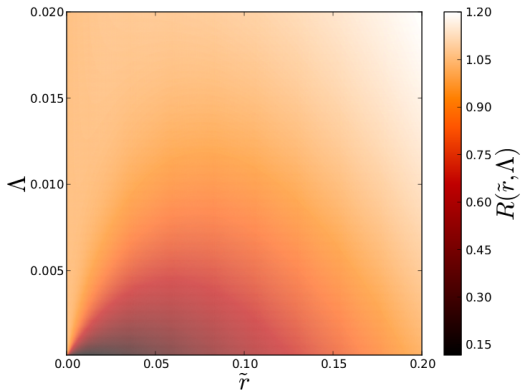
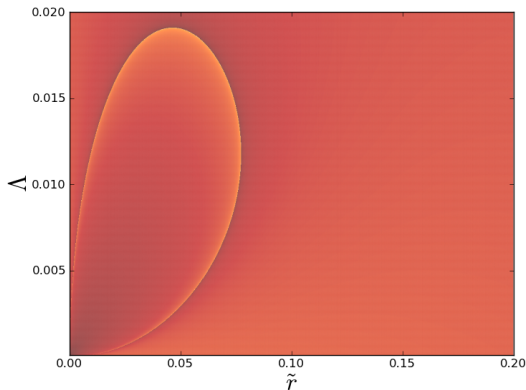


Figure: $\alpha = 2$ illustrates the HC mode better.

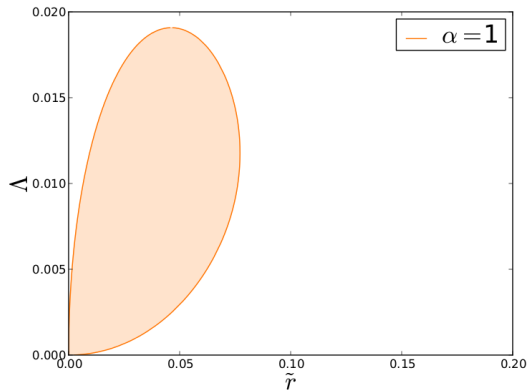
Mode-Space



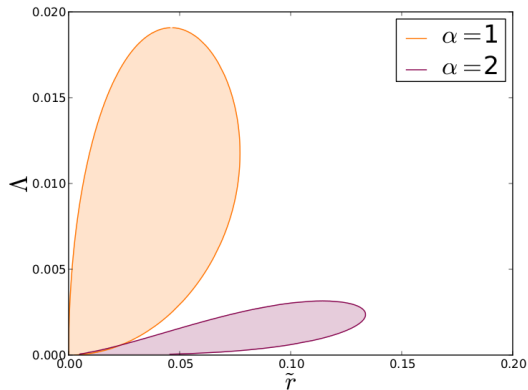
Mode-Space



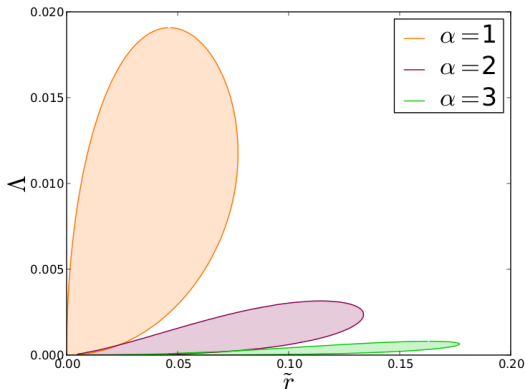
Mode-Space



Mode-Space



Mode-Space



Normal-mode operation enclosed by steric-mode. For $\alpha = 3$, normal-mode can extend as far as 18% the channel height.

Stress over Surface Area

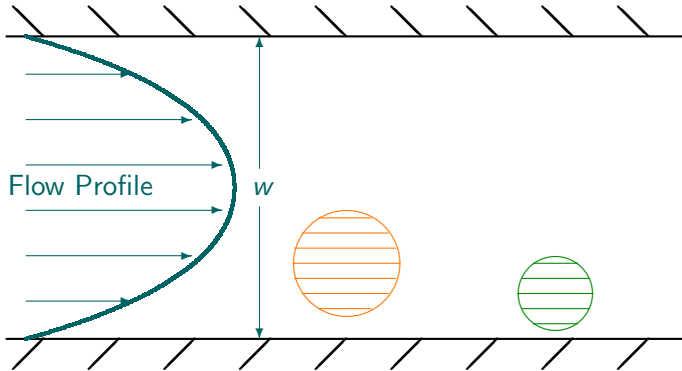


Figure: Schematic of surface area integration of stress on particle.

