FFF VERIFICATION OF FAXEN MODE

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ABSTRACT

Unified ideal retention theory for Field-Flow Fractionation (FFF) in microfluidic chips predicts the existence of an operational-mode, termed Faxén-mode FFF. When particle sizes approach the channel height, their velocity is poorly estimated by assuming that they move at the same speed as the fluid at their centre of mass. It is better estimated by utilizing Faxén's Law. The resulting correction to the retention theory produces the transition from Steric-mode FFF to Faxén-mode, which is predicted to have the same elution order as normal-mode FFF. We experimentally verify this prediction for sedimentation-FFF of polystyrene microspheres eluting in 21μm microchannels using video microscopy and demonstrate that the range of some of the FFF operational-modes (hydrodynamic chromatography, normal and steric-mode) is well approximated by unified ideal retention theory but that the extent of Faxén-mode is severly under-estimated in low flow rates. Simulations using multi-particle collision dynamics (MPCD) explain a number of the differences between experiment and theory; namely that friction and wall interaction forces become significant for large particles and that solid particles have perturbative effect on the local flow near the surface of solute particles.

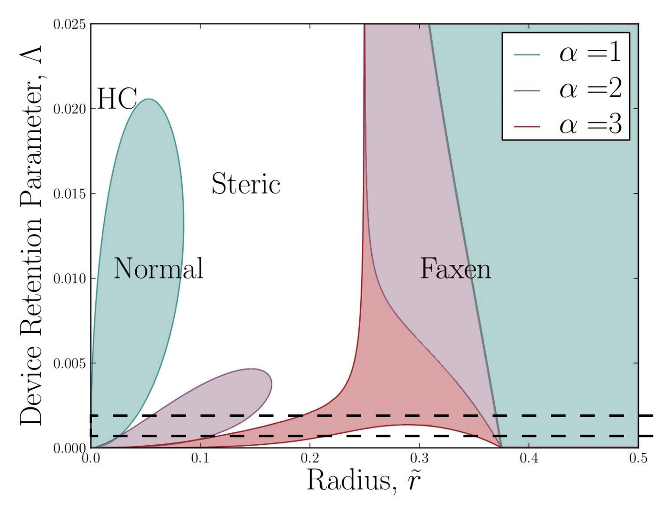
THEORETICAL MAPS

By defining the device retention parameter $\Lambda = \lambda \tilde{r}^{\alpha}$, the solute velocity becomes an explicit function of particle size $\tilde{r} = r/w$. The retention ratio is the average solute velocity normalized by the average solvent velocity

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

where

$$\mathcal{F}_f(x) = 6x\left(1-4x/3\right), \quad \mathcal{L}(x) = \coth(x) - 1/x.$$

