RICE UNIVERSITY

**Brownian Dynamics Simulations of
Single-Wall Carbon Nanotube Separation by
Type using Dielectrophoresis**

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Abstract

We theoretically investigate the separation of individualized metallic and semiconducting single-wall carbon nanotubes (SWNT) in a dielectrophoretic (DEP) flow device.

The SWNTs motion is simulated by a Brownian Dynamics (BD) algorithm which includes the translational and rotational effects of hydrodynamic, Brownian, dielectrophoretic, and electrophoretic forces. The device geometry is chosen to be a coaxial cylinder, because it yields effective flow throughput, the DEP and flow fields are orthogonal to each other, and all the fields can be described analytically everywhere. We construct a flow-DEP phase map, showing different regimes depending on the relative magnitudes of the forces in play.

The BD code is combined with an optimization algorithm that searches for the conditions which maximize the separation performance. The optimization results show that a 99% sorting performance can be achieved with typical SWNT parameters by operating in a region of the phase map where the metallic SWNTs completely orient with the field, whereas the semiconducting SWNTs partially flow align.

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Chapter 1

Introduction

The unique characteristics of SWNTs make them potentially effective in a wide range of applications in electronics, energy, multifunctional materials, and biomedicine.

The most common techniques used in the synthesis of SWNTs are Carbon Arc-Discharge [1], Laser Ablation [2], Chemical Vapor Deposition [3], Gas-phase catalytic growth [4], and Catalytic decomposition on bimetallic CoMo catalysts [5]. As-produced nanotubes from these processes contain a broad range of (n,m) chiralities with different diameters and electronic structure [6]. SWNTs with $n - m$ equal to a multiple of 3 are metallic, and the other two thirds correspond to direct band-gap semiconductors [7]. Whereas some applications (e.g. structural composites, fluids filtration, biomedical imaging, etc.) could be achieved with mixed-type SWNTs, others would benefit greatly from single-type (metallic vs. semiconducting) or single-chirality samples (e.g., molecular electronics, field emission displays, wires for long-distance electrical power transmission, etc.).

The type enrichment methods studied so far make use of distinct physico-chemical principles: covalent functionalization [8, 9], selective elimination [10], selective absorption [11, 12], ion exchange chromatography [13], elec-

trophoresis (EP) [14, 15], dielectrophoresis (DEP) [16, 17, 20, 18] and density gradient ultracentrifugation [29]. Each of these methods has different selectivity towards type or diameter, and different potential for scaling to bulk quantities. One potentially scalable route is to couple the type selectivity of DEP with the high-throughput provided by continuous flow devices.

Promising results were recently reported by our group. *H. Peng* and coworkers [30] developed a continuous flow through SWNT sorting process: *Dielectrophoresis Field Flow Fractionation* (DEP-FFF). In their work they use a chamber whose bottom is filled with an array of interdigitated gold electrodes driven by an AC voltage of 1 MHz and 10 V peak to peak. A solution with 1% SDBS dispersed SWNTs is injected in the mobile phase of the liquid that continuously flows through the chamber, and the eluent is collected and analyzed fractionally at certain time intervals. By comparing the absorption and emission spectra of the eluent with the starting solution spectra, as well as looking at the Raman spectra on the electrodes, the authors concluded that metallic tubes got 70% depleted from the initial solution.

Flow-through DEP (FT-DEP) is characterized by a large, complex parameter space; therefore, modeling can be invaluable in identifying the potential of the technique and the optimal range of operating parameters where sorting efficiency and throughput can be maximized.

The basic physics controlling DEP of rods is well-understood in terms of frequency-dependent polarizability, application of the theory to SWNTs still needs input from experimental results in terms of specific SWNT properties. Therefore, at this stage it is prudent to analyze FT-DEP in terms of a dimensionless parameter space and, based on current estimates of SWNT properties, to evaluate which regions of a FT-DEP diagram are accessible and desirable.

Here we present a computational study of the response of individual SWNTs under positive DEP, and apply it to the separation of metallic and

semiconducting SWNTs with polydisperse length in a new type of FT-DEP device with a coaxial cylindrical geometry. Earlier simulation articles studied the motion of dispersed SWNTs under the influence of DEP [20, 28]. Here, we include the important effect of fluctuating exchange of momentum between the SWNTs and the liquid. We also combine in the algorithm a pattern search optimization method which requires no derivative information.

Chapter 2

Dielectrophoresis on SWNTs

Dielectrophoresis is the motion of matter caused by polarization effects in a nonuniform electric field [21]. When a polarizable particle is placed in an electric field $\mathbf{E}$, it acquires an induced dipole moment caused by the charge separation within the particle material. If the field is spatially nonuniform, the polarizable object experiences a force imbalance which results in its translation along the field gradient direction, even if the object is globally uncharged. The translational DEP force is proportional to the field gradient at the particle position and to its induced dipole moment $\boldsymbol{\mu}$:

$$\mathbf{F}^{\text{DEP}} = \boldsymbol{\mu} \cdot \nabla \mathbf{E} \quad (2.1)$$

Because, in turn, $\boldsymbol{\mu}$ is proportional to $\mathbf{E}$ the DEP force is proportional to $\nabla E^2/2$. Thus, the particle DEP motion is independent of the field direction and can be driven by a DC or AC field. This effect has proven useful for nanoscale object manipulation [31] and separation [22] due to the differences in the polarizabilities of particles with distinct material properties and/or geometries.

Carbon nanotubes are long thin rods which can be modeled as slender prolate ellipsoids to calculate their induced dipole moment $\boldsymbol{\mu}_{NT}$. It is as-

sumed that the nanotubes are seen as point particles by the field gradient, i.e., that their size is very small compared to the spatial change of ∇E :

$$|\nabla E| \gg l_{NT} |\nabla \nabla E| \quad (2.2)$$

where l_{NT} is the tube length. If condition 2.2 is valid, $\boldsymbol{\mu}_{NT}$ can be written as [23]:

$$\boldsymbol{\mu}_{NT} = V_{NT} \epsilon_m \mathbf{E} \cdot \underline{\underline{\mathbf{P}}} \quad (2.3)$$

where $\underline{\underline{\mathbf{P}}} = Re[K^{\parallel}] \mathbf{u}\mathbf{u} + Re[K^{\perp}] (\mathbf{I} - \mathbf{u}\mathbf{u})$ is the polarizability tensor, $\mathbf{u}$ is the unit vector along the SWNT axis, V_{NT} the SWNT volume, ϵ_m the medium permittivity, and $Re[K^{\perp, \parallel}]$ the real parts of the radial (or perpendicular) and axial (or parallel) Clausius-Mossotti factors which depend on the difference between the dielectric constants of the particle material (ϵ_{NT}^*) and the medium (ϵ_m^*):

$$K^{\perp, \parallel} = \frac{\epsilon_{NT}^* - \epsilon_m^*}{\epsilon_m^* + (\epsilon_{NT}^* - \epsilon_m^*) L^{\perp, \parallel}} \quad (2.4)$$

where $L^{\perp, \parallel}$ are depolarization factors which have distinct values due to the particle shape anisotropy. In the case of long prolate ellipsoids these factors are [23]:

$$L^{\parallel} = \frac{4r_{NT}^2}{l_{NT}^2} \left(\log \left[\frac{l_{NT}}{r_{NT}} \right] - 1 \right) \quad , \quad L^{\perp} = \frac{1 - L^{\parallel}}{2} \quad (2.5)$$

where r_{NT} is the SWNT radius. This results in a higher polarizability along the longer axis ($\parallel$) of the ellipsoid.

