Polyelectrolyte Dynamics in Confined Flows

Petr Hotmar

Department of Chemical and Biomedical Engineering
Florida State University

Dissertation Defense

February 11, 2013

Outline

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1. Introduction: polyelectrolyte dynamics and confinement
2. Voltage-driven polymer translocation through entropic traps and nanopores
3. Kinetic theory of a charged FENE dumbell in confined flow under applied pressure and electric fields
4. Brownian dynamics of polymer migration in combined pressure-driven and electrophoretic flows
5. Green's function for Stokes flow in a rectangular channel

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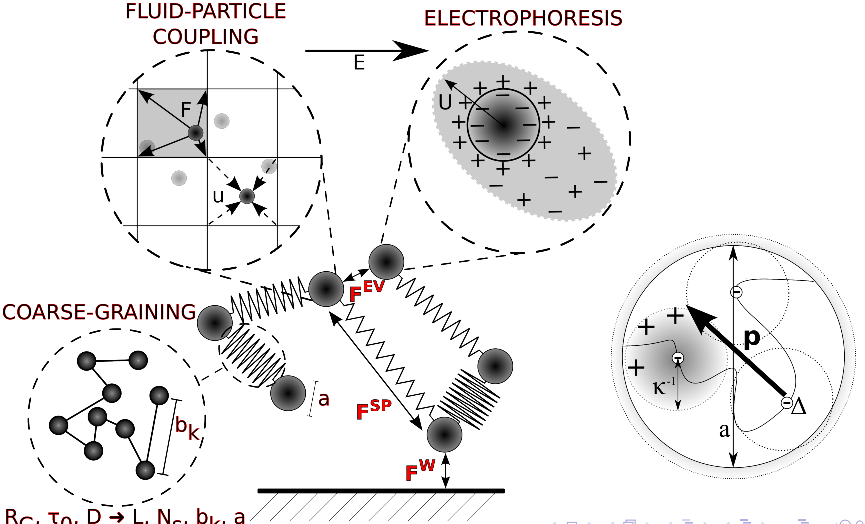
1. Introduction: HIs in confinement
2. Translocation through entropic traps
3. Kinetic theory of non-linear dumbell in electrolyte
4. Brownian dynamics of polymer migration
5. Stokeslet in a rectangular channel

Introduction

Forces acting on beads results in long-range velocity perturbations that favor cooperative motion of chain segments.

- In bulk, polyectrolyte chains diffuse essentially as non-draining spherical objects of size R_g (Zimm behavior, $D \sim N^{3/5}$).
- However, polymer segments appear to be electrophoresing independently (free-draining Rouse behavior) under applied external electric fields ($\mu \sim N^0$).
- In confinement, inclusion of hydrodynamic interactions due to applied electric fields is critical in explaining polymer migration behavior consistent with experimental observations.

Polymer model



$R_G, \tau_0, D \rightarrow L, N_s, b_k, a$

Hydrodynamic interactions for non-electric forces

- Stokes flow with $(\nabla \cdot \mathbf{v}' = 0)$:

$$-\nabla p + \eta \Delta \mathbf{v}' = \sum_{j}^{N_b} \mathbf{F}_j \delta(\mathbf{r} - \mathbf{r}_j)$$

- Velocity perturbation due to $\mathbf{F}$: $\mathbf{v}'_i = \sum_j \boldsymbol{\Omega}_{ij} \cdot \mathbf{F}_j$
- Hydrodynamic-interaction tensor (Green's function, Stokeslet)

$$\boldsymbol{\Omega}_{ij} \equiv (1-\delta_{ij})\boldsymbol{\Omega}_{ij}^{OB} + \boldsymbol{\Omega}_{ij}^{W}, \text{ where } \boldsymbol{\Omega}_{ij}^{OB} = \frac{1}{8\pi\eta r_{ij}}\left(\mathbf{I} + \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2}\right) \propto \frac{1}{r}$$

- Mobility tensor $\boldsymbol{\mu}_{ij} = \delta_{ij}\mu\mathbf{I} + \boldsymbol{\Omega}_{ij}$

Hydrodynamic interactions in electrolyte

- Stokes flow with $(\nabla \cdot \mathbf{v}' = 0)$:

$$-\nabla p + \eta \Delta \mathbf{v}' = \sum_{j}^{N_b} \left(\mathbf{F}_j \delta(\mathbf{r} - \mathbf{r}_j) + \rho_f(\mathbf{r} - \mathbf{r}_j) \mathbf{E}_0 \right),$$

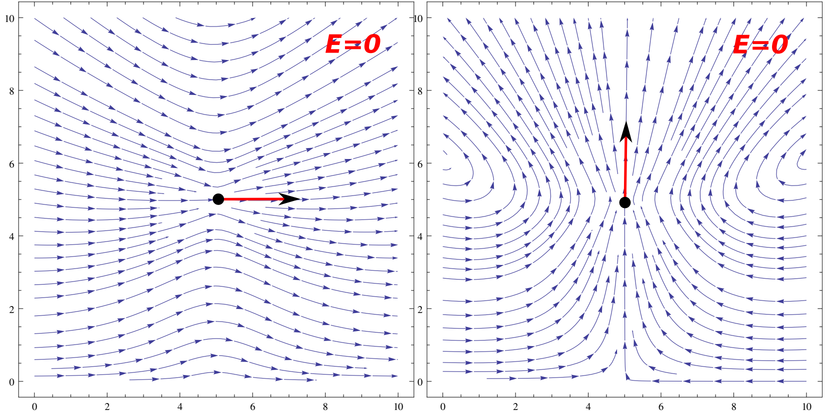
where free-charge density $\rho_f(\mathbf{r}) = -Q\kappa^2 \exp(-\kappa r)/(4\pi r)$

