Steric Mode Separation of Nanotubes Using Electric Field, Field-Flow Fractionation*

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ABSTRACT

A Brownian dynamics simulation has been used to study the separation of rodlike particles in Electric Field, Field-Flow Fractionation (EF-FFF), in which in addition to the FFF cross-flow, a uniform AC field acts in the gradient direction. Under these conditions, the electric field acts to align the tubes in the gradient direction in competition with both the shear field and Brownian motion. The simulation results show that as the rods become increasingly aligned, they undergo a transition from normal mode to steric mode separation. By exploiting field conditions in which either metallic or semi-conducting types are preferentially oriented relative to the other, this can be used in the context of nanotube separation as a means for separating tubes by type.

Keywords: Brownian Dynamics, Field-Flow Fractionation, Nanotubes, Separations, SWNT

1 INTRODUCTION

For nanotubes to achieve their full potential in applications, it is desirable to be able to separate them according to their physical properties of length, diameter and chirality. One possible technique for achieving this is field-flow fractionation (FFF), depicted in Figure 1.

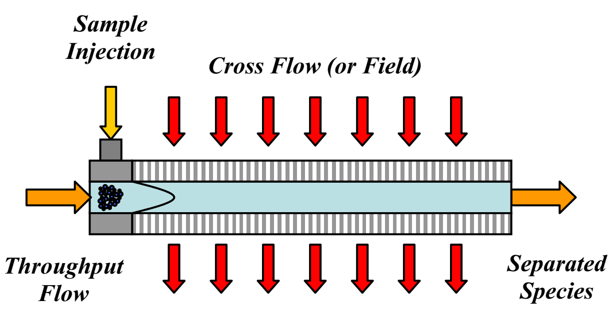

Figure 1: Schematic of frit-inlet symmetrical, field-flow fractionation, i.e., flow-FFF. In the asymmetric variation, only the lower wall is porous.

Classical flow-FFF is a separation technique in which a perpendicular cross flow is imposed upon a channel flow of dilute particulates [1-3]. The cross flow exits through a porous accumulation wall which is impermeable to the particulates. Competition between various flow mechanisms drives particles of unlike size to different average positions in the cross flow direction. Separation is achieved due to the different residence times of the particles based upon their position in the parabolic velocity profile in the throughput direction. Classical flow-FFF can be expected to produce sized based separations. In conjunction with other FFF based process variants incorporating electric fields or centrifugal forces, it might also potentially be used to produce separations based on chirality or diameter.

A number of different mechanisms can be exploited to achieve separation in FFF operations. Normal mode separation applies to particles which are small enough to undergo significant Brownian motion, and whose size is small compared to the cross flow gap size. In this case, smaller particles, which are more diffusive, have an average position closer to the centerline and elute faster than larger particles. Steric mode separation occurs when the particle layer in FFF is strongly compressed along the accumulation wall and due to size exclusion, larger particles are more highly entrained by the throughput flow and elute more quickly than smaller ones. This turnaround is called steric inversion.

Particle separation in flow-FFF can be described by a theoretical variable called the retention, R, which represents the ratio of the average residence time of non-retained tracers, t_0, to the average retention time of the particles, t_r, *i.e.*, $t_r = t_0 / R$, where $0 \le R \le 1$. For the case of normal mode separation, the retention is given by

$$R = 6\lambda\left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right] \tag{1.1}$$

where λ is an inverse Peclet Number (Pe) given by

$$\lambda = \frac{D}{|v_c|H} = \frac{1}{Pe} \tag{1.2}$$

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v_c is the cross flow velocity, D is the diffusion coefficient of the particle in the cross flow direction, and H is the cross-flow thickness.

A Retention model which takes into account both normal mode diffusion and steric effects for spheres in FFF was derived by Giddings [1]

$$R = 6\left(\alpha - \alpha^2\right) + 6\lambda\left(1-2\alpha\right)\left[\coth\left(\frac{1-2\alpha}{2\lambda}\right) - \frac{2\lambda}{1-2\alpha}\right] \quad (1.3)$$

where $\alpha = r/H$ is the ratio of the particle radius to gap thickness. For the case of negligible particle size, Eq. (1.3) reduces to Eq. (1.1). It can be seen that, theoretically, normal mode elution is independent of the particle shape and depends only on the particle diffusion coefficient. Steric mode elution becomes independent of diffusion, and depends mainly on the particle dimensions. However, little is known about how steric mode separations are effected by different particle shapes.