In an AC field the material polarization is frequency dependent due to the losses associated with internal charge displacement. Therefore, the dielectric constants are complex quantities which can be written in a simplified form in terms of the material permittivity ϵ and conductivity σ :

$$\epsilon^* = \epsilon - i\frac{\sigma}{\omega} \quad (2.6)$$

where $\omega = 2\pi f$ is the AC field angular frequency.

The SWNT is assumed to be a homogeneous material, i.e., ϵ_{NT} and σ_{NT} are the same for $K^{\parallel}$ and $K^{\perp}$ in eq. 2.4. The parallel permittivity and conductivity of SWNTs are expected to be higher than the perpendicular ones due to the SWNT unidimensional structure, as measured by [24, 25]. However, considering this anisotropy in dielectric constant would yield a small effect in the overall polarizability of the SWNTs, because of their high aspect ratio accounted for by the depolarization factors. For typical SWNT aspect ratios $\max(Re[K^{\parallel}]) \sim 1/L^{\parallel} \gg \max(Re[K^{\perp}]) \sim 1/L^{\perp}$; thus, taking ϵ_{NT}^* in $K^{\perp}$ different than the one in $K^{\parallel}$ would have minimal influence on the overall DEP response because the radial polarizability is negligible.

ϵ_{NT} and σ_{NT} are taken to be frequency independent. Optical experiments on nanotube networks show that these quantities differ from their DC values only for frequencies in the THz range or higher [26, 27]. Fits to the measured conductivity values with the Drude model yield mean scattering times on the order of 10^{-14} s. The frequencies of interest for SWNT DEP separation lie in the MHz range, as described later in chapter 5, [16, 17, 19, 18, 39] which are well below the expected SWNTs Drude resonance.

The Clausius-Mossotti factors in eq 2.4 are complex quantities whose magnitude and phase are functions of ω . The corresponding phase angle represents the phase lag between the applied field and the induced moment. Such ohmic, dispersive behavior is a consequence of the finite time required to build up charge at the particle-medium interface, due to the material finite conductivity. The characteristic buildup or decay time of charge at the nanotube surface, in response to an applied field, is given by the Maxwell-Wagner relaxation time constant τ [23]:

$$\tau^{\perp,\parallel} = \frac{(1 - L^{\perp,\parallel})\epsilon_m + L^{\perp,\parallel}\epsilon_{NT}}{(1 - L^{\perp,\parallel})\sigma_m + L^{\perp,\parallel}\sigma_{NT}} \quad , \quad \omega^C = \frac{1}{\tau^{\parallel}} \quad (2.7)$$

Every material has a *critical frequency* ω^C above which the charge can no longer follow the alternating field switching, thereby resulting in a reduced induced dipole moment. SWNTs exhibit longitudinal polarizabilities much higher than the radial ones; therefore, the relevant critical frequency is the one associated with the axial relaxation time. Figure 2.1 shows a schematic plot of the real part of the parallel Clausius-Mossotti factor expected for metallic and semiconducting SWNTs as a function of ω . This factor is constant at low frequencies, but drops dramatically above ω^C and can even reach negative values depending on the SWNT-medium dielectric constants difference.

SWNTs in the solvent medium must be wrapped in surfactant micelles to be dispersed in liquids [32]. The presence of surfactants influences the medium permittivity and conductivity as well as the effective properties of wrapped SWNTs, as has been observed by several reports on SWNT dielectrophoresis [16, 17, 19, 18, 39]. Therefore, ϵ_{NT}^* is, more correctly, the effective dielectric constant of the SWNT-surfactant complex. Figure 2.1 shows schematically how the Clausius-Mossotti factor of a semiconductor SWNT changes due to the wrapper effect.

The $Re[K]$ factors in the DEP force expression differ between metallic and semiconducting SWNTs since they have distinct effective dielectric constants. Type separation is possible if $Re[K_M]$ and $Re[K_S]$ differ sufficiently. This motivates the definition of the Polarization Ratio:

$$P(\omega) = \frac{Re[K_M^{\parallel}]}{Re[K_S^{\parallel}]} \quad (2.8)$$

where only the parallel K factors are considered due to SWNTs pronounced

Figure 2.1: Schematic plot of the parallel Clausius-Mossotti factor for metallic (M) and semiconducting (S) SWNTs, and how it changes with the surfactant effect. The main role of the surfactants is to increase the medium conductivity and reduce the effective one of wrapped SWNTs.

shape anisotropy, as previously discussed.

Chapter 3

The DEP Separation Device

This study considers a coaxial cylindrical channel composed of a hollow outer metallic tube and an inner metallic wire that is stretched along the cylinder axis, as depicted in fig. 3.1. The liquid flows between the inner wire and the hollow cylinder; and a voltage is applied between them to generate an electric field within the flow region. The SWNT suspension is injected near the internal cylinder wall at radial position R_2 .

Applying a pure AC voltage V_{AC} yields an inward radial DEP force, which scales as $F^{DEP} \propto V_{AC}^2/r^3$, where r is the distance from the cylinder axis.

The coaxial flow channel has two advantages over the previously used interdigitated electrode array [20, 30, 22]; it is expected to perform better, because, unlike the interdigitated array, F^{DEP} is always greater than zero inside the device, and it can be modeled simply because the flow and electric fields can be determined analytically if the channel length L is much longer than R_2 .

Figure 3.1: Sketch of separation device for metallic vs. semiconductors separation. The dilute SWNT solution is injected at the top of the hollow cylinder. Dielectrophoretic (DEP) and Electrophoretic (EP) forces are generated inside the flow region using an AC voltage with a DC offset. The objective is to collect metallic SWNTs in the inner wire and let the semiconductors flow out of the device.

Chapter 4

Brownian Dynamics Algorithm

The SWNTs equations of translational and rotational motion are determined using the force and torque balances, where inertia terms are ignored due to the minimal nanotube mass. The rapid process of inertia-friction relaxation of momentum occurs in picoseconds for these particles, which is a time scale much lower than the time scales of interest [38].

For simple systems with uniformly distributed fields over the whole space, the diffusive motion is best studied numerically by solving the appropriate partial differential equation for the probability distribution function in the space of possible configurations. However, in this case the fields are spatially dependent. The system can be studied more effectively by following the trajectories of N particles; such trajectories obey stochastic differential equations including deterministic as well as Brownian terms. Here the stochastic equations of motion are integrated by a Forward Euler scheme due to the presence of the Brownian term.

4.1 Force Balance and Translational Motion

The SWNT center of mass position $\mathbf{R}(t)$ is displaced according to the force balance:

$$\mathbf{F}^T + \mathbf{F}^H + \mathbf{F}^B = 0 \quad (4.1)$$

where $\mathbf{F}^T = \mathbf{F}^{\text{DEP}} + \mathbf{F}^{\text{EP}}$ is the total electric force that consists on the sum of DEP and electrophoretic (EP) forces. The hydrodynamic force $\mathbf{F}^H$ is composed of two terms, a flow and a viscous force:

$$\mathbf{F}^H = \underline{\underline{\zeta}} \cdot \left(\mathbf{v}_f - \frac{d\mathbf{R}}{dt} \right) \quad (4.2)$$

where $\mathbf{v}_f$ is the fluid velocity and $\underline{\underline{\zeta}}$ is the friction tensor of a rigid rod calculated using [34]:

$$\underline{\underline{\zeta}} \equiv \zeta^{\parallel} \mathbf{u}\mathbf{u} + \zeta^{\perp} (\mathbf{I} - \mathbf{u}\mathbf{u}) \quad (4.3)$$

The components of this tensor are the parallel and perpendicular friction coefficients, given by:

$$\zeta^{\parallel} = \frac{2\pi\eta l_{NT}}{\log[l_{NT}/(2r_{NT})]} \quad , \quad \zeta^{\perp} = 2\zeta^{\parallel} \quad (4.4)$$

where η is the fluid viscosity. The velocity profile of a laminar incompressible fluid flow can be analytically determined in a hollow tube [40] solving the Navier-Stokes equation with the following boundary conditions: $v_f(R_1) = 0$ and $v_f(R_2) = 0$.