- Velocity perturbation due to $\mathbf{F} = Q\mathbf{E}_0$: $\mathbf{v}'_i = \sum_j \mathbf{\Omega}^e_{ij} \cdot \mathbf{F}_j$
- Electrophoretic Stokeslet $(c = 4\pi\eta\kappa^2)$:

$$\mathbf{\Omega}^e_{ij} \equiv (1-\delta_{ij})\mathbf{\Omega}^{LA}_{ij} + \mathbf{\Omega}^{W,e}_{ij}, \text{ where } \mathbf{\Omega}^{LA}_{ij} = \frac{1}{c r_{ij}^3}\left(\mathbf{I} - 3\frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2}\right) \propto \frac{1}{r^3}$$

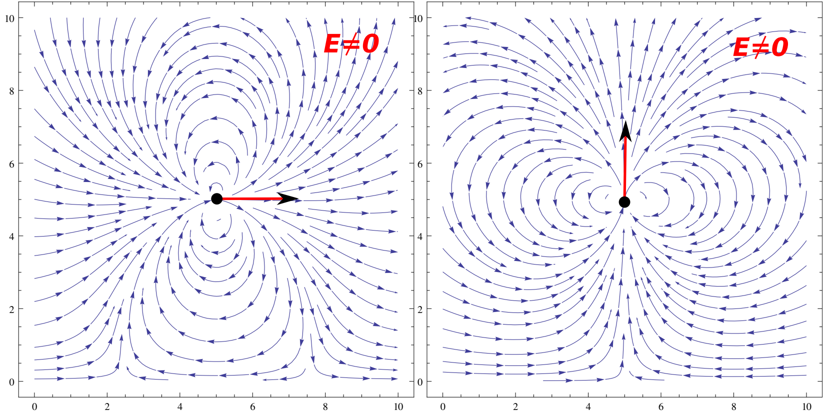
- Electrophoretic mobility tensor: $\boldsymbol{\mu}^e_{ij} = \delta_{ij}\mu_0 \mathbf{I} + \mathbf{\Omega}^e_{ij}$

Disturbance due to regular Stokeslet



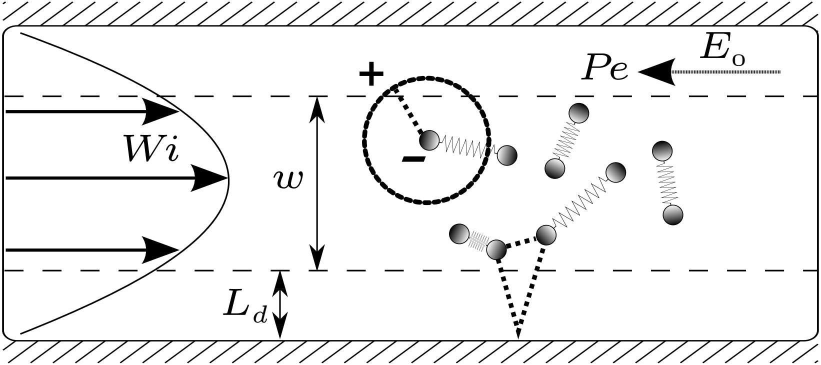
Disturbance velocity field due to point-force of unit strength and oriented parallel (left) and perpendicular (right) to the wall at $y = 0$.

Disturbance due to electrophoretic Stokeslet



Disturbance velocity field due to potential dipole of unit strength and oriented parallel (left) and perpendicular (right) to the wall at $y = 0$.

HIs under flow and electric field in confined electrolyte



Outline

Model description

- **Solvent**: Newtonian, low *Re* limit on overlapping, structured, FD grids
- **Polyelectrolyte**: modified Langevin system subject to relevant forces
- **Coupling**: a semi-empirical hydrodynamic force, interpolation between lattice and off-lattice points

Objective

Model dynamics of polyelectrolytes under electric fields while accounting for hydrodynamic interactions and thermal fluctuations in the fluid.

Hydrodynamic forces

Newton's equations of motion

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i,$$
$$m\frac{d\mathbf{v}_i}{dt} = \underbrace{-\zeta\left[\mathbf{v}_i(t) - \mathbf{U}(\mathbf{r}_i,t)\right] + \mathbf{F}_i^B(t)}_{\mathbf{F}_i^H(t)} + \underbrace{\mathbf{F}_i^{NH}(t),}_{\mathbf{F}^{SP}+\mathbf{F}^{EV}+\mathbf{F}^{W}\left(+\mathbf{F}^{EP}+\mathbf{F}^{DEP}\right)}$$

where fluctuation-dissipation theorem (FDT) requires

$$\left\langle F^B(t)\right\rangle = 0, \quad \left\langle F^B(t)F^B(t')\right\rangle = 2k_bT\zeta\delta(t-t').$$

$\mathbf{F}^B(t)$ is then

$$\mathbf{F}^B(t) = \left(\frac{6k_bT\zeta}{dt}\right)^{0.5}\cdot\mathbf{n}(t).$$