$$R = \frac{\langle \mathcal{V} \rangle}{\langle v \rangle} = \frac{\langle c \mathcal{V} \rangle}{\langle c \rangle \langle v \rangle} = \frac{1}{\langle v \rangle} \frac{\int_0^w c(y) \mathcal{V}(y) dy}{\int_0^w c(y) dy}$$

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Finite-Size Effects

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but $\mathcal{V}(\tilde{y}) \neq v(\tilde{y})$

Faxén's Law

$$\begin{aligned} \nu(\tilde{y}) &= \left(1 + \frac{\tilde{r}^2}{6} \nabla^2\right) \nu(\tilde{y}) \\ &= 6 \langle \nu \rangle \left[\tilde{y} - \tilde{y}^2 - \frac{\tilde{r}^2}{3} \right] \end{aligned}$$

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Retention Ratio

$$R = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_f(\tilde{r})$$

where $\mathcal{F}_f(r, w) = 6\tilde{r} \left(1 - \frac{4}{3}\tilde{r}\right)$

Comparison

Steric Mode

$$R = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_p$$

$$\mathcal{F}_p = 6\tilde{r} (1 - \tilde{r})$$

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Faxén's Mode

$$R = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_f$$

$$\mathcal{F}_f = 6\tilde{r} \left(1 - \frac{4}{3}\tilde{r} \right)$$

Comparison

Steric Mode

$$R = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_p$$

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Faxén's Mode

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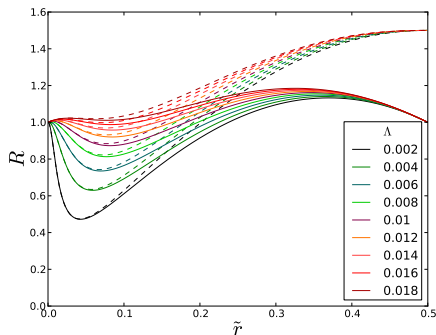
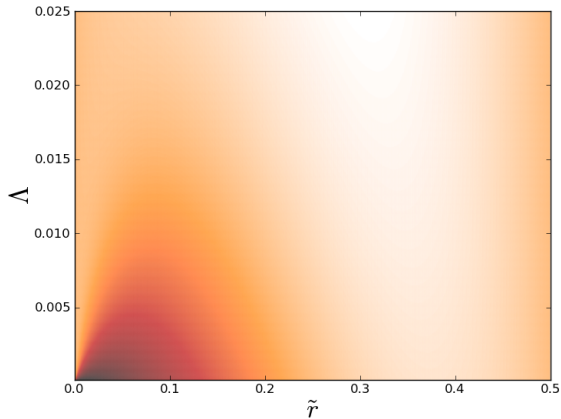
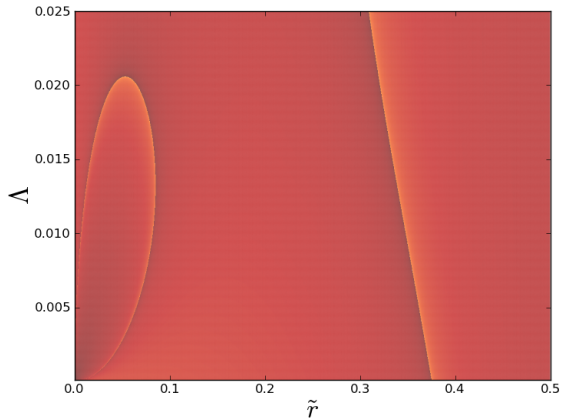


Figure: Retention ratios for $\alpha = 1$.

