Faxén Mode: Field Flow Fractionation

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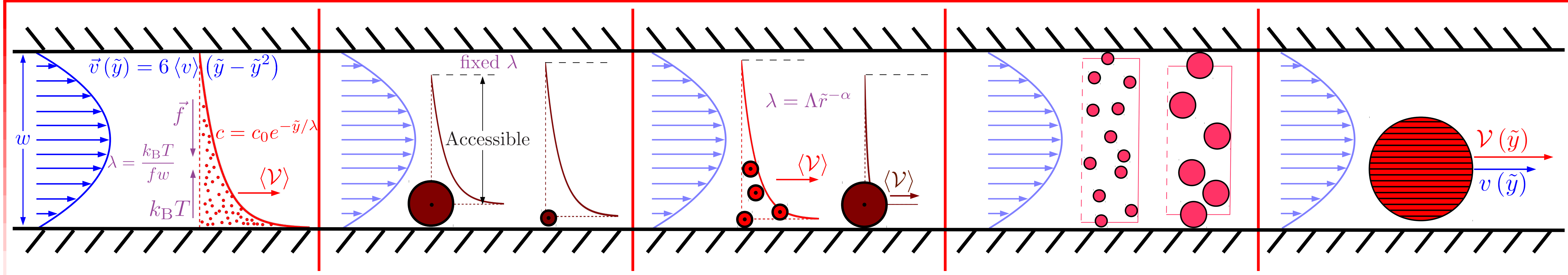
Field Flow Fractionation Schematics



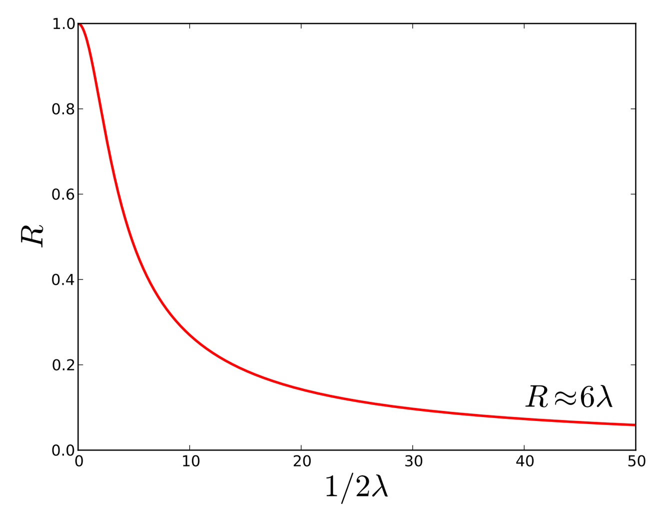
Normal-Mode FFF

- An ensemble of **point-like** solute particles in a channel of height w $(= 1)$ is subject to a force f and thermal noise,

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

- The resulting concentration gradient $c(\tilde{y})$ is pushed by a parabolic flow profile $\vec{v}(\tilde{y})$
- The solute moves with an average velocity $\langle \mathcal{V} \rangle$, which normalized by solvent velocity is $R = \langle \mathcal{V} \rangle / \langle v \rangle = \langle cv \rangle / \langle c \rangle \langle v \rangle$ [1]

$$R = \frac{\langle \mathcal{V} \rangle}{\langle v \rangle} = 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right] = 6\lambda \mathcal{L}\left(\frac{1}{2\lambda}\right)$$



Strong Force Limit If $\lambda \ll 1$ then

$$R \approx 6\lambda$$

Elution Order Smaller particles elute before larger particles whenever force is an implicit function of particle size

Conclusion Ideal retention theory for normal-mode FFF works well for small particles subject to a relatively strong force