Non-hydrodynamic forces

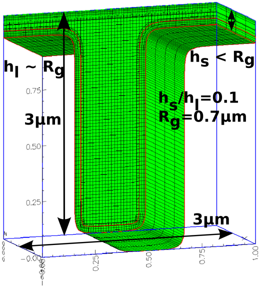
- Spring: semi-flexible Marko-Siggia
- Excluded-volume: soft, Öttinger's potential
- Bead-wall repulsion: Jendrejack's potential
- Normal wall distance: solve Eikonal equation (for complicated domains, e.g. trap)
  - Method of lines, stabilized Adams-Bashforth, neighbor search on Kd-tree
- Electric field: Debye-Hückel approximation, linearized Poisson-Boltzmann equation
- $\mathbf{U} = \mathbf{u} + \mathbf{u}'$: solve Navier-Stokes
  - $\mathbf{f}^{tot}(\mathbf{r}, t) = \mathbf{f}(\mathbf{r}) + \mathbf{f}^{prt}(\mathbf{r}, t) + \underbrace{\mathbf{f}^{thm}(\mathbf{r}, t)}_{\nabla \cdot \mathbf{S}}$, where Landau-Lifshitz stochastic flux tensor $\mathbf{S}$ has covariance given by the FDT

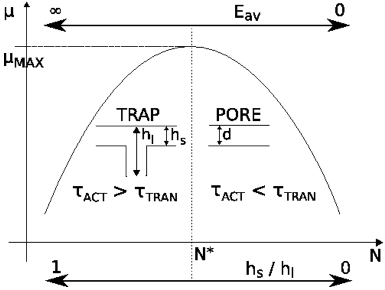
Predictor-Corrector

- To solve the coupled system at discrete times t_n for $n \in [0, \ldots N_t - 1]$:
  1. Solve, off-lattice, Langevin system with $\mathbf{F}_n^{prt} = \mathbf{F}^{prt}(\mathbf{R}_n, \mathbf{u'}_{SS,n})$ to obtain $\mathbf{R}_{n+1}$.
  2. Predict particle force $\mathbf{F}_*^{prt}(\mathbf{R}_{n+1}, \mathbf{u'}_{SS,n})$ and extrapolate to neighboring nodes.
  3. Solve, on-lattice, Navier-Stokes system with $\mathbf{f}_*^{prt}$ to obtain $\mathbf{u'}_{SS,n+1}$.
  4. Interpolate velocity perturbation to bead locations and correct particle force $\mathbf{F}_{n+1}^{prt}(\mathbf{R}_{n+1}, \mathbf{u'}_{SS,n+1})$.
- Model validation: Long-time tail of VAF, free-draining and HIs in bulk (stretch-coil, Rouse, Zimm)

Entropic trapping, theory

- EP separation: free-solution vs gel vs “artificial” gel
- Long molecules will travel faster than the short ones!

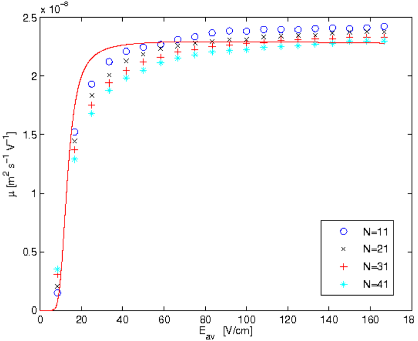


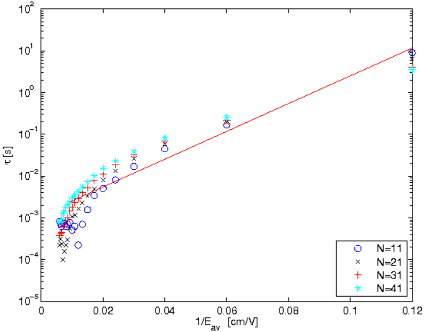


$$\tau_{trap} \sim \tau_0 \exp(\Delta F), \quad \Delta F \sim m - E_s m^2, \quad \tau_0 \sim N^{-\nu} D^{-1}$$

Entropic trapping, simulations

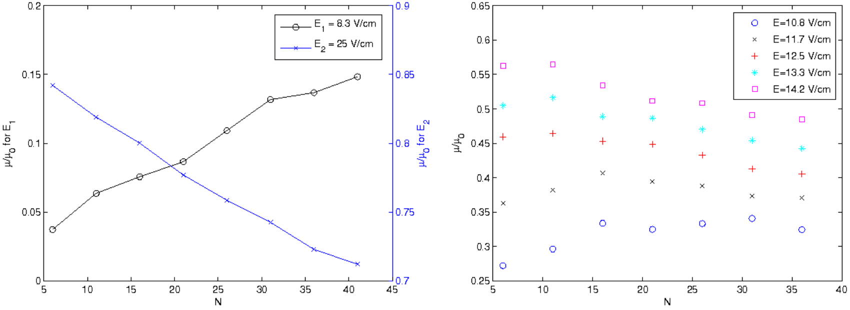
- Charge screening due to counter-ion condensation. Using Rouse model and experimental μ_0, we estimate counter-ion screening at 24 %



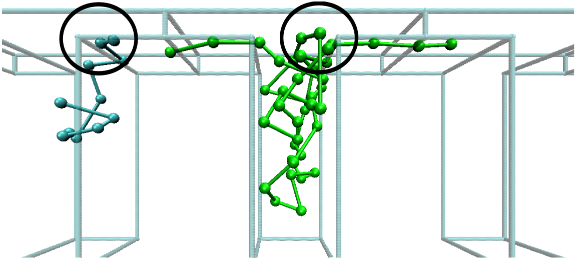


Entropic trapping, predictions

- Limiting behaviors of μ observed for $E = 8.3$ V/cm and $E = 25$ V/cm. The maximum occurs for $E \sim 12$ V/cm.



Entropic trapping, animation snapshot



Snapshots of short (N=11) and long (N=41) chains at time t=1s. Long chain has more beads facing the slit than the short chain and thus higher probability of transit (activation regions circled). While the long chain successfully migrated into the middle trap and nucleated into the next shallow region, the short chain is delayed in the activation stage negotiating the free energy barrier.