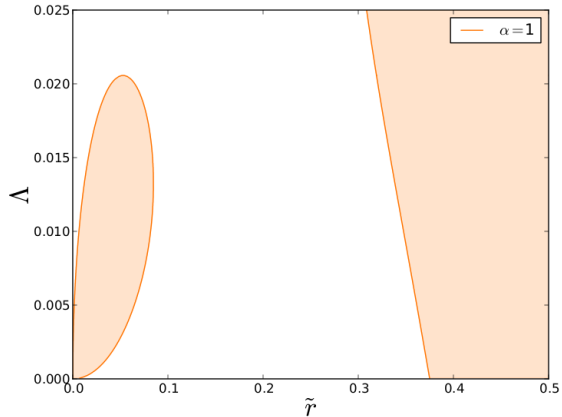
Mode-Map



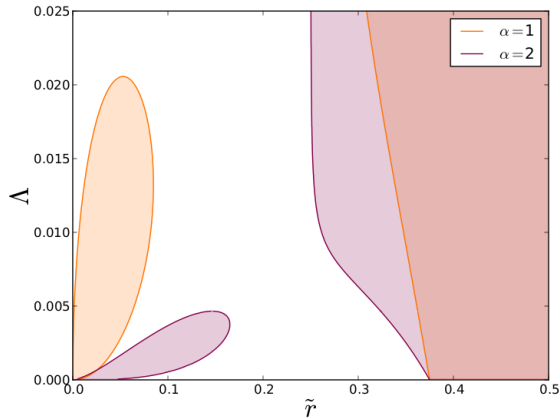
Mode-Map



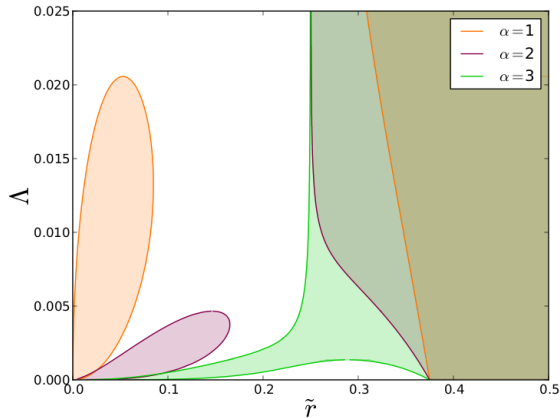
Mode-Map



Mode-Map



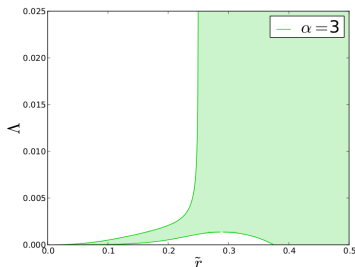
Mode-Map



Map (experimentally relevant)

Retention Parameter

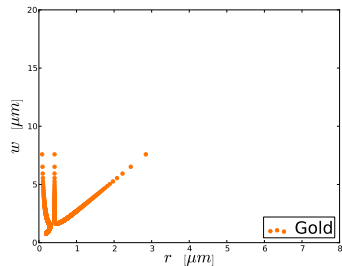
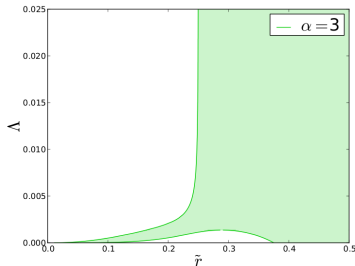
FFF-Method	Sedimentation	Flow	Thermal	Magnetic	Electrical
Λ	$\frac{3}{4\pi} \frac{k_B T}{g \Delta \rho w^4}$	$\frac{k_B T}{6\pi \eta w^3} \frac{V_0}{V_c}$	$\frac{k_B T}{6\pi w \eta D_T \Delta T}$	$\frac{6k_B T}{w^4 \Delta \mu H} \left(\frac{dH}{dy} \right)^{-1}$	$\frac{k_B T}{6\pi \eta \mu_e E w}$



Map (experimentally relevant)

Retention Parameter

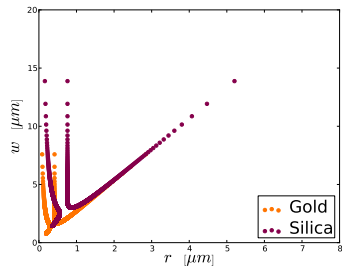
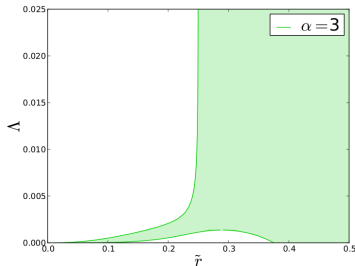
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Retention Parameter