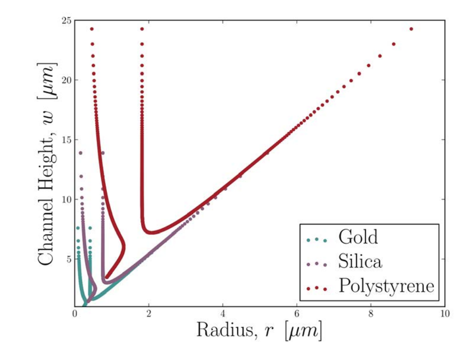


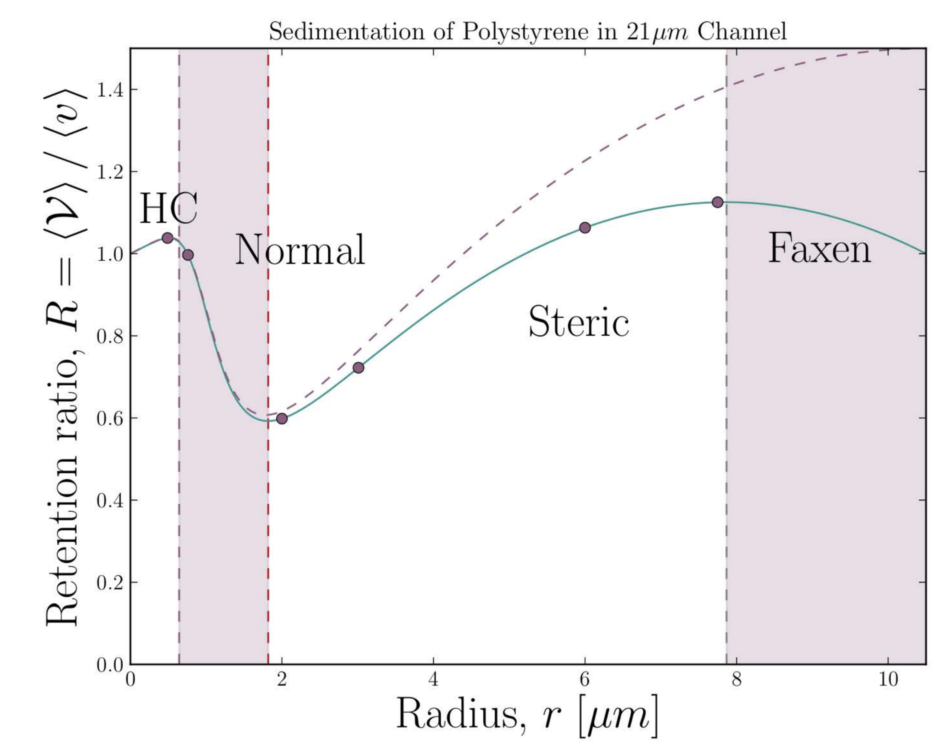
The unified ideal retention theory's mode-diagram maps out the four distinct operational regimes. It can be used to design microfluidic channels to function in one specific operational-mode or be employed to interpret all possible elution times[3] .

The device retention parameter is determined entirely by the experimental apparatus. For sedimentation in a microfluidic channel

$$\alpha = 3, \qquad \Lambda = \frac{3}{4\pi}\frac{k_B T}{g\Delta\rho w^4}.$$

Different choices of channel height and solute material were considered; polystyrene beads in a 21μm channel were chosen.





These choices produce an individualized retention curve describing the elution of polystyrene beads through a 21μm channel. HC is a small but accessible region with only a meager change in retention ratio over the size range. Faxén-mode is predicted to exist for particles with a diameter over 70% the channel height. Not only will the elution order change in this regime but the retention ratio should also be less than other wise expected.

INTRODUCTION

When a mixture of different solute particles are eluted through a channel by a nonuniform, flow profile and simultaneously subjected to an external field applied perpendicular to the flow, the constituent species size separate. This is called Field-Flow Fractionation (FFF)[1]. The competition between thermal energy and the external field results in a different exponential concentration distribution for each ensemble of solutes. Solutes with an average height near the wall are subject to slower fluid velocity than solutes with an average height far into the channel.

Although simple in concept, FFF is a flexible technique because

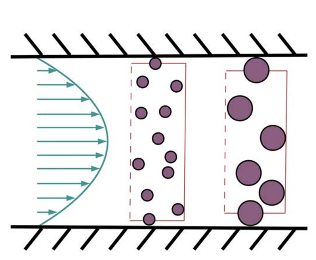
1) FFF can use a wide variety of external fields

Sedimentation, cross flows (both symmetrical and asymmetrical), thermal-gradients, electrical fields, pressure, magnetic fields, dielectrophoretic forces, acoustic forces, photophoretic fields have all been demonstrated to work.

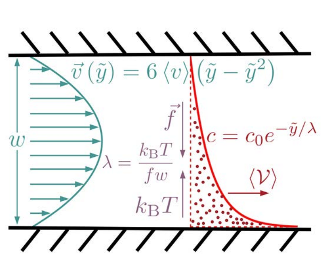
2) FFF can run in several operational-modes

By ignoring complicating effects such as particle slip, nonparabolic solvent flow or attraction to the accumulation wall, a single unified, ideal, retention theory can predict all four operational-modes

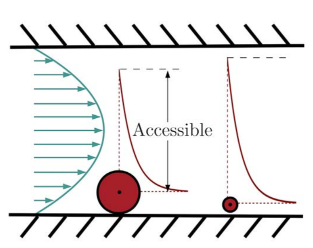
- **Hydrodynamic-chromatograghy (HC):** When the external force is negligible, the solute particles are free to diffuse across the entire channel and are only limited by steric interactions with the walls. This is why larger particles elute before smaller particles[2].