Conclusions

Developed a new hybrid discrete-continuum model (Langevin-Navier-Stokes with semi-empirical coupling) for polymer dynamics of dilute solutions under confinement suitable for complicated domains.

- Predicted and quantified mobility transition from the trapping to the free flowing behavior in entropic traps
- Described translocation time dependences of short chains in nanopores

Outline

The overall picture

- Elastic dumbells $(\mathbf{r}_c, \mathbf{Q})$ in Newtonian electrolyte
- Continuity + eq. of motion = Fokker-Planck eq.

$$0 = \left\{ -\frac{\partial}{\partial \mathbf{Q}} \cdot \mathbf{D}(\mathbf{Q}) + \frac{\partial}{\partial \mathbf{Q}} \cdot \frac{\partial}{\partial \mathbf{Q}} \mathbf{\Delta}(\mathbf{Q}) \right\} \psi$$

- Solve by perturbation series $\rightarrow$ distribution of orientations $\psi(\mathbf{Q}, \mathbf{r}_c)$
- Form averages and let wall-normal COM flux $\mathbf{j}_c$ vanish $\rightarrow$ distribution of positions $n(\mathbf{r}_c)$
- What's new: stiffness (FENE) and wall-mediated HIs due to counter-ion clouds

Fokker-Planck equation for ψ

$$\frac{\partial}{\partial \mathbf{Q}} \cdot (\dot{\mathbf{Q}}\psi) = 0, \frac{\partial}{\partial \mathbf{r}_c} \cdot (\langle \dot{\mathbf{r}}_c \rangle n) = 0, \text{ where } \langle \cdot \rangle = \int \cdot \psi d\mathbf{Q}.$$

Balancing Brownian, spring, electric and hydrodynamic forces:

$$\dot{\mathbf{r}}_c = \mathbf{u} + \frac{1}{8}\mathbf{QQ} : \nabla\nabla\mathbf{u} + \frac{1}{2}\bar{\mathbf{\Omega}} \cdot \mathbf{F}^s + \frac{2}{k_b T}\mathbf{D_K} \cdot \mathbf{F}^e - \mathbf{D_K} \cdot \frac{\partial \ln(n\psi)}{\partial \mathbf{r}_c},$$

$$\dot{\mathbf{Q}} = \mathbf{Q} \cdot \nabla\mathbf{u} - 2\mu\mathbf{I} \cdot \mathbf{F}^s - \bar{\bar{\mathbf{\Omega}}} \cdot \mathbf{F}^e - k_b T 2\mu\mathbf{I} \cdot \frac{\partial \ln \psi}{\partial \mathbf{Q}},$$

where $\mathbf{D_K}, \bar{\mathbf{\Omega}}$ and $\bar{\bar{\mathbf{\Omega}}}$ are linearized functions of the HI tensor $\mathbf{\Omega}_{ij}$.

Fokker-Planck equation

$$\frac{2k_b T}{\zeta}\frac{\partial}{\partial \mathbf{Q}} \cdot \frac{\partial}{\partial \mathbf{Q}}\psi - \left(\hat{\boldsymbol{\kappa}} : \frac{\partial \psi}{\partial \mathbf{Q}}\mathbf{Q}\right) + \frac{2a}{\zeta}\mathbf{Q} \cdot \frac{\partial \psi}{\partial \mathbf{Q}} + \frac{2}{\zeta}\left[Q\frac{da}{dQ} + 3a\right]\psi = 0$$

Distribution functions ψ and n

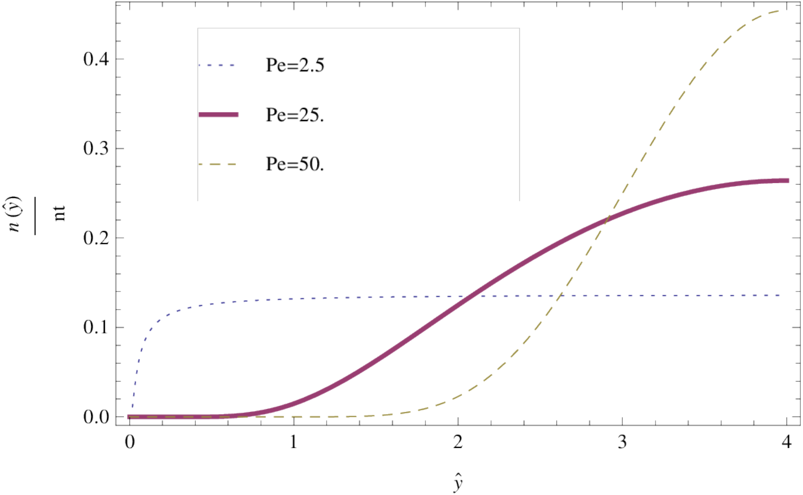
- **Dumbell** $(a, b \equiv \frac{HQ_0^2}{2k_b T})$ under **Poiseuille flow** (Wi) and **electric field** (Pe) in a **slit** $(h, W \equiv y(h-y))$
- Perturbation series solution