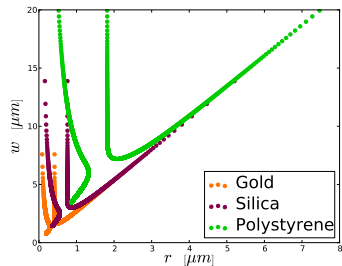
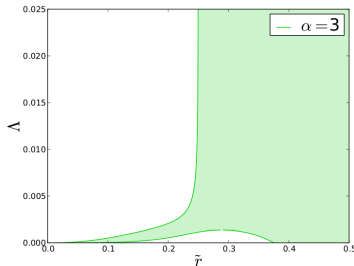
FFF-Method	Sedimentation	Flow	Thermal	Magnetic	Electrical
Λ	$\frac{3}{4\pi} \frac{k_B T}{g \Delta \rho w^4}$	$\frac{k_B T}{6\pi \eta w^3} \frac{V_0}{V_c}$	$\frac{k_B T}{6\pi w \eta D_T \Delta T}$	$\frac{6k_B T}{w^4 \Delta \mu H} \left(\frac{dH}{dy} \right)^{-1}$	$\frac{k_B T}{6\pi \eta \mu_e E w}$



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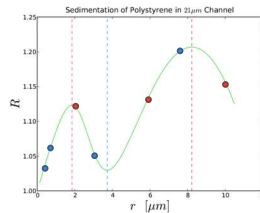
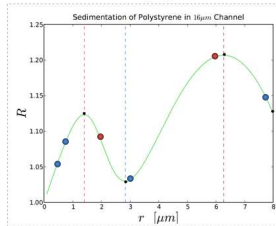
Retention Parameter

FFF-Method	Sedimentation	Flow	Thermal	Magnetic	Electrical
Λ	$\frac{3}{4\pi} \frac{k_B T}{g \Delta \rho w^4}$	$\frac{k_B T}{6\pi \eta w^3} \frac{V_0}{V_c}$	$\frac{k_B T}{6\pi w \eta D_T \Delta T}$	$\frac{6k_B T}{w^4 \Delta \mu H} \left(\frac{dH}{dy} \right)^{-1}$	$\frac{k_B T}{6\pi \eta \mu_e E w}$



Our Choices

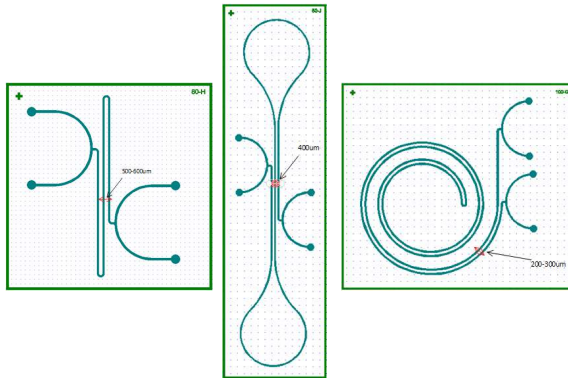
Where Particle Sizes are found on the Retention Ratio Curve



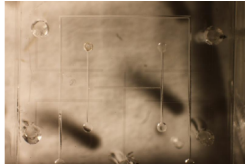
- Particle Sizes we have (R (μm)= 0.49, 0.76, 3.01, 7.75)
- Particle Sizes we are ordering (R (μm)= 2.0, 6.0, 10.0)

Microfluidic Devices

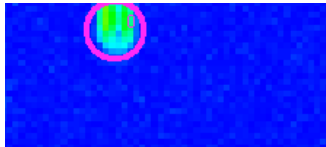
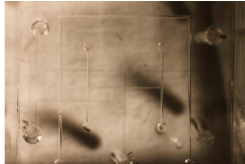
Mask Designs



Video Microscopy



Video Microscopy

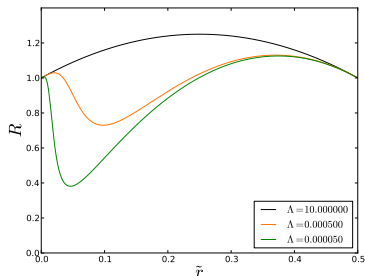


Approximations

$$R = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_f = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \left[\coth \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) - \frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right] + \mathcal{F}_f$$

$$\mathcal{F}_f = 6\tilde{r} \left(1 - \frac{4}{3}\tilde{r} \right)$$

Limits



Approximations

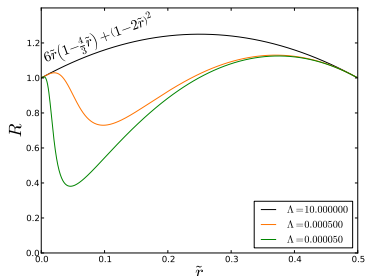
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Limits