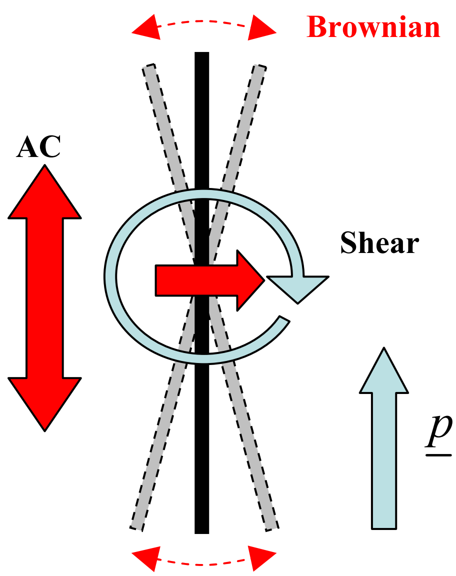

Figure 2: Forces on a rodlike particle subject to both shear flow, translational and rotational Brownian motion, and an AC electric field. Such a situation acts to induce "wobbly" alignment and modifies the FFF elution characteristics.

The steric inversion of spheres suggests that an even stronger steric effect might be obtained for rodlike particles due to their great length, if they could be oriented normal to the flow direction. This could be useful in the context of nanotube separation if either metallic or semi-conducting types could be preferentially oriented relative to the other. One way in which to induce an orientation of nanotube particles is by the use of an electric field, as in Electric Field, Field-Flow Fractionation (EF-FFF). In EF-FFF, in addition to the usual FFF cross-flow, an electric field acts in the gradient direction. The field may be AC or DC, and either uniform or non-uniform. When an anisotropic particle is subject to an electric field, a net torque which acts to align the particle in the field direction is produced [4]. In the case of EF-FFF, the orientation torque produced by the electric field is in competition with both the shear field and Brownian motion as depicted in Figure 2. The degree of alignment depends on the polarizability of the particle, and the electric field strength.

In what follows, the separation of rodlike particles in EF-FFF under the condition of a uniform, AC electric field is investigated using a Brownian dynamics simulation. First, single particle behavior in a uniform shear field is examined in order to determine parameter conditions necessary in order to align the particle under the conditions of shear and Brownian motion. Then, we look at the elution of oriented rods and elucidate a steric mode separation mechanism that can potentially be used to separate rods based on chirality.

2 SIMULATION

Full details of the Brownian dynamics simulation used to investigate the separation of rodlike particles in flow-FFF and EF-FFF are found in references [5-8]. A summary of pertinent details of the numerical method are discussed below.

2.1 EF-FFF Model Equations

The rodlike nanotubes are modeled as prolate ellipsoids, with major axis radius a and minor axis radius b. The translational particle motions are governed by a Langevin equation with orientation dependent drag and diffusion coefficients, and the rotational motion by the Jeffrey equation with rotational diffusion [5,9,10]

$$\frac{d}{dt}\left(\underline{R}^{(i)}\right) = \underline{v}\left(\underline{R}^{(i)}\right) + \left[\underline{\underline{\zeta}}^{(i)}\right]^{-1} \cdot \left(\underline{F}_B^{(i)} + \underline{F}_{DEP}^{(i)} + \underline{F}_{EP}^{(i)}\right) \quad (1.4)$$

$$\frac{d}{dt}\left(\underline{p}^{(i)}\right) = -\underline{\underline{W}} \cdot \underline{p}^{(i)} + \lambda_p^{(i)}\left(\underline{\underline{D}} \cdot \underline{p}^{(i)} - \underline{\underline{D}} : \underline{p}^{(i)}\underline{p}^{(i)}\underline{p}^{(i)}\right) - \underline{p}^{(i)} \times \left[\underline{\underline{\xi}}^{(i)}\right]^{-1} \cdot \left(\underline{\mathrm{T}}_B^{(i)} + \underline{\mathrm{T}}_E^{(i)}\right) \quad (1.5)$$

where $\underline{R}$ and $\underline{p}$ are the position and orientation vectors of the particles, $\underline{F}_B$ and $\underline{\mathrm{T}}_B$ are the Brownian force and torque, $\underline{F}_{DEP}$ is the dielectrophoretic force, $\underline{F}_{EP}$ is the electrophoretic force, $\underline{\mathrm{T}}_E$ is the torque due to the electric field , $\underline{\underline{\zeta}}$ and $\underline{\underline{\xi}}$ are hydrodynamic resistance tensors, $\underline{\underline{D}}$ and $\underline{\underline{W}}$ are the stretching and vorticity tensors, respectively, $\lambda_p = \frac{\Re^2 - 1}{\Re^2 + 1}$ with $\Re = \frac{a}{b}$.