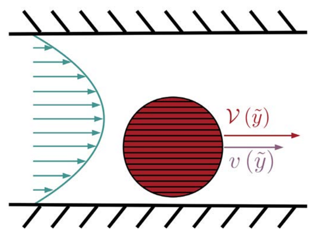
- **Normal-mode FFF:** Ensembles of small solutes can be thought of as point particles and the Boltzmann distribution gives them an exponential concentration from the accumulation wall. Because the average height of smaller particles is higher into the faster moving solvent flow, smaller particles elute before larger particles[1].



- **Steric-mode FFF:** Larger particles are pushed against the wall. Hard, steric interactions with the wall exclude the particle from sampling the slow moving velocity near the wall. The excluded region is larger for larger particles, so they elute more quickly[2].



- **Faxén-mode FFF:** At very large sizes, a significant portion of the particle's surface sees a very different velocity than the velocity at the particle's centre of mass. Integrating the fluid stress over the surface area causes larger particles to move more slowly than they would otherwise[3]. Faxén-mode has been theoretically predicted but is currently unverified by experiments.



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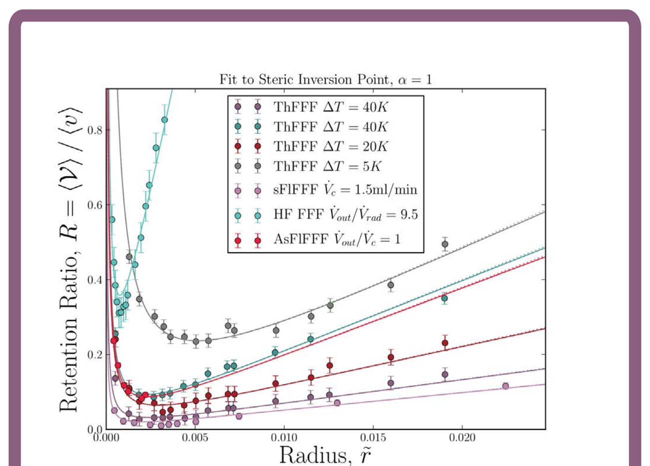
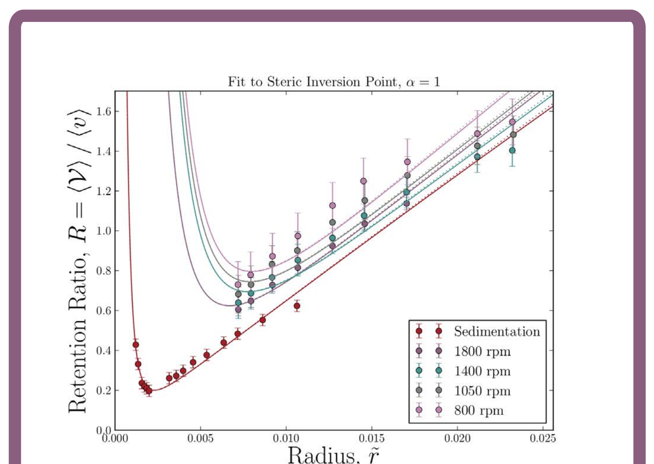
TRANSITION

The transition between normal- and steric-mode FFF (sometimes called the steric-inversion point) is most often avoided by experimentalists, who seek to work in one mode or the other. However, there are a handful of experimental measurements in the literature around this non-monotonic region of the retention ratio (and even some predictions of the transition point for specific fields).



