On the hydrodynamic diffusion of rigid particles

O. Gonzalez
Introduction

**Basic problem.** Characterize how the diffusion and sedimentation properties of particles depend on their shape.

**Applications.** Molecular separation techniques, structure determination; particle transport, mixing in microfluidic devices.
Outline

Introduction

Spherical bodies

Arbitrary bodies

Asymptotic analysis

Application to DNA

(Numerical method, if time permits)
Spherical bodies
Classic model for spherical bodies

**Setup.** Consider a dilute solution of identical spheres in a fluid subject to external loads.

\[
\rho(x, t) \quad \# \text{spheres per unit volume of } E.
\]
\[
f^{\text{ext}}(x, t) \quad \text{external body force.}
\]
\[
\mu, T \quad \text{fluid viscosity, temperature.}
\]
Modeling assumptions

Consider locally time-averaged forces and motion for each particle and assume:


\[
\begin{align*}
\mathbf{f}^{\text{ext}} + \mathbf{f}^{\text{hydro}} + \mathbf{f}^{\text{osmotic}} &= 0.
\end{align*}
\]

2. Hydrodynamic force model.

\[
\mathbf{f}^{\text{hydro}} = -6\pi \gamma \mu \nu, \quad \gamma \text{ radius.}
\]
Modeling assumptions

3. Osmotic force model.

\[ f_{\text{osmotic}} = -\nabla \psi, \quad \psi = kT \ln \rho. \]


\[ \frac{\partial}{\partial t} \int_B \rho \, dV + \int_{\partial B} \rho \mathbf{v} \cdot \mathbf{n} \, dA = 0, \quad \forall B \subset E. \]
Resulting model on $E$

**Equations.** Combining 1-3 and localizing 4 we get

$$f^{\text{ext}} - 6\pi \gamma \mu v - \frac{kT}{\rho} \nabla \rho = 0,$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot [\rho v] = 0.$$

Eliminating $v$ gives

$$\frac{\partial \rho}{\partial t} = \nabla \cdot [D \nabla \rho - C \rho f^{\text{ext}}].$$

$$D = \frac{kT}{6\pi \mu \gamma}, \quad C = \frac{1}{6\pi \mu \gamma}.$$

**Remark.** Various experiments can measure $D$ or $C$ and hence $\gamma$. 
Example: centrifuge experiment

\[ D \text{ and/or } C \text{ can be determined from speed of moving front } r_f(t). \]
Arbitrary bodies
**Model for arbitrary bodies**

**Setup.** Consider a dilute solution of identical bodies in a fluid subject to external loads.

\[
\rho(q, \eta, t) \quad \# \text{ bodies per unit volume of } E \times SO_3.
\]

\[
(f^{\text{ext}}, \tau^{\text{ext}})(q, \eta, t),
\]

\[
\mu, T
\]

external body force, torque.

fluid viscosity, temperature.
Modeling assumptions

Consider locally time-averaged loads and motion for each particle and assume:

1. Net force and torque balance.

\[
\begin{bmatrix} f^{\text{ext}} \\ \tau^{\text{ext}} \end{bmatrix} + \begin{bmatrix} f^{\text{hydro}} \\ \tau^{\text{hydro}} \end{bmatrix} + \begin{bmatrix} f^{\text{osmotic}} \\ \tau^{\text{osmotic}} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}
\]

or

\[
\mathcal{F}^{\text{ext}} + \mathcal{F}^{\text{hydro}} + \mathcal{F}^{\text{osmotic}} = 0 \in \mathbb{R}^6
\]

where

\[
\mathcal{F} = \Lambda^T \begin{bmatrix} f \\ \tau \end{bmatrix} \text{ local basis components.}
\]
Modeling assumptions