The Brownian force $\mathbf{F}^B$ is a Gaussian random variable with zero mean and second moment given by a Dirac δ -function [35]:

$$\langle \mathbf{F}^B(t') \mathbf{F}^B(t'') \rangle = 2k_B T \underline{\underline{\zeta}} \delta(t' - t'') \quad (4.5)$$

where T is the temperature and k_B the Boltzman constant. At a given time step from t to $t + \Delta t$ the Brownian force produces a Gaussian random displacement $\mathbf{b}(t)$ of the center of mass position with zero mean and second moment:

$$\langle \mathbf{b}(t)\mathbf{b}(t) \rangle = 2\underline{\underline{\mathbf{D}}}\Delta t \quad (4.6)$$

where $\underline{\underline{\mathbf{D}}}$ is the diagonal diffusivity tensor, which can be written in terms of the friction coefficient tensor:

$$\underline{\underline{\mathbf{D}}} = k_B T \underline{\underline{\zeta}}^{-1} \quad (4.7)$$

Combining eqs 4.1-4.6 and discretizing the equation of motion with the forward Euler scheme yields the expression for the center of mass displacement,

$$\mathbf{R}(t + \Delta t) - \mathbf{R}(t) = \frac{\Delta t}{k_B T} \underline{\underline{\mathbf{D}}} \cdot \mathbf{F}_T + \mathbf{v}_f \Delta t + \mathbf{b}(t) \quad (4.8)$$

4.2 Torque Balance and Rotational Motion

The evolution of the unit vector $\mathbf{u}$ aligned along the tube axis obeys a torque balance:

$$\mathbf{M}^T + \mathbf{M}^H + \mathbf{M}^B = 0 \quad (4.9)$$

where the indices T , H and B refer to total electric, hydrodynamic, and Brownian torques.

The electric torque $\mathbf{M}^E$ is related to the applied field $\mathbf{E}$:

$$\mathbf{M}^E = \boldsymbol{\mu}_{NT} \times \mathbf{E} \quad (4.10)$$

For the case of an AC field, the time-average of this torque over the period of the applied AC voltage is [23]:

$$\mathbf{M}^{\mathbf{E}} = V_{NT}\epsilon_m Re [K^{\parallel}K^{\perp}] (L^{\perp} - L^{\parallel}) E_{RMS}^2 (\mathbf{u} \cdot \mathbf{r})(\mathbf{u} \times \mathbf{r}) \quad (4.11)$$

where E_{RMS} is the RMS value of the applied field's magnitude, and $\mathbf{r}$ is the unit vector in the $\mathbf{E}$ direction. The factors $K^{\perp,\parallel}$ are obtained using eq 2.4. In a DC field the torque expression is the same but the dielectric constants ϵ are only given by their real parts (permittivities), and therefore the Clausius-Mossotti factors $K^{\perp,\parallel}$ are also real quantities. In the general case of an AC voltage with a DC offset, the total electric torque $\mathbf{M}^{\mathbf{T}}$ is the sum of the AC and DC torques.

The hydrodynamic torque $\mathbf{M}^{\mathbf{H}} = \mathbf{M}^{\mathbf{F}} + \mathbf{M}^{\mathbf{V}}$ can be broken into the sum of so-called flow ($\mathbf{M}^{\mathbf{F}}$) and viscous ($\mathbf{M}^{\mathbf{V}}$) components. To calculate this torque we assume that the SWNT is a slender rigid rod [34, 36]:

$$\mathbf{M}^{\mathbf{H}} = \zeta^R \mathbf{u} \times \left(\underbrace{\underline{\mathbf{k}} \cdot \mathbf{u} - \mathbf{u}(\mathbf{u}\mathbf{u} : \underline{\mathbf{k}})}_{\text{Flow}} - \underbrace{\frac{d\mathbf{u}}{dt}}_{\text{Viscous}} \right) \quad (4.12)$$

where $\underline{\mathbf{k}} = \nabla \mathbf{v}_f$ is the fluid velocity gradient. The rotational friction coefficient is given by [37]:

$$\zeta^R = \frac{\pi\eta l_{NT}^3}{3} \xi f(\xi) \quad (4.13)$$

with,

$$\xi = 1/\log(l_{NT}/r_{NT}) \quad \text{and} \quad f(\xi) = \frac{1 + 0.64\xi}{1 - 1.5\xi} + 1.659\xi^2. \quad (4.14)$$

The Brownian torque $\mathbf{M}^{\mathbf{B}}$ generates two Gaussian random orientational displacements along the two directions orthogonal to $\mathbf{u}$. If we denote the sum of these displacements by the unit vector $\hat{\beta}$, then this vector has zero mean and second moment:

$$\langle \hat{\beta}(t)\hat{\beta}(t) \rangle = 2D^R(\underline{\mathbf{I}} - \mathbf{u}\mathbf{u})\Delta t \quad (4.15)$$

where $D^R = k_B T / \zeta^R$ is the rotational diffusivity.

After discretization, the expression for the orientational displacement is:

$$\mathbf{u}(t + \Delta t) - \mathbf{u}(t) = \Delta t \left(\frac{\mathbf{M}^T}{\zeta^R} \times \mathbf{u}(t) + (\underline{\mathbf{k}} \cdot \mathbf{u} - \mathbf{u}(\mathbf{u}\mathbf{u} : \underline{\mathbf{k}})) \right) + \hat{\beta}(t) \quad (4.16)$$

The new vector $\mathbf{u}(t + \Delta t)$ must be normalized at the end of the iteration step to avoid accumulation of numerical error. The maximum torque experienced by the particles determines the maximum time step that can be used for the integration of the equations of motion:

$$\Delta t < \frac{\zeta^R}{M_{max}} \quad (4.17)$$

4.3 Initial and Boundary Conditions

In practice, the SWNTs are injected from an aperture in the cylinder outer wall (see fig. 3.1); this aperture should be as small as possible to avoid dispersion of the sorted species [33]. In the simulations, all SWNTs are “injected” at the same location with zero velocity and a random orientation $\mathbf{u}$. The starting radial position R_i depends on the ratio between the main flow Q and the SWNT solution injection flow Q_{inj} . As described in Appendix A, when $Q/Q_{inj} \approx 100$ it is reasonable to assume that all SWNTs initiate their motion at $R_i = 0.9R_2$.

The flow region boundaries are considered to be sticky walls. Once a SWNT reaches the cylindrical walls at R_1 or R_2 it remains fixed at that final position and the calculations terminate for that particle.

Chapter 5

Flow-DEP Phase Portrait

The DEP translational motion of polarizable rigid rods is tightly connected to their rotation under the influence of the torques in play. In our device, the hydrodynamic torque acts so as to align the rods normal to the electric field, i.e., along the streamlines. However, the DEP force is most effective in moving the rods along the field (across streamlines) when they are aligned in the field direction, because in this configuration the induced dipole moment is largest and the drag is lowest. This condition is realized when the characteristic magnitude of M^T is larger than M^B and M^H in eq 4.9. Hence, eq 4.9 reduces to $M^T \approx 0$, and this implies that $\mathbf{u}$ has to lie parallel to the $\mathbf{E}$ field according to eq 4.11. Conversely, the DEP force is least effective when the rods are aligned perpendicularly to the electric field gradient, i.e., along the flow streamlines. This is realized when M^H dominates over the other terms in eq 4.9. Thus, eq 4.9 reduces to $M^H \approx 0$, and according to eq 4.12 this implies flow alignment since the dominant term is $\underline{\mathbf{k}} \cdot \mathbf{u} \approx 0$.