$$\psi = f(a, b, \mathbf{Q}, \hat{\dot{\gamma}}, \hat{\omega})$$

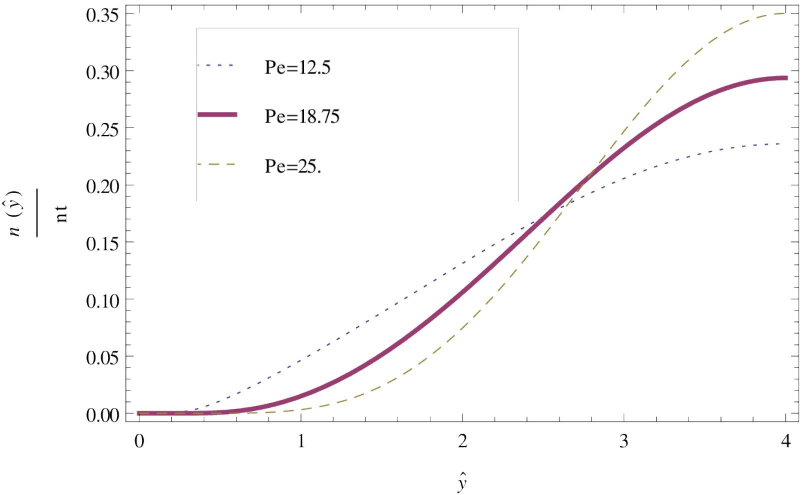
- In SS, the flux of the center-of-mass PDF $n(\mathbf{r}_c)$ normal to the wall must vanish, yielding an ODE for $n(y)$:

$$n\langle \dot{\mathbf{r}}_c \rangle \cdot \mathbf{e}_y = 0 = f(a, b, Wi, Pe, h, W)$$

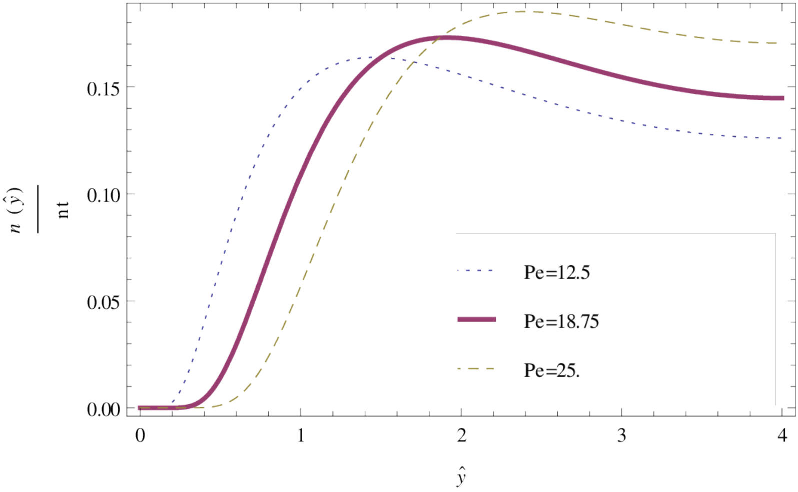
Force only



Flow and force in cooperation

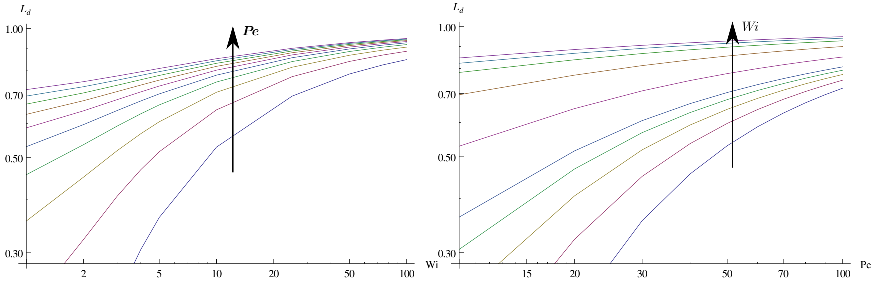


Flow and force in opposition



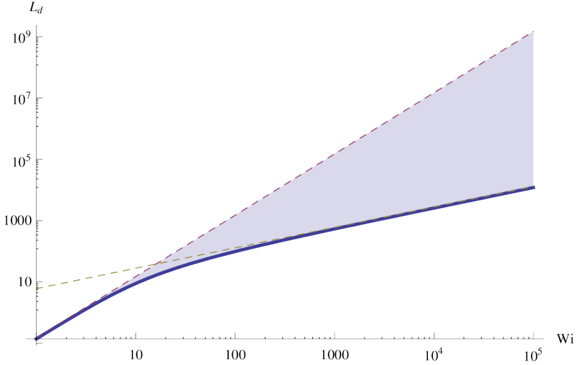
Depletion layer (Wi, Pe)

$$L_d^W = \frac{75M(b)h}{4}Pe^2 + \frac{81N(b)ah}{8}Wi^2 \qquad \left(W \ll \frac{h}{2}\right).$$



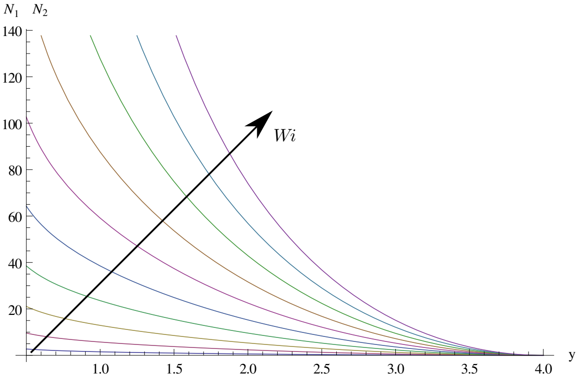
Left: L_d dependence on Wi, for $Pe = 10, 20 \ldots 100$ with $b = 10$ (stiff dumbell). Right: L_d dependence on Pe for $Wi = 1, 2 \ldots 100$ with $b = 10$.

Scaling transition



Left: $L_d \propto Wi^{\alpha_{1,2}}$. Deviation from the quadratic scaling ($\alpha_1 = 2$) is shaded. As $Wi \to \infty, \alpha_2 \to 2/3$. b=500.