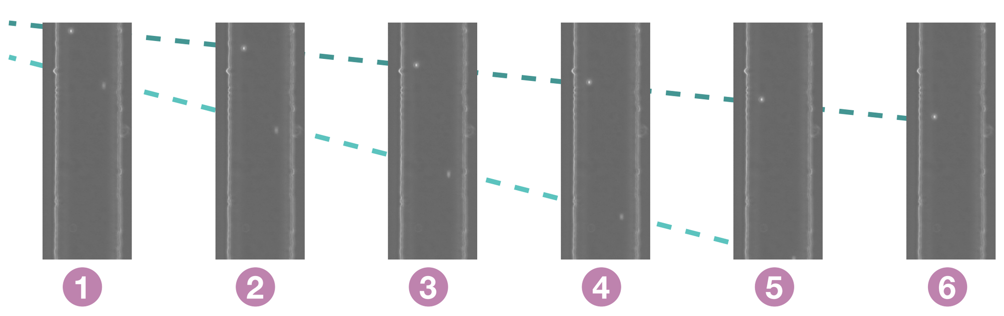
Flow FFF (FlFFF)[4,5] and thermal FFF (ThFFF)[6] are the most commonly utilized forms of FFF and for these cases α=1. In FlFFF, Λ depends on the volumetric cross flow, while in ThFFF, Λ depends on the temperature difference between the plates.



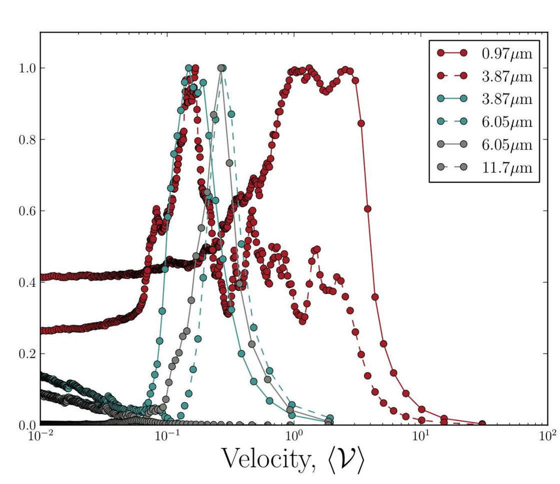
The most obvious examples of α=3 are gravitational[7] and sedimentation FFF[8]. Increasing the centripetal acceleration pushes particles against the accumulation wall and so decreases the retention ratio.

Despite the wide variety of field types, field strengths and particle sizes, the ideal unified retention ratio consistently and accurately fits the retention ratio in this critical region.

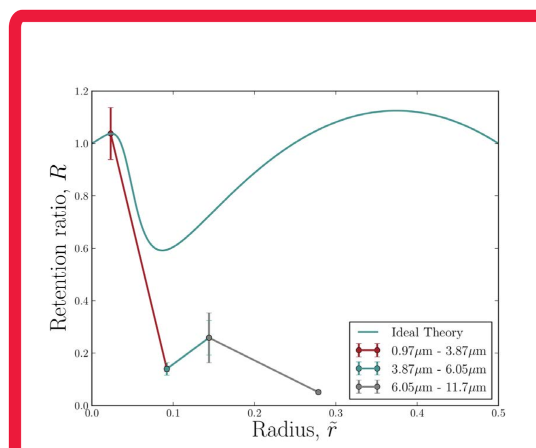
MICROFLUIDICS



To measure the velocity of polystyrene microbeads in a 21μm PDMS channel, an automated video-microscopy system has been developed. Particles are recorded over multiple frames and sorted by pixel-count. The Fourier transform of the resulting track of particle-events reveals the velocity distribution.



Since the retention ratio is normalized by average solvent velocity, the absolute velocity is not required; only velocity differences. For this reason, mixtures of two particle sizes transverse the microfluidic device simultaneously and the velocity is matched between pairs to create a preliminary chromatogram.