2. Hydrodynamic force model.

\[
\begin{bmatrix}
  f_{\text{hydro}} \\
  \tau
\end{bmatrix}
= - \begin{bmatrix}
  L_1 & L_3 \\
  L_2 & L_4
\end{bmatrix}
\begin{bmatrix}
  v \\
  \omega
\end{bmatrix}
\]

or

\[
\begin{bmatrix}
  v \\
  \omega
\end{bmatrix}
= - \begin{bmatrix}
  M_1 & M_3 \\
  M_2 & M_4
\end{bmatrix}
\begin{bmatrix}
  f_{\text{hydro}} \\
  \tau
\end{bmatrix}
\]

or

\[V = -M\mathbf{f}_{\text{hydro}} \in \mathbb{R}^6\]

where

\[L = L(\Gamma, c), \quad M = M(\Gamma, c) \in \mathbb{R}^{6 \times 6}\]

\[\mathcal{M} = \Lambda^{-1} M \Lambda^{-T}, \quad \mathcal{V} = \Lambda^{-1} \begin{bmatrix}
  v \\
  \omega
\end{bmatrix}.\]
Modeling assumptions

3. Osmotic force model.

\[ F_{\text{osmotic}} = -\nabla \psi \]
\[ \psi = kT \ln \rho, \quad \nabla = (\nabla q, \nabla \eta). \]


\[ \frac{\partial}{\partial t} \int_B \rho g \, dV + \int_{\partial B} \rho g \nabla \cdot \mathbf{N} \, dA = 0 \]
\[ \forall B \subset \mathcal{E} \times \mathcal{A}. \]
Resulting model on $E \times SO_3$

**Equations.** Combining 1-3 and localizing 4 we get

\[
\mathcal{F}^{\text{ext}} - \mathcal{M}^{-1} \mathcal{V} - \frac{kT}{\rho} \nabla \rho = 0, \quad \frac{\partial (\rho g)}{\partial t} + \nabla \cdot [\rho g \mathcal{V}] = 0.
\]

Eliminating $\mathcal{V}$ gives

\[
\frac{\partial \rho}{\partial t} = g^{-1} \nabla \cdot [g \mathcal{D} \nabla \rho - g \rho \mathcal{C} \mathcal{F}^{\text{ext}}],
\]

\[
\mathcal{D} = kT \mathcal{M}(\Gamma, c), \quad \mathcal{C} = \mathcal{M}(\Gamma, c).
\]

**Remark.** Model is fully coupled b/w translations and rotations.
Detail on hydrodynamic model

\[
\begin{bmatrix}
    f \\
    \tau
\end{bmatrix}^{\text{hydro}} = - \begin{bmatrix}
    L_1 & L_3 \\
    L_2 & L_4
\end{bmatrix} \begin{bmatrix}
    v \\
    \omega
\end{bmatrix}
\]
Detail on hydrodynamic model

\[ \mu \Delta u = \nabla p \quad \text{in } \mathbb{R}^3 \setminus \Omega \]
\[ \nabla \cdot u = 0 \quad \text{in } \mathbb{R}^3 \setminus \Omega \]
\[ u = v + \omega \times (x - c) \quad \text{on } \Gamma \]
\[ u, p \to 0 \quad \text{as } |x| \to \infty \]

\[ \Rightarrow \quad \begin{bmatrix} f \end{bmatrix}_{\text{hydro}} = - L^1 \begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix} \begin{bmatrix} v \\ \omega \end{bmatrix} \]

\[ M(\Gamma, c) = L(\Gamma, c)^{-1} \in \mathbb{R}^{6 \times 6}, \text{ where } L(\Gamma, c) \text{ is a Dirichlet-to-Neumann map.} \]
Asymptotic analysis
Basic question

**Question.** What does the coupled model imply about various observable densities of interest?

\[ \frac{\partial \rho_c}{\partial t} = ? \]

where \( \rho_c \) is the number of reference points \( c \) per unit volume of \( E \).