Steric-Mode FFF

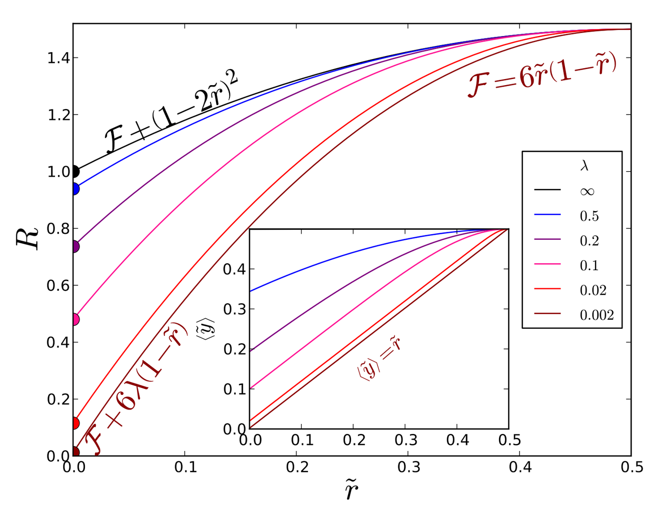
- Strong forces push the particles right against the wall. Traditionally the analysis holds λ fixed for all sizes [2, 3]

$$\lambda \approx \text{constant}$$

- If **finite sized particles** (radius $\tilde{r}$) are in contact with the wall, there is steric repulsion
- Only a fraction $1 - 2\tilde{r}$ of the channel is accessible to finite particles

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

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



Strong Force Limit If $\lambda \ll 1$ then

$$R \approx \mathcal{F} + 6\lambda(1 - \tilde{r}) - 12\lambda^2$$

Elution Order Larger particles see a faster flow profile and elute before smaller particles [4]

Conclusion Steric-mode retention theory describes the elution of large particles but two separate theories are needed one for normal-mode and a second for steric-mode

Transition

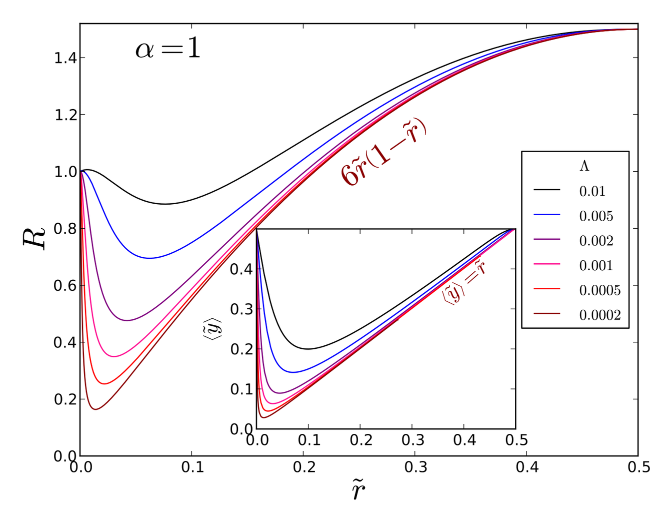
- In reality, the force isn't fixed. It **varies with size**. To replace the implicit size dependence and be completely explicit let

$$\lambda = \Lambda \tilde{r}^{-\alpha}$$

- The scaling exponent α describes the nature of the force: in a gravitational field f increases with volume so $\alpha = 3$; in a cross-flow f goes with drag so $\alpha = 1$

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

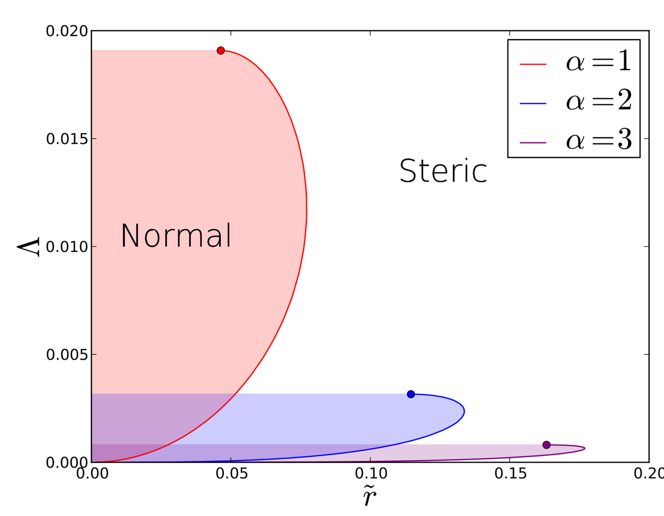
$$\mathcal{F} = \textbf{unchanged} = 6\tilde{r}(1 - \tilde{r})$$



Approximation If $\Lambda \ll 1$ then

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

Elution Order R is non-monotonic. Small, light particles elute before larger ones but large, heavy particles elute before smaller ones