Three distinct regimes characterize the rotational behavior of nanotubes considering DEP as the only electric torque. These are depicted in the phase diagram of fig. 5.1, and they depend on the relative intensities of the DEP rotational energy over thermal energy ($U_R^{DEP}/k_B T$) and the rotational Peclet

number (Pe). U_R^{DEP} is equal to the maximum DEP torque magnitude, given by eq. 4.11, and $Pe = \frac{\partial v_f}{\partial r} / D^R$ is a ratio between the shear flow and Brownian torques.

Figure 5.1: Different regimes that characterize the SWNT rotational motion. The separation lines are shown for metals (M) and semiconductors (S). Sorting between both species should be performed in the shaded areas where the semiconductors are randomly oriented (SB) or preferentially aligned with the flow direction (SH), whereas the metallic SWNTs are aligned with the E field.

There are two preferential regimes for type separation. In the regime denoted as SB , the DEP and the hydrodynamic torques on semiconductor SWNTs are too low to overcome the Brownian motion, whereas the DEP

torque on metallic SWNTs is sufficiently strong to induce field-alignment. In regime *SH*, the semiconductor SWNTs align with the flow and the metallic SWNTs with the field.

The size of these regions is proportional to the polarization ratio $P(\omega)$, defined in eq 2.8, which depends on the frequency dependent Clausius-Mossotti factors. These factors can be estimated by assuming reasonable literature values for the SWNT and medium material parameters.

The medium is taken to be water with a small percentage of surfactant salt ($\epsilon_m = 80\epsilon_0$, $\sigma_m = 1 \times 10^{-3} \text{ S/m}$). The whole system is assumed to be isothermal.

The semiconductors permittivity ϵ_S is expected to be inversely proportional to the square of the band gap energy, according to the theoretical model described in [45]. This yields values on the order of $\epsilon_S = 5\epsilon_0$, which is consistent with the experimental observations of [25]. The permittivity of metallic SWNTs is expected to be higher, on the order of $10^4\epsilon_0$ [20, 28].

The semiconducting SWNTs effective conductivity σ_S can be determined by their critical frequency ω_S^C , using eq 2.7 and assuming a typical aspect ratio $l_{NT}/r_{NT} = 800$ for as-produced HiPco nanotubes [42, 41]. Previous studies on DEP separation [16, 17, 19, 18, 39] report that the semiconductors critical frequency is on the order of $f_S^C = 1 \text{ MHz}$. Therefore here we consider $\omega_S^C = 2\pi f_S^C$. These studies also reveal that the metallic tubes $Re[K_M^{\parallel}]$ factor remains approximately constant for frequencies around ω_S^C , as sketched in fig. 2.1. Thus, here we take $\sigma_M = 10^3\sigma_S$ for the metallic SWNTs conductivity.

The polarization ratio $P(\omega)$ becomes a function of only the field frequency considering these material parameters. Frequencies higher than ω_S^C , and lower than the metallic SWNTs critical frequency ($\approx 10^3\omega_S^C$), allow sufficiently broad regions *SB* and *SH*, in fig. 5.1, for separation. As an example, a frequency $\omega = 3\omega_S^C$ yields one order of magnitude difference between the metallic and semiconducting SWNTs polarizability ($P(\omega) \simeq 10$).

Chapter 6

SWNT Dimensions

The statistics of HiPco generated SWNT lengths have been studied using AFM imaging, and the Weibull distribution function (W) was shown to have the best fit to the measured length histograms [41]. The general expression for this distribution is:

$$W(l) = ab(l - l_{min})^{b-1} e^{-a(l-l_{min})^b} \quad , \quad l > l_{min} \quad (6.1)$$

where a and b are the scale and shape parameters, and l_{min} is the minimum length considered.

All the forces and torques listed in eqs 4.1,4.9 are length dependent, so broad distributions make sorting harder. Typical HiPco SWNT length distributions [42, 41] range from $l_{min} \approx 0$ to a few microns. However, recent length separation studies [43, 44] have shown that short nanotubes can be removed in a feasible way up to a significant minimum length, achieving narrower distributions devoid of short SWNTs. These distributions are preferred for type separation; therefore, in this work the length l_{NT} of each SWNT is generated through a random number following a length sorted distribution depicted in fig. 6.1.

All SWNTs are taken to have the same radius $r_{NT} = l^p/800$, where l^p is

Figure 6.1: Weibull SWNT length distribution. The parameters assumed for the distribution are: $a = 6 \times 10^{-6}$, $b = 2.29$, $l_{min} = 0.625l^p$. The standard deviation is $\sigma \simeq 0.2l^p$.

the Weibull distribution peak length.

Particularly the Clausius-Mossotti factor is very sensitive to the rod aspect ratio l_{NT}/r_{NT} , as depicted in the plots of fig. 6.2. Fig. 6.2(a) shows that the critical frequency ω^C decreases monotonically with length, because it takes more time for the charge buildup at the SWNT/medium interfaces (eq 2.7). The semiconductors critical frequency ($\omega_S^C = 1/\tau_S^p$) is taken to be the critical frequency of a SWNT whose length is l^p . Fig. 6.2(b) shows how the $Re[K^{\parallel}]$ factor changes with length at that frequency ω_S^C . For low aspect ratios the induced dipole moment μ_{NT} , given in eq 2.3, scales with $l_{NT}^3/\log(l_{NT})$; for high lengths it just increases proportionally to the volume (V_{NT}), because $Re[K^{\parallel}]$ becomes length independent.

The contour plot of fig. 6.3 depicts the logarithm of the polarization ratio

$P(\omega)$ as a function of frequency and SWNT length. The dashed vertical lines represent the limits of the length distribution in fig. 6.1. The ratio of the curves in fig. 6.2(b) corresponds here to $\omega\tau_S^p = 1$. The length at which those curves split corresponds approximately to the minimum length considered for this study (l_{min}), so that the Weibull distribution lies in a favorable region for separation: $P(\omega_S^C, l_{min}) \geq 1.4$, as shown in fig. 6.3.

For simplicity, when referring to the polarization ratio $P(\omega)$ on the following chapters of this paper it is the one corresponding to the peak length $l_{NT} = l^p$, unless stated otherwise.

Figure 6.2: (a) Critical frequency ω^C in units of $\omega_s^C = 1/\tau_s^p$ as a function of the SWNT length l_{NT} in units of l^p . (b) Real part of the parallel Clausius-Mossotti factor as a function of length at the semiconductors critical frequency ω_s^C . The curve $W(l)$ corresponds to our length distribution in fig. 6.1. Both quantities are shown for Metals (*blue*) and Semiconductors (*red*).

Figure 6.3: Color contour plot of the polarization ratio $P(\omega)$ (in logarithmic scale) as a function of frequency ω , in units of $\omega_S^C = 1/\tau_S^p$, and the SWNT length l_{NT} in units of l^p . The region inside the dashed lines corresponds to the length distribution in fig. 6.1.