Because we are considering the case of a uniform electric field, both the dielectrophoretic force and electrophoretic force are zero. The time-average torque in Eq. (1.5) due to the AC electric field is given by

$$\langle \underline{T}_E \rangle = \frac{1}{2} V^{(i)} \operatorname{Re}\left[\Delta\hat{\alpha}^{(i)} \left(\underline{p}^{(i)} \underline{p}^{(i)} \cdot \hat{\underline{E}} \right) \times \hat{\underline{E}}^* + \hat{\alpha}_{\perp}^{(i)} \hat{\underline{E}} \times \hat{\underline{E}}^* \right] \quad (1.6)$$

where $\hat{\underline{E}}$ is the electric field phasor vector, $\hat{\underline{E}}^*$ is the complex conjugate, V is the particle volume, $\hat{\underline{\underline{\alpha}}}$ is the complex polarizability, $\hat{\alpha}_{\parallel}$ and $\hat{\alpha}_{\perp}$ are the axial and perpendicular components of the polarizability, and $\Delta\hat{\alpha} = \hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}$.

Eqs. (1.4) and (1.5) are integrated for an ensemble of particles with respect to initial conditions described by FFF flow-focusing [5,7]. The degree of particle orientation obtained in EF-FFF depends on the ratio of the dimensionless groups $N_{DE} = \frac{V \operatorname{Re}[\Delta\hat{\alpha}] E_{rms}^2}{kT}$, which is the ratio of the dielectrophoretic potential energy to kT, and $Pe_r = \frac{\eta \dot{\gamma} Y_c^{(i)}}{kT}$ which is the Peclet number for rotational diffusion (where $Y_c^{(i)}$ is rotational friction coefficient). At lower values of Pe_r where the particles are more diffusive, higher values of N_{DE} are needed to orient the particles.

2.2 Boundary Conditions

An important part of the scheme is the interaction of the particles with the boundaries. The cross flow velocity continually drives the particles towards the accumulation wall and the diffusion step being random may also cause the particles to collide with this boundary. To handle this, a no-penetration boundary condition is used, based on the rod size and 3-D orientation [7,8] as show in Figure 3, in which the particle velocity is set to its center of mass value with respect to its distance from the wall in the local velocity field.

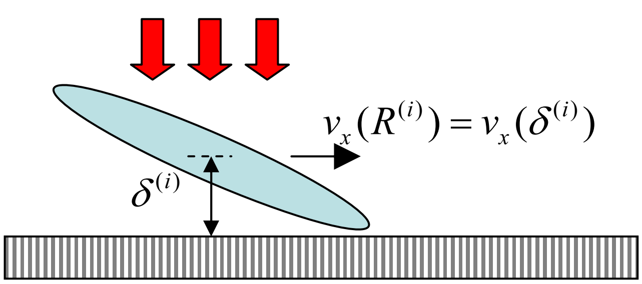

Figure 3: Boundary condition for ellipsoidal particles.

3 RESULTS

3.1 Orientation

The orientation behavior of rodlike particles in a steady shear flow subject to a uniform AC electric field and Brownian motion was examined. Invoking the ergodic hypothesis, we look at single particle behavior, as the time average of a single particle is the same as the instantaneous average of an ensemble. The motivation for this calculation is to determine the effect of shear on particle orientation, and to determine range of electric field and polarizability needed to orient particles in EF-FFF.

The particle orientation in a uniform electric AC field is characterized by an order parameter given by [11,12]

$$S = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle \quad (1.7)$$

where θ is the angle between the particle orientation and the electric field vector, $\langle \ldots \rangle = \int_0^{\pi} (\ldots) f(\theta) \sin\theta \, d\theta$, denotes an average over a potential, $f(\theta)$ is the potential

$$f(\theta) = \frac{e^{-\frac{U(\theta)}{kT}}}{\int_0^{\pi} e^{-\frac{U(\theta)}{kT}} \sin\theta \, d\theta} \quad (1.8)$$

and $U(\theta)$ is the interaction energy between the particle and the electric field

$$U(\theta) = -\frac{1}{2} V \operatorname{Re}[\Delta\hat{\alpha}] E_{rms}^2 \cos^2\theta \quad (1.9)$$

The value of S is equal to 1 when the particles are perfectly oriented with the field direction, 0 when they are oriented randomly with respect to the field direction, and a value of -½ when they are oriented normally to the field.