Conclusion By explicitly taking into account particle size, ideal retention theory predicts the transition from normal- to steric-mode

HC-Mode FFF

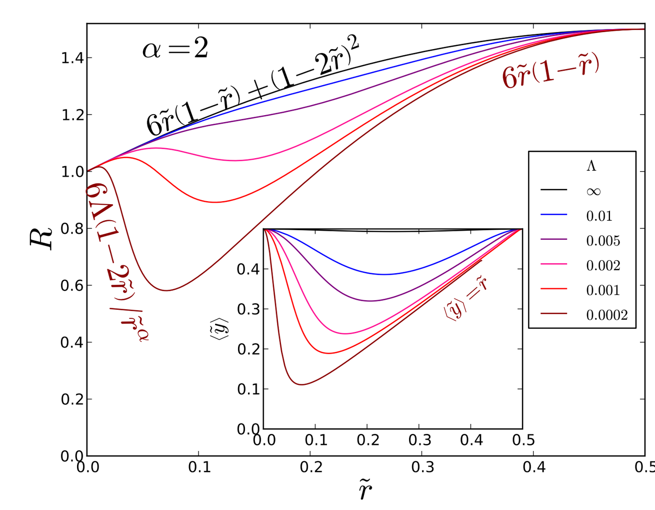
- If $f = 0$ then c is homogeneous and the excluded region leads to separation
- In a weak field, the excluded region dominates

$$\Lambda \gg 1$$

- This is the **hydrodynamic chromatography** (HC) limit of FFF
- FFF retention theory automatically includes HC **if** size is included by setting $\lambda = \Lambda \tilde{r}^{-\alpha}$

$$R = \textbf{unchanged}$$

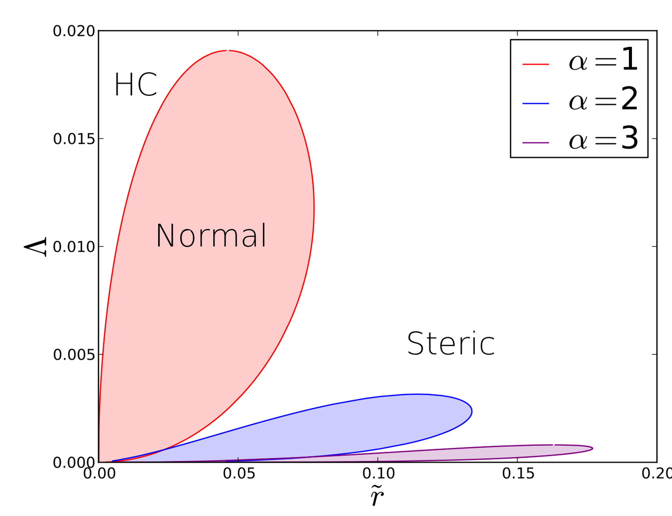
$$\mathcal{F} = \textbf{unchanged} = 6\tilde{r}(1 - \tilde{r})$$



Approximation If $\Lambda \gg 1$ then

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

Elution Order There always exists a regime of the tiniest sizes when thermal energy dominates over potential energy and FFF operates as HC



Conclusion Normal-mode FFF exists as a lobe below a critical Λ_c surrounded by steric-mode FFF and the hydrodynamic chromatography limit

Faxén-Mode FFF

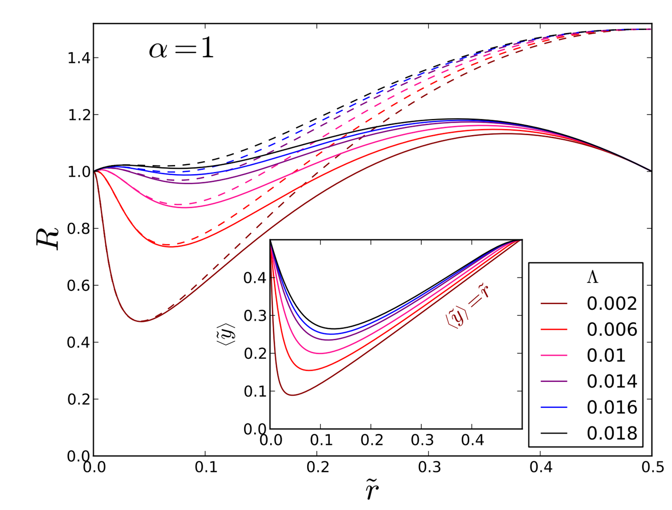
- We included finite size with the wall but retained $\mathcal{V}(\tilde{y}) = v(\tilde{y})$. We improve this by using **Faxén's Law** [5]

$$\mathcal{V}(\tilde{y}) = \left(1 + \frac{\tilde{r}^2}{6}\nabla^2\right) v(\tilde{y})$$