Chapter 7

Initial Separation Conditions

The initial device conditions shall be chosen by setting the following dimensionless ratios relative to a metallic SWNT with length l^p :

$$\frac{R_2}{l^p} = 10^3 \quad (7.1)$$

$$\frac{U_R^{DEP}(R_2)}{k_B T} = 10 \quad (7.2)$$

$$\frac{T^{DEP}(R_2 \rightarrow R_1)}{T^{BM}(R_2 \rightarrow R_1)} = 0.1 \quad (7.3)$$

$$Pe(R_1) = \frac{\partial v_f / \partial r|_{R_1}}{DR} = 0.01 \quad (7.4)$$

$U_R^{DEP}(R_2)$ is the rotational DEP energy (equal to the maximum torque magnitude) at R_2 . $T^{DEP}(R_2 \rightarrow R_1)$ is the analytically calculated transit time for a SWNT aligned with the field lines to cross the channel radially with just the DEP and viscous force ($F_{DEP}^{\parallel}(r) = \zeta^{\parallel} \frac{dr}{dt}$). This time interval is given by:

$$T^{DEP}(r_i \rightarrow r_f) = \frac{\zeta^{\parallel}(r_i^4 - r_f^4)}{4V_{NT}\epsilon_m Re[K_M^{\parallel}]} \left(\frac{\log[R_2/R_1]}{V_{AC}/\sqrt{2}} \right)^2 \quad (7.5)$$

$T^{BM}(R_2 \rightarrow R_1)$ is the time to randomly diffuse a distance $d = R_2 - R_1$, obtained with the Einstein diffusion equation: $d^2 = 6Dt$. The inverse of the dimensionless number in eq 7.3 is the ratio of the average DEP velocity over diffusion.

The last ratio (eq 7.4) is the Peclet number (Pe) at the position of highest shear, which relates the flow and Brownian torque. With such low Pe shear cannot overcome Brownian motion to cause flow alignment. In this case the magnitude of the DEP torque on metals (eq 4.11) versus the flow torque (eq 4.12) is $M_M^{DEP}/M^F = 1551.28$ at R_2 .

At the channel entrance ($r = R_2$), our system is placed in the preferential regime *SB* of fig. 5.1 using the parameters in eqs 7.1-7.4, and provided that $P(\omega) \geq 10$.

Chapter 8

Simulation Conditions

The Brownian dynamics algorithm was implemented in Fortran 90 code using Message Passing Interface (MPI) for parallel computation on distributed memory systems (typically 20-100 processors). The Rice ADA Cray cluster was the computational environment used to run the programs. It is a 632 AMD64 CPU core machine with dual core CPUs and Rapid Array Interconnect. Each CPU is a 2.2 GHz AMD Opteron with 1 MB L2 cache.

Every simulation was performed using 9000 SWNTs from which 3000 were metallic and 6000 were semiconductors, to mimic equidistribution of SWNT chiralities (n,m) . This is statistically a sufficiently high number of particles for all the calculations, as discussed in Section 10.2 below.

The time step used was always chosen to be less than the maximum time step allowed for the integration of a metallic tube's rotational motion, calculated using eq 4.17.

Chapter 9

Results using only DEP

A convenient natural time unit to use in the analysis of the SWNTs' translational motion is the analytically calculated transit time for a metallic tube, of length l^p and aligned with the field lines, to go from the injection point R_i to the inner wire R_1 ($T_M^{DEP}(R_i)$); determined with eq 7.5.

The simulation runs until all metallic tubes are collected; the transit or collection time t^{Col} is recorded. Figure 9.1 displays the number of collected SWNTs (N^{Col}) as a function of t^{Col} in units of $T_M^{DEP}(R_i)$. For both polarization ratios $P(\omega)$ shown in the graphic, the behavior of metallic tubes is the same because this would correspond to changing the frequency next to ω_S^C , where the Clausius-Mossotti factor on metals remains invariant.

The histogram of polydisperse length metallic tubes is compared with the one of a monodisperse length $l_{NT} = l^p$ population. The polydisperse peak is shifted left relative to the monodisperse due to the Weibull distribution right skewness. This yields slightly more tubes with $l_{NT} > l^p$, which implies a higher average DEP force since the induced dipole moment on metallic SWNTs scales with $l_{NT}^3 / \log(l_{NT})$ (see chapter 6).

For $P(\omega) = 10$ the DEP energy on semiconducting SWNTs is low. The ratio in eq 7.2 gives $U_R^{DEP}(R_2)/k_B T = 0.9$ for semiconductors, which positions

Figure 9.1: Histograms of the number of collected SWNTs N^{Col} , normalized by the corresponding number of injected tubes N^{Inj} , as a function of the transit or collection time t^{Col} in units of $T_M^{DEP}(R_i)$. Results are shown for metallic tubes with a polydisperse Weibull length and with a monodisperse length equal to the Weibull distribution peak $l_{NT} = l^p$. The behavior of polydisperse length semiconductors is shown for $P(\omega) = 3$ and $P(\omega) = 10$. For both polarization ratios the behavior of metallic tubes is the same. The peak at $t^{Col}/T_M^{DEP}(R_i) \approx 0.3$ for semiconductors corresponds to the tubes that diffused from R_i to the outer wall at R_2 .

them in the Brownian regime of the phase map in fig. 5.1. That explains the existence of a single semiconductors collection peak at $t^{Col}/T_M^{DEP}(R_i) \approx 0.3$,

which corresponds to the tubes that just diffuse from the injection point to the outer cylinder wall at R_2 . For $P(\omega) = 3$ this diffusion peak is also present, however there is also some collection at R_1 corresponding to the small peaks present for $t^{Col} > T_M^{DEP}(R_i)$.

To quantify the degree of separation we used two normalized quantities [20]:

- **Separation Efficiency (α):** This function is mainly dependent on the collection of metallic SWNTs. It is one if all metallic tubes have been collected and there are still some semiconductors left in solution:

$$\alpha = \frac{N_S^{sol.}}{N_S^{sol.} + N_M^{sol.}} \quad (9.1)$$

where the superscript *sol.* denotes SWNTs left in solution (not collected).

- **Yield of Semiconductors (Y):** Fraction of semiconducting SWNTs that remain dispersed and exit the device:

$$Y = \frac{N_S^{sol.}}{N_S^{inj.}} \quad (9.2)$$

The ideal situation is when both of these ratios are equal to one, meaning that all metallic SWNTs were collected and all semiconductors were left in solution. The graphics in fig. 9.2 show the efficiency and yield values as a function of the channel aspect ratio L/R_2 , for three different polarization ratios $P(\omega)$.

These plots give us information about the axial position (y) at which SWNTs are collected for both species. The α curves in fig. 9.2(a) show a minimum at the position where the semiconducting tubes reach the outer wall at R_2 by simple diffusion. When all the metallic tubes are collected the function reaches unity.

Figure 9.2: (a) Efficiency α as a function of the channel aspect ratio L/R_2 , for three polarization ratios $P(\omega)$. The initial α is equal to the fraction of injected semiconductors ($2/3$). (b) Yield Y as a function of L/R_2 . When α reaches its maximum value, Y is lower than 0.4 for the three $P(\omega)$. The behavior of the system for $P(\omega) > 10$ does not change significantly.

It is observed that α and Y do not change considerably for polarization ratios $P(\omega) > 10$. This is because the dimensionless parameters listed in chapter 7 were chosen so that semiconducting SWNTs with polarizability at least one order of magnitude lower than the one of metallic tubes will have almost no DEP response (regime *SB* of phase diagram in fig. 5.1).

At the channel length where α reaches its maximum ($L \approx 125R_2$) the Yield is no longer good ($Y < 40\%$). That is due to the significant percentage of semiconductors which diffuse to R_2 , and therefore get collected before the metals (see histogram in fig. 9.1).