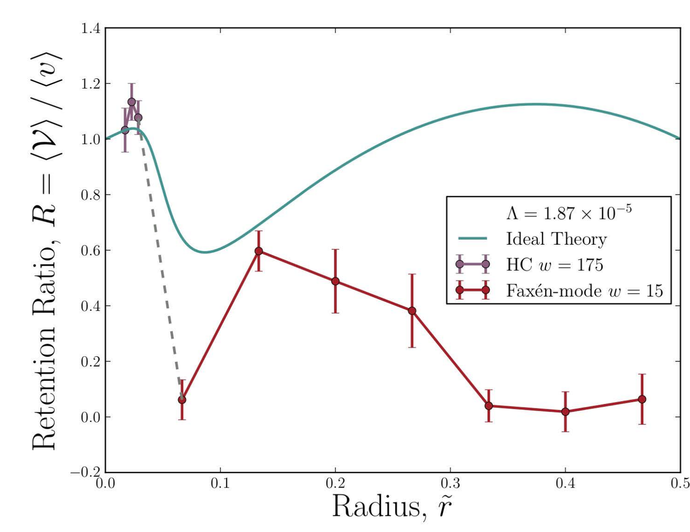


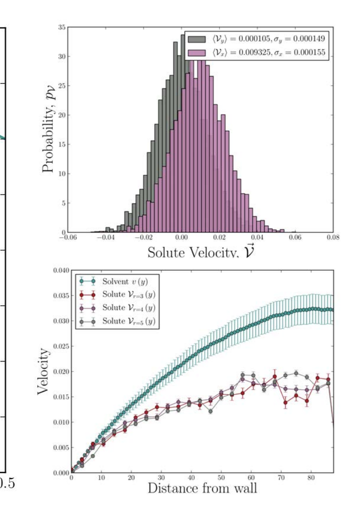
The average velocities are presented as a retention ratio by normalization of the 0.97μm bead.

- Greater than predicted change in the normal-mode regime.
- Steric-mode does not rise as high as predicted.
- Faxén-mode exists.
- The transition from steric- to Faxén-mode occurs much earlier than predicted.

SIMULATIONS

Investigations of the HC-limit and of Faxén-mode FFF are experimentally challenging. Therefore, we use a 2D Multi-Particle Collision Dynamics (MPCD) algorithm to simulate the solvent while modeling solute particles as hard spherical beads. The instantaneous coordinates of the solute particles are tracked and the retention ratio is determined from the velocity distribution. Simulations of small particle sizes show a slight maximum indicating the transition from HC to normal-mode. In agreement with experimental data, simulations of large particles demonstrate the existence of Faxén-mode FFF.





MPCD ALGORITHM

MPCD is a mesoscopic fluid model that replaces detailed interactions between fluid particles with non-physical, multi-particle collision events[9]. The collision is constructed to naturally reproduce thermal noise and hydrodynamic motion on sufficiently long length and time scales[10].

- During the streaming-step, the MPCD particles move ballistically:

$$\vec{r}_i(t+\delta t) = \vec{r}_i(t) + \vec{v}_i(t)\,\delta t$$

- The collision sorts the particles into cells and randomly re-assigns their velocities while conserving the cell momentum. The collision is controlled by an Andersen thermostat[11]:

$$\vec{v}_i(t+\delta t) = \vec{v}_{CM}(t) + \mathbf{R}\left(\vec{v}_i(t) - \vec{v}_{CM}(t)\right) = \vec{v}_{CM} + \vec{v}_i^{ran} - \frac{1}{N_{cell}}\sum_j^{N_{cell}} \vec{v}_j^{ran}$$