● $\tilde{r} \rightarrow 0$

$$R \approx \mathcal{F}_f + (1 - 2\tilde{r})^2$$



Approximations

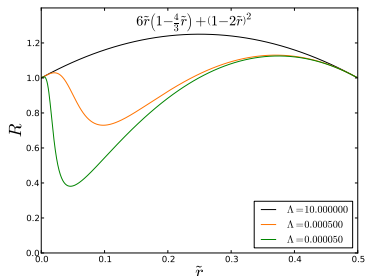
$$R = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_f = \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \left[\coth \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) - \frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right] + \mathcal{F}_f$$

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• $\tilde{r} \rightarrow 0$ $R \approx \mathcal{F}_f + (1 - 2\tilde{r})^2$

• $\Lambda \gg 1$ $R \approx \mathcal{F}_f + (1 - 2\tilde{r})^2$



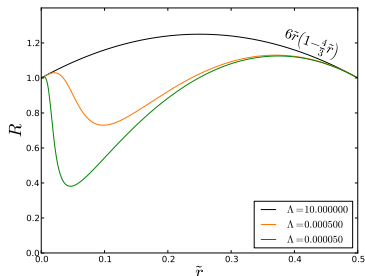
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- $\tilde{r} \rightarrow 1/2$ $R \approx \mathcal{F}_f + (1 - 2\tilde{r})^2$



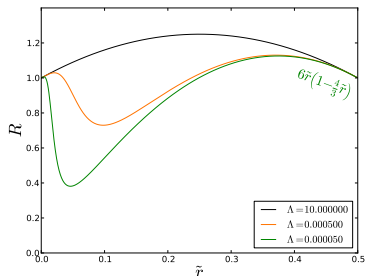
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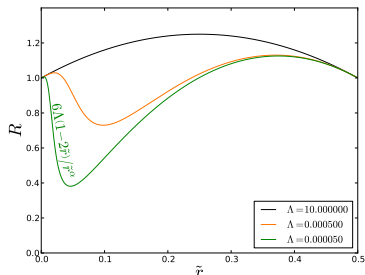
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- $\Lambda \ll 1$ $R \approx \mathcal{F}_f + \frac{6\Lambda}{\tilde{r}^\alpha} \left(1 - 2\tilde{r} - \frac{2\Lambda}{\tilde{r}^\alpha} \right)$



Quadratic Approximations of Transition

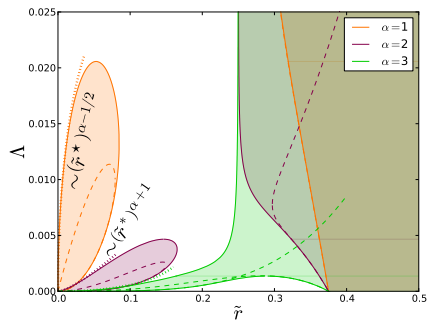
$\Lambda \ll 1$ ($\tilde{r}^*$ dashed)

$$\frac{\partial R}{\partial \tilde{r}} \approx 6 \left[a + b\Lambda + c\Lambda^2 \right]$$

$$a \equiv 1 - \frac{8}{3}\tilde{r}$$

$$b \equiv \frac{2\alpha\tilde{r} - 2\tilde{r} - \alpha}{\tilde{r}^{\alpha+1}}$$

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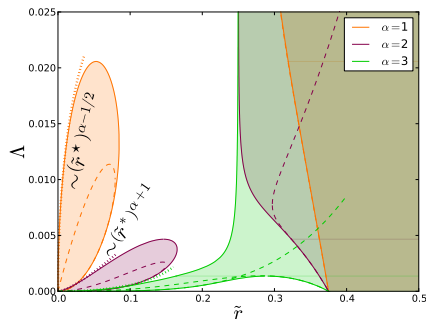
Quadratic Approximations of Transition

$\tilde{r} \ll 1$ ($\tilde{r}^*$ dotted)

$$\frac{\partial R}{\partial \tilde{r}} = A + \frac{B}{\Lambda^2} + \mathcal{O}(\tilde{r}^{2\alpha+2})$$

$$A \equiv 2 - 8\tilde{r}$$

$$B \equiv \frac{1}{5} \left[-\frac{\alpha}{6} \tilde{r}^{2\alpha-1} + \frac{2(2\alpha+1)}{3} \tilde{r}^{2\alpha} - 4(\alpha+1) \tilde{r}^{2\alpha+1} \right].$$



Conclusion

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 - To be experimentally verified
 - Neglects HI with walls
 - No hyperlayer-mode FFF
 - No perturbation to the flow field by the particle