This diffusion problem can be eliminated by using an additional small electrophoretic (EP) force that acts on the charged surfactant micelles of both SWNT species and forces the semiconductors to remain in solution, pushing them away from the top electrode.

Chapter 10

Separation with Dielectrophoresis (DEP) and Electrophoresis (EP)

10.1 Electrophoresis on SWNTs

An EP force F^E can be added to the DEP force by adding a DC offset V_{DC} to the AC voltage. This force is proportional to the net charge on the nanotubes, q_{NT} , and to the DC electric field E^{DC} generated by the offset voltage:

$$\mathbf{F}^E(\mathbf{r}) = q_{NT}\mathbf{E}_{DC}(\mathbf{r}) = \frac{q_{NT}V_{DC}}{\log[R_2/R_1]} \frac{\hat{\mathbf{r}}}{r} \quad (10.1)$$

The SWNTs' net charge comes from the polar surfactant molecules wrapped around their surface [14, 15]. Therefore, this force is taken to act equally on metallic and semiconducting tubes because there is no type selective attachment between the surfactants and SWNTs.

The EP force can considerably increase the amount of semiconductors

that remain in the flow region; improving the output yield Y . For that purpose, the DC positive electrode must be applied to the inner wire (for negatively charged surfactants), so that $\mathbf{F}^E$ points inward (like $\mathbf{F}^{DEP}$).

The value of q_{NT} for a certain tube depends on the type of surfactant and should be proportional to the nanotube length l_{NT} , assuming a fixed diameter for all SWNTs. Therefore, the product $q_{NT}V_{DC}$ in eq 10.1 is treated as a single variable which obeys:

$$q_{NT}V_{DC} = C_q l_{NT} \quad (10.2)$$

The constant of proportionality C_q is initially fixed by taking the DEP and EP forces on a metallic SWNT with $l_{NT} = l^p$ to be equal at R_2 :

$$\frac{F_M^{DEP}(R_2)}{F^E(R_2)} = 1 \quad (10.3)$$

F^{DEP} scales with $1/r^3$ and F^E scales with $1/r$; thus, condition 10.3 ensures that the highest possible EP force is used without overcoming DEP anywhere inside the flow region. In this way the adding electrophoresis only increases the semiconductor yield without reducing the separation efficiency.

10.2 Results with DEP and EP

The quantities α and Y were calculated as a function of channel aspect ratio and polarization ratio, using the dimensionless parameters in chapter 7 and the additional electrophoretic force previously introduced.

Fig. 10.1 shows that the sorting efficiency α is almost independent of $P(\omega)$. For sufficiently long channels, all metallic SWNTs are collected on the inner wire. The width of the contour regions increases with the broadening of the length distribution; therefore these regions are wider for polydisperse than for monodisperse SWNTs.

Figure 10.2 shows the yield Y . This quantity depends strongly on $P(\omega)$ because it is a function of the amount of semiconducting SWNTs that stay dispersed in solution. Excessively long channels lead to lower Y as more semiconductors get collected. The strongest contribution to the motion length dependence comes from the DEP response when the system is operating in regime SB of the phase diagram in fig. 5.1. Hence, no pronounced differences are expected for the monodisperse and polydisperse SWNTs yield, since this quantity mainly depends on the semiconductors diffusive behavior.

The analysis of these contour plots reveals that L/R_2 should be sufficiently high for good efficiency but, at the same time, it must be low enough to achieve a reasonable yield. To determine the best channel length, we define the performance:

$$\Pi = \frac{N_M^{col.}}{N_M^{inj.}} \frac{N_S^{sol.}}{N_S^{inj.}} \quad (10.4)$$

This ratio gives a quantity that is similar to the efficiency multiplied by the yield, but is also independent of the initial fraction of injected semiconductors versus injected metals. The performance contour plot is shown in fig. 10.3. The region of highest Π for polydisperse SWNTs is the band centered around the optimal channel aspect ratio $L/R_2(opt) = 54.2$. This band is wider for monodisperse SWNTs and slightly shifted towards lower aspect ratios. Moreover, the performance becomes nearly independent of the polarization ratio when $P(\omega) \gtrsim 10$, because that is the threshold above which semiconducting SWNTs cease to exhibit a significant DEP response.

Figure 10.4 depicts the number of collected SWNTs as a function of the collection time, using $L/R_2(opt) = 54.2$. This graph can be compared with fig. 9.1, which shows the same histograms for DEP-only separation. The additional EP force reduces substantially the semiconductor collection peak corresponding to diffusion to the outer wall at R_2 , i.e., a greater portion of the semiconducting SWNTs remain in the flow and the yields are substantially

higher. Moreover, the device performs faster; the monodisperse metallic SWNTs peak is now at $t^{Col} \simeq 0.7T_M^{DEP}(R_i)$, whereas in the case of DEP alone the peak collection was at $T_M^{DEP}(R_i)$.

In order to confirm that the ensemble size (3000 metals + 6000 semiconductors) used for the simulations is large enough, error bars were computed for the curves in fig. 10.4 corresponding to polydisperse length metals and semiconducting SWNTs with $P(\omega) = 10$. These errors were calculated by running two simulations for each case, with distinct random number seeds in every processor, and then calculating the absolute value of the difference between the quantities given by both trials. For the $P(\omega) = 10$ semiconductor curve, the error bars are so small that can barely be distinguished, and for the polydisperse metallic SWNTs they are less than 10% of the mean.

Fig. 10.5 shows the average tube orientation relative to the radial direction $\mathbf{r}$, as a function of time. Metallic SWNTs quickly align with the field direction, whereas semiconductors remain more randomly oriented at frequencies close to the critical one, as expected from the diagram in fig. 5.1. The same was observed by [19] in a recent contribution. The orientation fluctuations shown in the inset are below 2%, which indicates that the total number of particles used is large enough both for metals and semiconductors.

Figure 10.1: Contour plots of the efficiency α (which means the collection of metallic SWNTs) as a function of the channel aspect ratio L/R_2 and polarization ratio $P(\omega)$. (a) Monodisperse length SWNTs with $l_{NT} = l^p$. (b) Polydisperse length SWNTs with a Weibull distributed l_{NT} .

Figure 10.2: Contour plots of the yield Y (which means the amount of semi-conducting SWNTs that remain in the flow) as a function of the channel aspect ratio L/R_2 and polarization ratio $P(\omega)$. (a) Monodisperse length SWNTs with $l_{NT} = l^p$. (b) Polydisperse length SWNTs with a Weibull distributed l_{NT} .

Figure 10.3: Performance Π contour plot. This quantity is similar to the efficiency multiplied by the yield but also independent of the initial fraction of injected semiconductors versus injected metals. (a) Monodisperse length SWNTs with $l_{NT} = l^p$. (b) Polydisperse length SWNTs with a Weibull distributed l_{NT} . The vertical dashed line marks the best channel length at $L/R_2(opt) = 54.2$.

Figure 10.4: Histograms of the number of collected SWNTs N^{Col} , divided by the corresponding number of injected tubes N^{Inj} , as a function of the transit or collection time t^{Col} in units of $T_M^{DEP}(R_i)$. Results are shown for polydisperse (with the distribution in fig. 6.1) and monodisperse ($l_{NT} = l^p$) length metallic tubes. The collection of polydisperse semiconductors is shown for $P(\omega) = 3$ and $P(\omega) = 10$. Error bars are present in the histogram points for Polydisperse Metals and Semic. with $P(\omega) = 10$. Comparing with fig. 9.1, we can see that the peak that was at $t^{Col} / T_M^{DEP}(R_i) \approx 0.3$, for semiconductors which diffused to R_2 , practically disappears due to the additional EP force.