Normal stress differences



The difference of normal stress differences N_1 and N_2 (scaled by nk_bT) across the channel width, with $b = 100$, $Pe = 1$ and $Wi = 0.5, 1, 1.5, \ldots 5$.

Stokeslet in Debye-Hückel electrolyte

Objective

Replace all $\mathbf{F}^e$-related HI functions in the equations of motion by the corresponding functions of the electrophoretic HI tensor $\boldsymbol{\Omega}^e_{ij} \equiv (1-\delta_{ij})\boldsymbol{\Omega}^{FS,e}_{ij} + \boldsymbol{\Omega}^{W,e}_{ij}$, retaining only its long-range part.

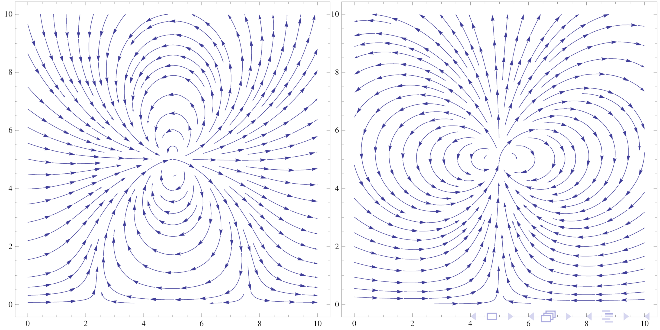
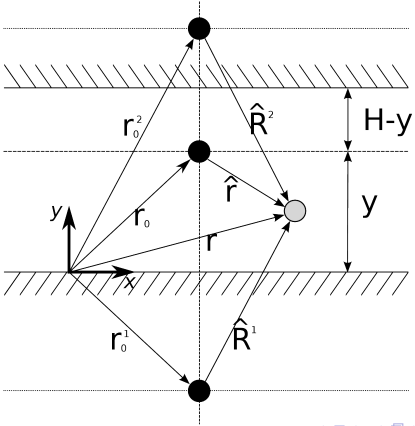


Image system in a slit

- Use an image system based on free-space dipole **D** and other degenerate singularities



Migration tensors $\rightarrow \psi \rightarrow n$

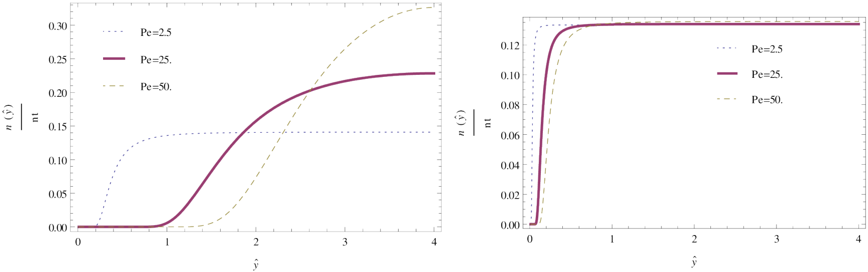
- Introduce reflection operators to ease computations and linearize HI functions around $\mathbf{q} = \mathbf{0}$, to obtain:

$$\bar{\bar{\mathbf{\Omega}}}^{12} = (\lambda^1 + \lambda^2)\bar{\bar{\mathbf{M}}} \cdot \mathbf{q},$$
$$\mathbf{D_K}^{12} = \mathbf{D_K}^1 - D_0\omega \left(\mathbf{I} + 3\mathbf{e}_y\mathbf{e}_y\right)$$

- HI functions $\rightarrow$ Eqs. of motion for $\mathbf{r}_c$ and $\mathbf{Q}$ $\rightarrow$ Fokker-Planck for ψ $\rightarrow$ SS wall-flux ODE $\frac{\partial \ln n(W)}{\partial W} =$

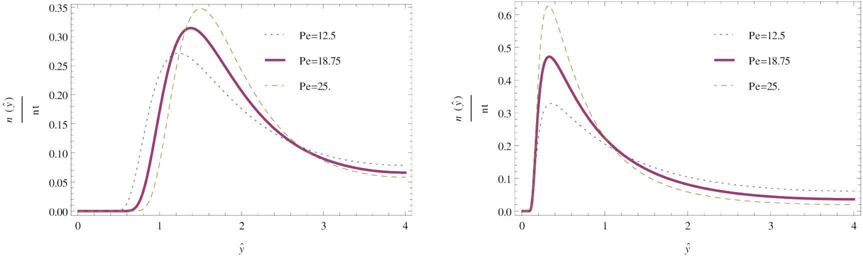
$$\frac{6M^E}{5h}\, Wi\, Pe + \frac{27M^E h(h^2 - 2W)}{320W^4}\, Pe^2 + \frac{81N^E a(h^2 - 4W)}{2hW^2} Wi^2$$

Force only (in electrolyte)



Center-of-mass distribution for different Pe. No imposed flow. Left: non-linear spring model, right: linear spring model.

Flow and force in opposition (in electrolyte)



Center-of-mass distribution. Flow and force in opposition, $Wi = 5/6$.
Left: non-linear spring model, right: linear spring model.

Conclusions

Extended the kinetic theory to include finite chain flexibility and take into account wall-mediated migration due to electric field, without explicit inclusion of counter-ion charges.

1. Predicted non-monotonic dependence of concentration layer thickness
2. Derived depletion layer scaling and its dependence on Pe
3. Showed dependence of normal stresses on Wi
4. Linear (Hookean) spring model under-predicts the thickness of the depletion layer compared to the non-linear model
5. HIs due to counter-ion cloud tend to decrease migration away from the walls in combined fields

Outline

The overall picture

Objective

Provide a comprehensive treatment of HIs in electric field under confinement within the framework of Brownian Dynamics.