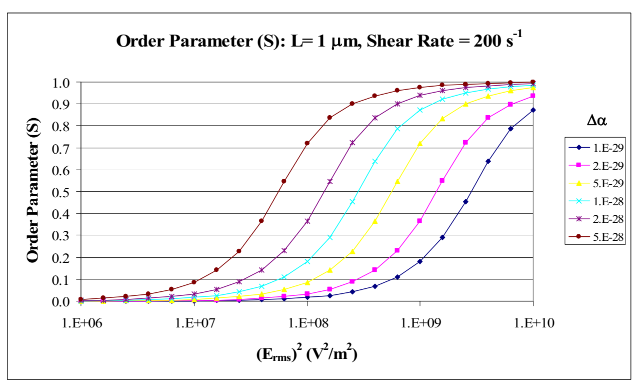

Figure 4: Order parameter at constant shear rate as a function of effective polarizability (*F-m*²).

Orientation results for a particle with a 1000 nm length and 1 nm diameter, at a constant shear rate of 200 are shown in Figure 4. Effective polarizibility values, $\Delta\alpha = V \cdot \mathrm{Re}\left[\Delta\hat{\alpha}\right]$, were chosen in a range consistent with values obtained in recent experimental investigations [12-15]. Shear rates were chosen in a range consistent with the maximum rates seen in experimental FFF studies [6,16]. This figure shows the expected behavior that higher effective polarizability leads to greater orientation at lower electric field values.

The particle orientation at constant polarizabilty as a function of shear rate is shown in Figure 5. These results indicate that on average at this size scale, the particle orientation is insensitive to the shear flow, and that the orientation is mainly a competition between the Brownian motion and the torque due to the electric field.

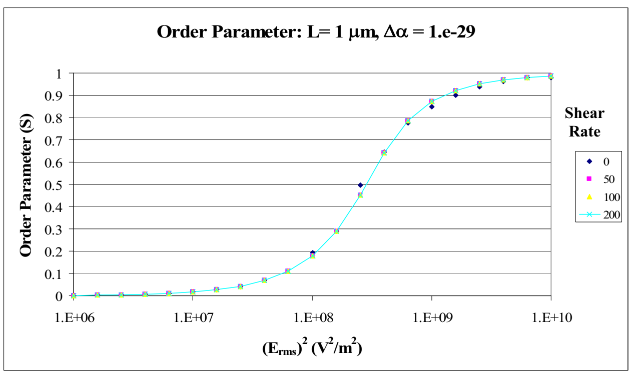

Figure 5: Order parameter at constant polarizability as a function of shear rate.

3.2 Retention Model and EF-FFF Results

For the case of perfect orientation, the boundary condition of the particle becomes as is shown in Figure 6, and the particle velocity will be at its maximum possible steric exclusion value, similar to the case for spheres. Under this condition, an appropriate expression for the Retention for the case of perfect orientation can be obtained by the modification of Eq. (1.3) with the substitutions $\alpha \to \alpha' = \frac{1}{2}\frac{L}{H}$, where L is the axial length of the rod, and $\lambda \to \lambda' = \frac{D_{\parallel}}{|v_c|H}$, where $D_{\parallel}$ is the axial diffusion coefficient of the rod, yielding the expression

$$R = 6\left(\alpha' - (\alpha')^2\right) + 6\lambda'(1-2\alpha')\left[\coth\left(\frac{1-2\alpha'}{2\lambda'}\right) - \frac{2\lambda'}{1-2\alpha'}\right] \qquad (1.10)$$

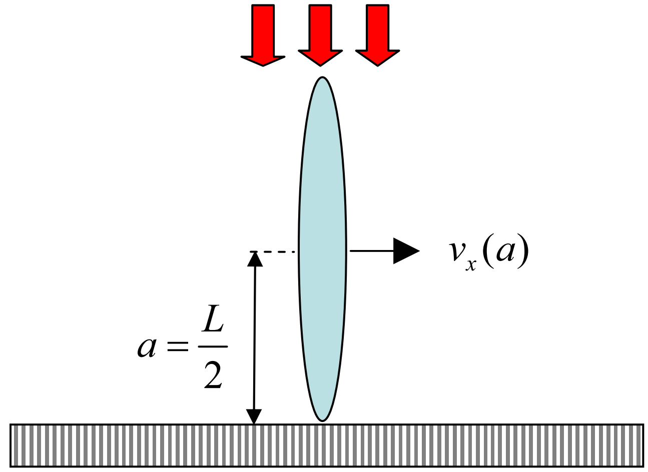

Figure 6: Boundary condition on a rodlike particle oriented normal to the flow direction.