Figure 10.5: Average SWNT orientation for polydisperse and monodisperse length metallic tubes, and polydisperse semiconductors using $P(\omega) = 3$ and $P(\omega) = 10$. θ is the angle between the nanotube direction $\mathbf{u}$ and the field direction $\mathbf{r}$. The inset shows the percentage difference between the results of two simulations with distinct random numbers. The time unit used here is the rotational diffusion relaxation time $\tau_R = \frac{1}{2D_R}$ for a tube with $l_{NT} = l^p$.

Chapter 11

Nelder and Mead Optimization algorithm

Conditions mentioned in chapter 7, together with the optimal channel aspect ratio calculated in the previous section, yield a performance of about 83% for $P(\omega) = 10$. However, these conditions can be tuned to improve the sorting.

To find the overall maximum performance Π , we make use of a multidimensional direct search algorithm known as the Nelder and Mead or Downhill Simplex method [46, 47]. This method has found widespread use in the optimization of nonlinear functions whose gradient is very expensive (or practically impossible) to calculate. It has also been shown to work well for stochastic problems, as in the present case where we want to determine the set of 6 dimensionless numbers, listed in the first column of table I, that maximize the performance function Π . These 6 quantities can be treated as the coordinates of a 6-dimensional space in which Π is defined.

The basic notion behind the Nelder and Mead technique for maximizing (or minimizing) a function with n variables is to pick $n+1$ starting points, at which the function is evaluated, forming an n -simplex (an n -dimensional analogue of a triangle). The procedure then iteratively moves and redimen-

sions the simplex along the coordinate space as better points are found, until some desired bound is obtained.

The range of each variable is restricted to avoid searching in physically forbidden regions, or where it is known *a priori* that the performance is going to be low. The two most crucial physical limits are:

- The flow regime must be laminar, i.e., the Reynolds number $Re < 1000$.
- The channel must be much larger than the SWNTs ($R_1/l^p > 10$ and $(R_2 - R_1)/l^p > 100$), in order for condition in eq 2.2 to be verified.

These boundaries set an upper limit to the *SH* separation regime in the phase portrait of fig. 5.1. Lower and upper bounds are assigned to each coordinate in the 6-dimensional space. To restrict the searching direction inside our chosen domain the maximizing function is set to a low value at any point outside the allowed region, so that out of bounds points are not considered for the new simplex in the next iteration.

The search for the global performance maximum, within the defined 6-dimensional domain, can be made substantially faster with a good choice of the initial 7-point simplex. This initial simplex must be nondegenerate, i.e., its 6D volume cannot be zero, and it should cover a significant portion of the total domain volume. Therefore, six of the initial simplex vertices are set close to different domain boundaries. The 7th point is set with the previous parameters used in the simulations of Section 10.2, which place our system in the *SB* regime of fig. 5.1. These conditions constitute a good initial guess for our searching direction, which cause the simplex to shrink in the first iterations towards the 7th point. Afterwards it reflects and expands towards regions of higher Π until it shrinks to a single point at the peak performance found.

A minimal polarization ratio $P(\omega) = 10$ is taken for the optimization, as significant differences are not expected for higher $P(\omega)$ according to fig.

Dimensionless quantity	(a) Polydisperse Weibull Length $W(l)$	(b) Bidisperse Length (l^p and $l^p/5$)
$\frac{R_2}{l^p}$	587.5	477.5
$\frac{U_R^{DEP}(R_2)}{k_B T}$	118.9	187.02
$\frac{T^{DEP}(R_2 \rightarrow R_1)}{T^{BM}(R_2 \rightarrow R_1)}$	9.42×10^{-3}	6.11×10^{-3}
$Pe(R_1)$	18.13	28.97
$\frac{F_M^{DEP}(R_2)}{F^E(R_2)}$	10.9	23.7
L/R_2	4765.96	6157.07
Performance Π	0.991	0.562

Table 11.1: Optimal operational conditions calculated by the Nelder and Mead direct search algorithm using $P(\omega) = 10$. These dimensionless numbers were defined in chapter 7 and 10.1.(a) Using these conditions almost total metallic vs. semiconducting SWNT separation is achieved for polydisperse length SWNTs.(b) In this bidisperse case the maximum Π that can be obtained is 0.5625.

10.3.

The algorithm is able to reach a maximum within about 60 iterations. However, generally this is a local maximum in the search domain. To find the global performance maximum, the Nelder and Mead program is sequentially run with different initial 7-point sets that include the previously obtained local maxima. Finally, the algorithm reaches the absolute peak performance with the dimensionless values shown in table I.

For polydisperse length SWNTs, the conditions in table I(a) result in almost total collection of metallic tubes with no collection of semiconductors. Interestingly, the optimization algorithm converges to points with higher Pe numbers than the one initially used (given by eq 7.4). With the quantities in Table I(a), the magnitude of the SWNT DEP torque (eq 4.11) versus the flow

torque (eq 4.12) is $M_M^{DEP}/M^F = 9.68$, for a metallic nanotube with length l^p at R_2 ; whereas for a semiconductor is $M_S^{DEP}/M^F = 0.88$. Therefore, near the outer channel wall, the optimized system is in region SH of the phase diagram in fig. 5.1. The SH regime is expected to yield higher performance than the SB since the semiconductors DEP response is substantially reduced upon flow alignment. Another advantage of using higher Pe is that it enables larger flow rate of separated SWNTs; a higher main flow allows higher injection flow, as discussed in Appendix A, i.e., higher throughput.

Column (b) of table I shows the results of a simulation using equal number of SWNTs of just two lengths (l^p and $l^p/5$), to mimic the effect of a sample where the short SWNTs have not been removed. The graphics in figs. 6.2(b) and 6.3 indicate that for $l_{NT} = l^p/5$ the semiconducting and metallic SWNTs DEP response should be very similar at frequencies on the order of ω_S^C . Therefore, if one metallic $l^p/5$ tube is collected then two semiconducting $l^p/5$ tubes should also be collected, because each simulation has twice the number of semiconductors ($N_S^{inj.} = 2N_M^{inj.}$). In these conditions the performance is badly degraded, and the maximum achievable value is $\Pi = 0.5625$.

Nevertheless, even if short SWNTs are present, good separation can still be achieved by using higher frequencies. The contour plot in fig. 6.3 shows that a polarization ratio $P(\omega, l^p/5) \approx 10$ is obtained for $l^p/5$ tubes at a frequency $\omega = 45\omega_S^C$. The bidisperse case optimization was repeated with these conditions and a high peak separation performance $\Pi = 0.998$ was achieved as expected.

Chapter 12

Conclusions

A novel DEP separation device using a coaxial cylindrical geometry is studied theoretically in this work.

The different regimes that characterize the behavior of metallic and semi-conducting SWNTs in a DEP-flow device are analyzed. Two preferential regimes are identified for separation between the SWNT types. A set of dimensionless conditions is given that place the system in the first regime SB , where the metallic SWNTs motion is DEP dominated and the semi-conductors motion is diffusive. The expected behavior of both SWNT types is confirmed with the numerical results presented. Moreover, it is shown that the sorted SWNTs yield can be substantially increased by adding an electrophoretic force acting on the charged surfactant micelles.

A direct search optimization algorithm is implemented to obtain the parameters that maximize the separation performance. The algorithm shows that optimal separation is achieved in the regime SH , where the semiconducting SWNTs align with the flow, whereas the metallic SWNTs orient with the field. We examine the effect of short SWNTs and we find that, at fixed frequency, short SWNTs can degrade performance significantly; however, they can be separated successfully by raising the DEP frequency to

establish a sufficiently large polarization ratio for the shorter SWNTs.