Thank you,



- Michel Godin
- Andrew Todd
- Christian Gigault
- Mykyta Chubynsky
- Yu-guo Tao
- Henk deHaan
- David Sean
- Owen Hickey

Expansions

Retention Ratio

$$\begin{aligned}
 R &= \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \mathcal{L} \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) + \mathcal{F}_f \\
 &= \frac{6\Lambda}{\tilde{r}^\alpha} [1 - 2\tilde{r}] \left[\coth \left(\frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right) - \frac{[1 - 2\tilde{r}] \tilde{r}^\alpha}{2\Lambda} \right] + 6\tilde{r} \left(1 - \frac{4}{3}\tilde{r} \right)
 \end{aligned}$$

Expansions

$$\begin{aligned}
 \coth(x) &\approx \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \dots \\
 \coth(x) &= \frac{e^{2x} + 1}{e^{2x} - 1} \approx (1 + e^{2x}) (1 + e^{-2x} + e^{-4x} \dots) \\
 &\approx 1
 \end{aligned}$$

Retention Ratio Derivative

$$\begin{aligned} \frac{\partial R}{\partial \tilde{r}} = & \left(-\frac{6\alpha\Lambda}{\tilde{r}^{\alpha+1}} \right) \left\{ \coth \left([1 - 2\tilde{r}] \frac{\tilde{r}^{\alpha}}{2\Lambda} \right) (1 - 2\tilde{r}) - \frac{2\Lambda}{\tilde{r}^{\alpha}} + \left(1 - \frac{4}{3}\tilde{r} \right) \frac{\tilde{r}^{\alpha+1}}{\Lambda} \right\} \\ & + \left[\left\{ 1 - \coth^2 \left([1 - 2\tilde{r}] \frac{\tilde{r}^{\alpha}}{2\Lambda} \right) \right\} \left([1 - 2\tilde{r}] \frac{\alpha \tilde{r}^{\alpha}}{2\Lambda \tilde{r}} - \frac{\tilde{r}^{\alpha}}{\Lambda} \right) [1 - 2\tilde{r}] \right. \\ & \left. - 2 \coth \left([1 - 2\tilde{r}] \frac{\tilde{r}^{\alpha}}{2\Lambda} \right) + \frac{2\alpha\Lambda}{\tilde{r}^{\alpha+1}} + [1 + \alpha] \left(1 - \frac{4}{3}\tilde{r} \right) \frac{\tilde{r}^{\alpha}}{\Lambda} - \frac{4}{3} \frac{\tilde{r}^{\alpha+1}}{\Lambda} \right] \frac{6\Lambda}{\tilde{r}^{\alpha}} \end{aligned}$$

Approximations of Derivative

$$\Lambda \ll 1$$

$$\frac{\partial R}{\partial \tilde{r}} \approx 6 \left[a + b\Lambda + c\Lambda^2 \right]$$

$$a \equiv 1 - \frac{8}{3}\tilde{r}, \quad b \equiv \frac{2\alpha\tilde{r} - 2\tilde{r} - \alpha}{\tilde{r}^{\alpha+1}}, \quad c \equiv \frac{4\alpha}{\tilde{r}^{2\alpha+1}},$$

$$\tilde{r} \ll 1$$

$$\frac{\partial R}{\partial \tilde{r}} = A + \frac{B}{\Lambda^2} + \mathcal{O}(\tilde{r}^{2\alpha+2})$$

$$A \equiv 2 - 8\tilde{r},$$

$$B \equiv \frac{1}{5} \left[-\frac{\alpha}{6} \tilde{r}^{2\alpha-1} + \frac{2(2\alpha+1)}{3} \tilde{r}^{2\alpha} - 4(\alpha+1) \tilde{r}^{2\alpha+1} \right].$$

Plate Height and Resolution

$$H = \frac{D_{\text{eff}}}{R \langle v \rangle}$$

$$= \frac{D_{\text{mol}}}{R \langle v \rangle} \left[1 + \chi \frac{R}{2} \left(\frac{\langle v \rangle w}{D_{\text{mol}}} \right)^2 \right]$$

$$\chi \propto \Lambda^3 r^{3\alpha}$$

$$D_{\text{mol}} \propto r$$

$$R_S = \frac{1}{2(H_1 + H_2)} \left(\frac{1}{\langle v_2 \rangle} - \frac{1}{\langle v_1 \rangle} \right)$$