- Use full electrophoretic Stokeslet (short-ranged + long-ranged parts)
- Include the corresponding wall correction

Model equations

$$\dot{\mathbf{r}}_i = \mathbf{u}(\mathbf{r}_i) + \sum_{j=1}^{N} \boldsymbol{\mu}_{ij} \cdot \left(\mathbf{F}_j^b + \mathbf{F}_j^s\right) + \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}^e \cdot \mathbf{F}_j^e$$

- Brownian dynamics:

$$d\mathbf{r} = \left[\mathbf{u} + \frac{1}{k_b T}\mathbf{D} \cdot \mathbf{F} + \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{D} + \boldsymbol{\mu}^e \cdot \mathbf{F}^e\right] dt + \sqrt{2}\mathbf{B} \cdot d\mathbf{w},$$

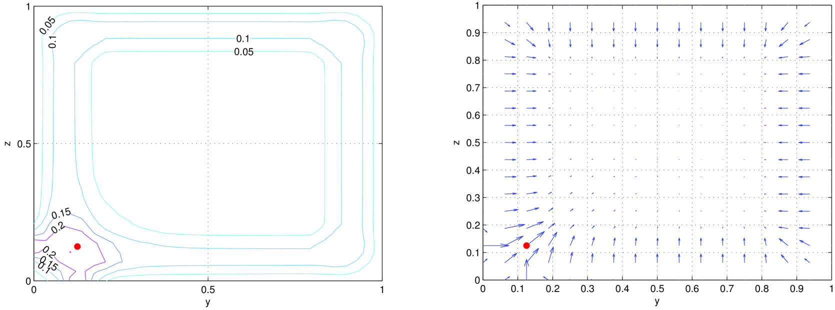
$$\mathbf{D} = \mathbf{B} \cdot \mathbf{B}^T.$$

- HI tensor splitting, $\mathbf{u} = \mathbf{u}^{OB} + \mathbf{u}^W$ circumvents the need to resolve Dirac delta function. Price is non-homogeneous BCs.

$$-\nabla p + \eta \Delta \mathbf{u}^W = 0, \quad \nabla \cdot \mathbf{u}^W = 0,$$

$$\mathbf{u}^W = -\mathbf{u}^{OB} \text{ at walls}$$

Divergence of diffusion tensor



The divergence field (right) and its contours (left) for the source point near a corner. $H = 10\,\mu\text{m}$.

Cross-stream migration

Migration flux $[\mathbf{j}_C]_{mig}$

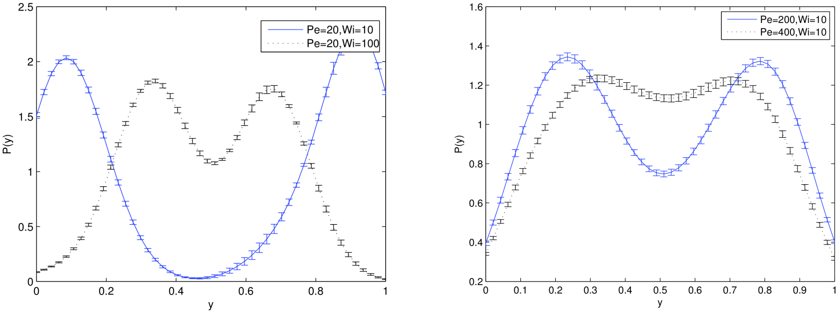
$$n\left[\frac{1}{2}\langle\bar{\mathbf{\Omega}}\cdot\mathbf{F}^s\rangle+\frac{2}{k_bT}\langle\mathbf{D_K}\cdot\mathbf{F}^e\rangle-\frac{\partial}{\partial\mathbf{r}_c}\cdot\langle\mathbf{D_K}\rangle+\frac{k_bT}{2}\langle\bar{\mathbf{\Omega}}\cdot\frac{\partial}{\partial\mathbf{Q}}\ln\psi\rangle\right]$$

Classification of HIs:

- Internally-induced: deterministic, due to $\mathbf{F}^S$, AFW/TW
- Externally-induced: deterministic, due to $\mathbf{F}^E$, AFW/TW
- Diffusion-induced (primary, secondary): Brownian, due to $\mathbf{F}^B$ (TW, AFW)

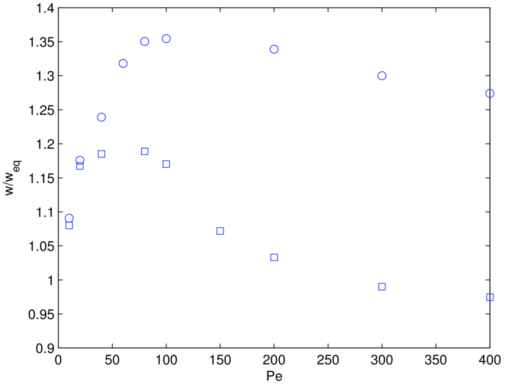
(TW=towards wall, AFW=away from wall)

Center-of-mass profiles



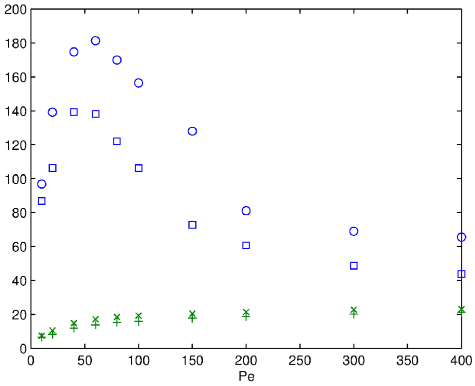
Flow field and electric field in opposition. Debye length $\lambda_D = 1\,\mu$m