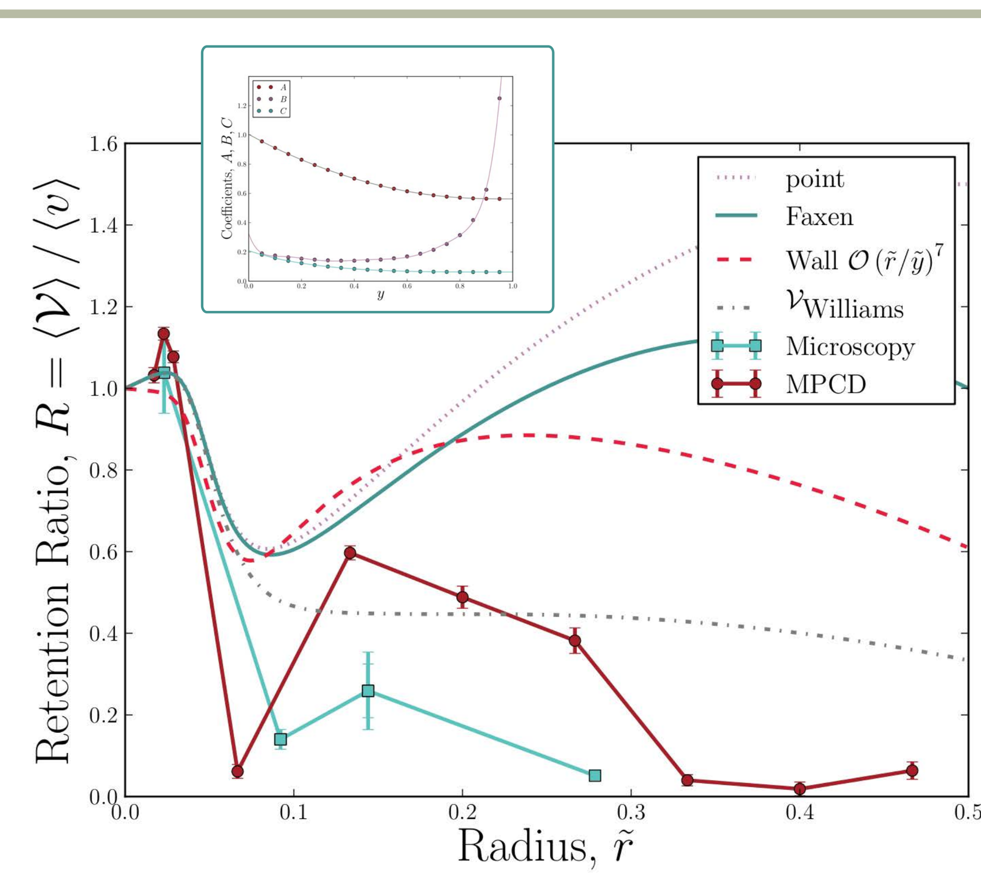
CONCLUSIONS

Results

- The unified ideal retention theory for FFF fits experimental data in the region of the steric-inversion point quite well. It does so despite large differences in particle size, device retention parameter and the field used.
- The predicted transition from HC to normal-mode FFF is observed in MPCD simulations with qualitative agreement.
- Both video-microscopy and MPCD simulations show a change in elution order at the largest particle sizes, verifying the existence of Faxén-mode FFF.

Open Questions

- Why does the ideal retention ratio accurately fit normal- and steric-mode FFF in macroscopic apparatuses yet under-predict the retention ratio in microfluidic devices?
- Can this decrease be used to increase resolution in microfluidic chips over traditional FFF apparatuses?
- Can microfluidic video-microscopy be extended into the HC-regime or further into the Faxén-mode regime?



- Can models for increased hydrodynamic drag explain the decrease?
  - Numerical integration of the retention ratio using series approximations[12] and empirical models[13] for increased drag between plates suggest:
    - The transition from steric- to Faxén-mode shifts to smaller particle sizes (series approximation).
    - The retention ratio is lowered to observed values by increasing drag (empirical model more successful)
    - Neither model shows quantitative agreement with experiments or simulations suggesting another mechanism - perhaps surface friction.
  - MPCD simulations suggest the solute velocity is slower in the centre of the channel than given by either model.
  - Simulations without gravity have the ability to these test models.
- Do inertial effects play a more important role due to the perpetual proximity of the microchannel walls or does the decreased Reynolds number ensure that they remain negligible?
  - Can simulations at different Reynolds numbers shed light on these theoretically intractable inertial effects (often called hyper-layer FFF)?