This work will be useful in developing and optimizing experimental devices for flow-DEP separation of SWNTs.

Chapter 13

Future Work

Our group is now engaged in the construction and testing of the DEP separation device proposed in this work. Preliminary tests have indicated a good match between predicted and experimental results for SWNTs dispersed in a non-ionic surfactant (pluronic F108).

In order to accurately compare theoretical and experimental results it is of key importance to develop other studies in parallel with these to measure the effective permittivity and conductivity values for the various SWNT chiralities and surfactants. These results are crucial for the improvement of the modelling on SWNT dielectrophoresis.

Several approaches can be taken to access these fundamental SWNT quantities. Our group is interested in the development of two particular bulk, non-contact approaches described below.

13.1 Dielectric Measurements with a Coaxial Probe

This work was initiated by Seth Marvel and coworkers to determine the approximate distribution of room temperature longitudinal conductivities in SWNT samples. This is obtained by applying a Maxwell Garnett model for randomly oriented prolate ellipsoids to empirical dielectric spectra of aqueous SWNT suspensions.

The dielectric spectra of solutions is measured using a single-port coaxial probe and vector network analyzer, in a fashion similar to that previously reported [50]. The current setup can measure the spectra of homogeneous solutions (without inclusions) very precisely. However, when measuring the dielectric response of well dispersed SWNT decants (concentrations $< 100\text{ mg/L}$) it does not resolve the SWNT inclusions dielectric contribution. High SWNT concentrations ($\sim 500\text{ mg/L}$) need to be used in order to distinguish the SWNT dielectric response from the surrounding medium. At these high concentration the SWNTs are mostly bundled, therefore the method probes a single conductivity distribution corresponding to the one of SWNT ropes.

Further improvement in the dispersion techniques and in the probe resolution may allow this process to distinguish different conductivity distributions for the different SWNT types.

13.2 Uniform Electric Field Alignment

The electric alignment of anisotropic particles (tobacco mosaic virus (TMV), attapulgite, gold nanorods [48], etc.) is often studied by electro-optical techniques such as birefringence, electric light scattering and dichroism [51]. The application of these techniques to carbon nanotubes can be used to determine

their dielectric properties.

The measurement of the alignment time of a nanotube in an applied field E yields the ratio between the electric and the viscous fluid torque. After alignment, if the field is turned off we can measure the relaxation time that it takes for the SWNTs to randomly orient. This time interval gives a ratio between the viscous and brownian torque ($k_B T$). The value of the viscous torque can be determined from this second relaxation regime; and then plugged in the ratio obtained in the first alignment regime to get the electric torque magnitude. The electric torque is proportional to $\Delta\alpha E^2$, where $\Delta\alpha = \alpha^{\parallel} - \alpha^{\perp}$ is the anisotropy in induced polarizability. This quantity is a function of the SWNT effective permittivity, conductivity and aspect ratio.

Both techniques described in this chapter can also be used to quantify the degree of type enrichment of a given solution after separation. Conclusive proof of total metallic vs. semiconductor separation should come from the match between the results given by these two methods plus Raman, Absorption and 4-point probe film conductivity measurements.

Appendix A

Analysis of SWNT starting condition

In this section the SWNT starting condition is modelled by considering that the nanotube solution is injected with a flow Q_{inj} into the solvent flow Q , from an aperture at the cylinder wall. This is illustrated in fig. A.1.

The position of the separation surface between the two converging flows can be determined by assuming the following conditions [49]:

- Both inlet and main flows are fully-developed and steady
- Fluids are perfectly miscible (no surface tension, similar fluids)
- The inlet and outlet have the same geometrical shape (circular)
- Injection flow inertia is sufficiently small, i.e., a Reynolds number $Re^{Inj} \leq 10$

If these conditions are verified, the interface can be assumed to be a planar surface at a position h calculated by the requirement:

$$\frac{Q_{inj}}{Q_T} = \frac{\int_{R_2-h}^{R_2} \int_0^{\sqrt{R_2-z^2}} v_f(x, z) dx dz}{\int_0^{R_2} \int_0^{\sqrt{R_2-z^2}} v_f(x, z) dx dz} \quad (\text{A.1})$$

where $v_f(x, z)$ is the fully-developed velocity profile inside the main hollow tube, and $Q_T = Q + Q_{inj}$ is the total volumetric flow rate in the main stream after the injection. The integration is performed in Cartesian coordinates since the interface is located at $z = R_2 - h$, as depicted in fig. A.1.

Figure A.1: Sketch of the planar layer boundary between the injection and main flow, at $z = R_2 - h$. It is assumed that the injection Reynolds number $Re^{Inj} \leq 10$.

If the injection Reynolds number Re^{Inj} is on the order of one the flow coming from the inlet becomes fully-developed within a few channel diameters downstream of the junction.

The separation layer position h depends mainly on the flow ratio $\frac{Q_{inj}}{Q_T}$. This position can be determined for the initial conditions considered in this article, determined by the ratios in chapter 7, considering a two order of magnitude difference between the flows:

$$\frac{Q_T}{Q_{inj}} = 100 \Rightarrow h = 0.128R_2 \quad (\text{A.2})$$

The SWNTs initial positions can be taken as random numbers located in a cross sectional area of the channel, at $y = 0$, between $z = R_2 - h$ and $z = R_2$. The probability p for a nanotube to be at a position (x, z) in that starting surface should be proportional to the fluid velocity at that point:

$$p(x, x + dx; z, z + dz) = C v_f(x, z) dx dz \quad (\text{A.3})$$

where C is a normalization constant given by the inverse of Q_{inj} .

The symmetry of v_f in x allows us to simplify the probability distribution to a single variable by integrating $p(x, z)$ over the x domain. This yields the contracted distribution function $f(z)$:

$$f(z, z + dz) = 2 \int_0^{\sqrt{R_2 - z^2}} p(x, x + dx; z, z + dz) \quad (\text{A.4})$$

which corresponds to the probability of finding a nanotube at a position z within the starting surface. The associated cumulative distribution function ($F(z)$) is obtained by integrating eq A.4 from $R_2 - h$ to z . The inverse function $G(R)$ outputs the z value that corresponds to a certain cumulative probability R . The position of 50% probability is located at $\bar{z}_i = G(0.5) = 0.905R_2$; this gives a mean value for the SWNTs starting radius.

In the simulations performed throughout the paper it is assumed that the SWNTs initiate their motion at $R_i = 0.9R_2$, which matches the mean starting position for a flow ratio $\frac{Q_T}{Q_{inj}} = 100$. In order to test the validity of single point injection at $R_i = G(0.5)$, two of the curves in fig. 10.4 are compared in fig. A.2 with the corresponding histograms using nanotubes initiated at random z positions within the starting surface (following distribution in eq A.4).

Figure A.2 shows that there is only a small distinction at the beginning of motion between the general case of random R_i and the assumption of point injection at $R_i = G(0.5)$. This is because the small SWNT fraction initiated close to R_2 , in the random R_i case, has a higher probability of sticking to the outer cylinder wall. This effect is more significant in the semiconducting SWNTs' motion, and results in a discrepancy of 0.06 in the calculated device performance.

Figure A.2: Comparison between the SWNT collection histograms of fig. 10.4 assuming point injection and with a random initial position in z inside the starting surface. Only the one polarization ratio $P(\omega) = 10$ is considered, for polydisperse length tubes. Using a flow ratio $Q/Q_{inj} \approx Q_T/Q_{inj} = 100$ there is a decrease of 0.06 in the performance of the device relative to single point injection.

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