Concentration layer thickness



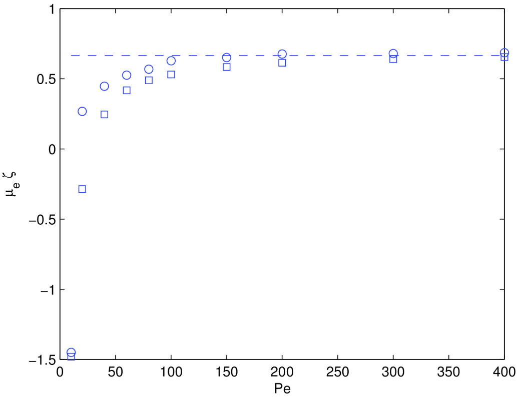
Concentration layer thickness. $Wi = 10$. Electrophoretic correction: $\bigcirc$ = excluded; $\square$ = included.

Shape descriptors



Shape descriptors ($\bigcirc, \square = S_{xx}/S_{yy}$ and $\times, + = Tr(S)$). $Wi = 10$.
Electrophoretic correction: $\bigcirc, \times$ = excluded; $\square, +$ = included.

Electrophoretic mobility



Electrophoretic mobility μ_e. $Wi = 10$. Flow reversal at $Pe_r \approx 50$.
Electrophoretic correction: $\bigcirc$ = excluded; $\square$ = included.

Conclusions

Used Brownian Dynamics in a channel with full electrophoretic Stokeslet to predict cross-stream migration patterns in an electrolyte of arbitrary Debye length.

- Predicted polymer center-of-mass distributions in confined electrolyte
- Described dependences of electrophoretic mobility and chain size on *Wi* and *Pe*
- Quantified neglect of electrophoretic wall correction, particularly significant in strong confinement

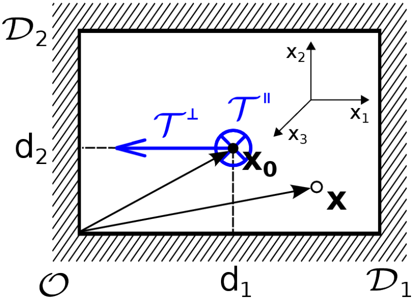
Outline

The overall picture

Objective

Derive an analytical form of the Stokeslet in a rectangular channel.

Background



Cross-section of an infinite rectangular channel of dimensions D_1 and D_2. The source point and field point are located at $\mathbf{x}_0 = [d_1, d_2, 0]$ and $\mathbf{x} = [x_1, x_2, x_3]$, respectively. General motion of the source point (T) is decomposed into the translation parallel ($T^{\parallel}$) and perpendicular ($T^{\perp}$) to the walls, $T = T^{\parallel} + T^{\perp}$.

Problem formulation

$$\eta\nabla^2\mathbf{v} + \delta(\mathbf{x}-\mathbf{x}_0)\mathbf{e}_3 = \nabla p,$$
$$\nabla\cdot\mathbf{v} = 0,$$
$$\mathbf{v} = 0 \qquad \text{at walls.}$$

Papkovich-Neuber formalism:

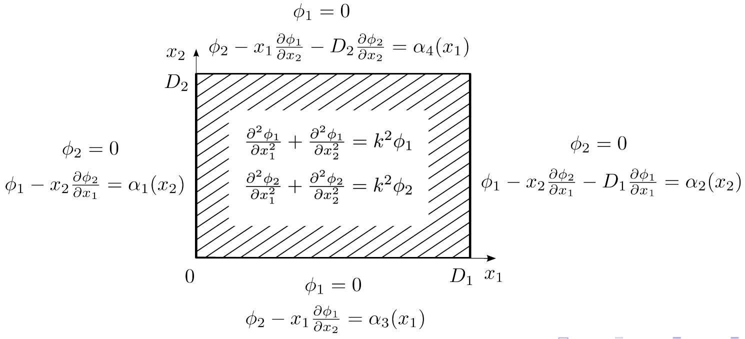
$$\mathbf{v} = \nabla(\mathbf{x}\cdot\boldsymbol{\phi} + \omega) - 2\boldsymbol{\phi}, \qquad p = 2\eta\nabla\cdot\boldsymbol{\phi},$$

with harmonic functions ω and $\boldsymbol{\phi} = (\phi_1, \phi_2, \phi_3)$ satisfying Laplace equations,

$$\nabla^2\omega = \nabla^2\phi_n = 0, \qquad n = 1, 2, 3.$$

Solution

1. Determine ϕ_3 as the Green's function associated with potential flow (rapidly convergent Fourier series).
2. Left with mixed-type BVP for ϕ_1 and ϕ_2, with no-slip BC at walls $\rightarrow$ FT w.r.t x_3 yields



Solution, cont'd

1. Use FFT (eigenfunction expansions) with the basis functions given by the corresponding Sturm-Liouville problems.
2. Truncate the sums at N terms to de-couple Fourier coefficients to arrive at linear system

$$\mathbf{z} = \mathbf{\Gamma} \cdot \mathbf{z} + \mathbf{p},$$

   where vector $\mathbf{z}$ contains $4N$ elements.
3. Solve for $\mathbf{z}$, compute Fourier coefficients, inverse transform $\hat{\phi}_1$ and $\hat{\phi}_2$ to obtain the desired solutions ϕ_1 and ϕ_2.

Questions

Thank you for your time. Questions?