- This is the result of integrating fluid stress over the particle's surface area
- Once again the average solute velocity $\langle \mathcal{V} \rangle = \langle c\mathcal{V} \rangle / \langle c \rangle$ can be found

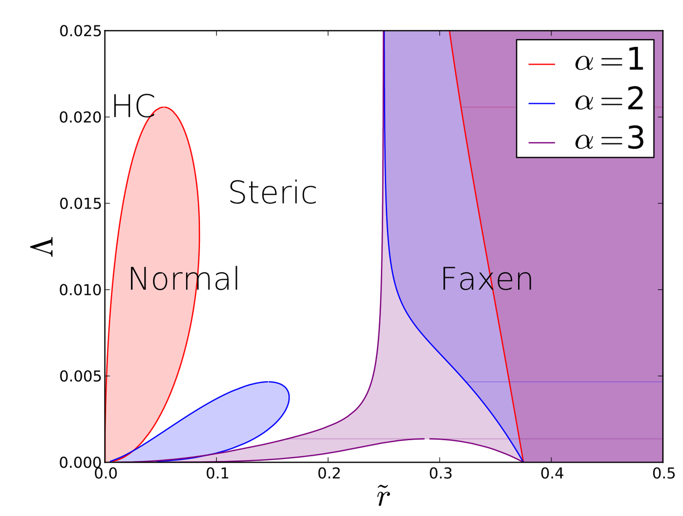
$$R = \textbf{unchanged}$$

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



Approximation The limits remain the same as long as one substitutes in the improved form of $\mathcal{F}$

Elution Order A 4th FFF regime emerges (Faxén-mode). Particles as large as the channel reside at the centre but sample the slow flow near the wall.



Conclusion The transition to Faxén-mode FFF exists for the largest particles. When $\alpha < 3$ normal-mode is distinct from Faxén-mode. When $\alpha < 3$ normal and Faxén-mode merge

Conclusion

The miniaturization of FFF apparatii is a tantalizing prospect for size separation in microfluidic chips. However, traditional retention theories deal with either point-like particles or hard particles in a field that does not depend on particle size. The theory for point-like particles describes normal-mode FFF, in which smaller particles elute before larger particles. On the other hand, the theory for hard particles gives the retention for steric-mode FFF in which larger particles elute before smaller particles. These theories implicitly assume an unspecified transition from normal-mode for small solutes to steric-mode operation for large solutes.

We extended the analysis to explicitly account for particle size and used Faxén's Law to better estimate the sample velocity. By doing so, we arrived at a retention theory that encompasses not only both normal- and steric-mode but also predicts two additional operational modes. At the tiniest particle sizes the external force must go to zero and so we found the hydrodynamic chromatography-limit of FFF below a critical particle size. At the other extreme, when the largest particle sizes approaches the height of the channel, a large portion of the particles' surfaces must sample the slow moving velocity near the walls. The retention time can not decrease with particle size indefinably and so there is a transition to a fourth FFF operational mode called Faxén-mode FFF. As FFF is added to microfluidic devices, the transitions between the four modes of operation become relevant and may have a significant impact on the ability to identify size based on retention time.

References

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[2] J. Giddings, "Displacement and dispersion of particles of finite size in flow channels with lateral forces. field-flow fractionation and hydrodynamic chromatography," *Separation Science and Technology*, vol. 13, no. 3, pp. 241–254, 1978.

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[4] H. Cölfen and M. Antonietti, *New Developments in Polymer Analytics I*, vol. 150 of *Advances in Polymer Science*, ch. Field-Flow Fractionation Techniques for Polymer and Colloid Analysis, pp. 67–187. Springer Berlin / Heidelberg, 2000.

[5] S. Kim and S. Karrila, *Microhydrodynamics: Principles and Selected Applications*. Dover, 2005.