Simulation results are shown in Figure 7 for the processing parameters given in Tables 1-2, and particle lengths ranging from 10 to 1000 nm, with a 1 nm diameter. An ensemble size of 1000 particles was used in all cases. Results for the steric inversion expression, Eq. (1.10), are plotted vs. EF-FFF results for $S = [0.1, 0.99, 1]$, and also the case of flow-FFF without any orientation. The results for $S = 1$ were obtained by setting the particle initial condition at an orientation normal to the flow direction, and turning off all rotational motion.

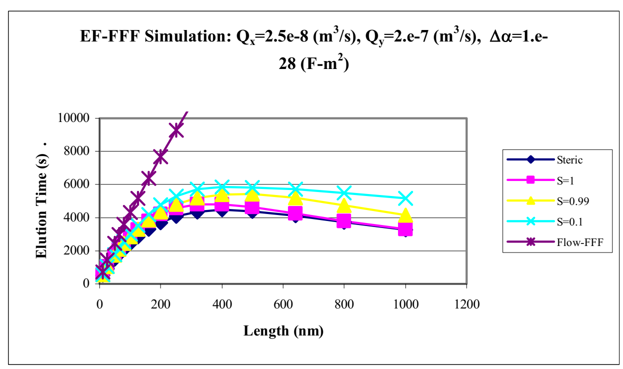

Figure 7: Comparison of elution time for rodlike particles under normal mode conditions, and for rods oriented perpendicular to flow direction.

A number of observations can be made from the Figure. First, the simulation results for $S = 1$ (constrained rotational motion) are in good agreement with the modified steric inversion theory of Giddings, *i.e.*, Eq. (1.10), and steric inversion is clearly observed. For the given conditions, the steric transition occurs when the particle length is approximately 400 nm. The data for $S = 0.99$ and $S = 0.1$ show that as the average particle orientation decreases, there is still steric inversion, but the elution times begin to significantly slow down. All the EF-FFF curves sharply diverge from the flow-FFF curve (which are governed by normal mode elution) at a length of about 100 nm.

The results show that oriented rods will exhibit steric inversion. This could be useful in the context of obtaining nanotube separation by chirality if either metallic or semi-conducting types could be preferentially oriented relative to the other by controlling the relative polarizability of the two different types by means of frequency, and appropriate solvent/surfactant combinations. Orienting one species relative to the other will allow the orienting and non-orienting types to be separated into two fractions. The first fraction will contain oriented rods of all sizes, and non-oriented Brownian rods whose size is such that their elution time is less than the elution time corresponding to the steric inversion point for the oriented rods. The second fraction will contain all the longer non-oriented rods. For the case shown in Figure 7, the non-orienting cutoff size in the first fraction is about 150 nm; smaller cutoff sizes can be obtained by optimizing parameter conditions. Both fractions may then be further refined using size separation only.

4 SUMMARY AND CONCLUSIONS

We have investigated particle separation mechanisms in EF-FFF using Brownian dynamics method. The following conclusions can be drawn from the present work.

- In the range shear rates common for FFF, shear flow has little effect on the orientation of rodlike particles in FFF, as Brownian motion is the dominant effect.
- Rods oriented normal to the flow direction can be expected to exhibit steric inversion. The steric effect grows stronger with increasing particle orientation. Eq. (1.10) provides a useful expression for the Retention of perfectly oriented particles.
- The use of steric inversion could be useful in the context of nanotube separation if either metallic or semi-conducting types could be preferentially oriented relative to the other by controlling the relative complex polarizability of the species.

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5 TABLES

Processing Parameters	
Length, L (m)	0.25
Thickness, H (m)	0.00025
Width, W (m)	0.02
Focus Point, x_f (m)	0.01
T (K)	293
Viscosity (Pa-s)	0.001
Q_x (m^3/s)	2.5×10^{-8}
Q_y (m^3/s)	2.0×10^{-7}
Q_f (m^3/s)	2.0×10^{-8}

Table 1 – Processing parameters used in the simulations.

Orientation Parameters	
E_{rms} (V/m)	S
8000	0.1
100,000	0.88

Table 2 – Electric field values used in the simulations for $\Delta\alpha = 1x10^{-29}\ F \cdot m^2$.

6 ACKNOWLEDGEMENTS

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