\[ E \subseteq \mathbb{R}^3 \]

\[ \rho_c \text{ per unit volume of } E \]
Basic question

**Question.** What does the coupled model imply about various observable densities of interest?

\[
\frac{\partial \rho_n}{\partial t} = ? \quad \text{where } \rho_n \text{ is } \# \text{ of ref points } n \text{ per unit area of } S_2.
\]


**Scale separation**

**Result.** For particles of arbitrary shape, there is a natural scale separation for dynamics on $E$ and $SO_3$.

Translations: \[ t_E = \text{time to diffuse across } E \]

Rotations: \[ t_S = \text{time to diffuse across } SO_3 \]

\[
\frac{t_S}{t_E} \sim \left(\frac{\ell}{L}\right)^2
\]

The two-scale structure is ideal setting for asymptotics; the small param is $\varepsilon = \ell/L << 1$. 
Limiting model on $E$

**Result.** For particles of arbitrary shape $\Gamma$ and mobility tensor $M(\Gamma, c)$, the leading-order equation on $E$ on the scale $t_E$ is

$$\frac{\partial \rho_c}{\partial t} = \nabla \cdot \left[ D_c \nabla \rho_c - \rho_c h^{\text{ext}} \right]$$

$$D_c = \frac{kT}{3} \text{tr}[M_1(\Gamma, c)], \quad h^{\text{ext}} = \text{avg ext load}$$

$$\rho_c = \# \text{ of ref points } c \text{ per unit volume of } E.$$
Property of model on $E$

**Result.** The diffusivity $D_c$ depends on body shape $\Gamma$ and ref point $c$. For each $\Gamma$, there is a unique $c_* \in \mathbb{R}^3$ such that

$$D_{c_*} = \min_{c \in \mathbb{R}^3} D_c.$$
Limiting model on $S_2$

**Result.** For particles whose shape $\Gamma$ and mobility tensor $M(\Gamma, c)$ satisfy an elongation condition wrt the body axis $n$, the leading-order equation on $S_2$ on the scale $t_S$ is

\[
\frac{\partial \rho_n}{\partial t} = D_n \Delta \rho_n
\]

\[
D_n = \frac{kT}{2} \text{tr}[P_n M_4(\Gamma, c) P_n], \quad P_n = \text{proj orthog to } n
\]

\[
\rho_n = \# \text{ of ref points } n \text{ per unit area of } S_2.
\]
Result. The diffusivity $D_n$ depends on body shape $\Gamma$ and ref vector $n$, but not ref point $c$. For each $\Gamma$, there is at least one $n_\ast \in S_2$ such that

$$D_{n_\ast} = \min_{n \in S_2} D_n.$$
Application
Estimation of hydrated radius

**Problem.** Given experimental measurements of $D_c$ and $D_n$ for various sequences, we seek to fit the radius parameter $r$ in a geometric model.

\[
\Gamma(S, r), \text{ } S = \text{DNA sequence.}
\]

\[
r = ?
\]

\[
D_c = \frac{kT}{3} \text{tr}[M_1(\Gamma(S, r), c)], \quad D_n = \frac{kT}{2} \text{tr}[P_n M_4(\Gamma(S, r), c) P_n].
\]
Results for straight model: $D_{c_*}$ vs sequence length

Curves: numerics w/ $r = 10, 11, \ldots, 15\text{Å}$ (top to bottom).

Symbols: experiments (ultracentrifuge, light scattering, electrophoresis).

Estimated radius: $r = 10 - 15\text{Å}$. 
Results for curved model: $D_{c*}$ vs sequence length

Curves: numerics on straight model (same as before).
Open symbols: experimental data (same as before).
Crosses, pluses: numerics on curved model $w/r = 10, r = 15$Å.
Estimated radius: $r = 12 – 17$Å.
Results for straight model: $D_{n*}$ vs sequence length

Curves: numerics $w/r = 12, 11, \ldots, 18\AA$ (top to bottom).

Symbols: experiments (birefringence, light scattering).

Estimated radius: $r = 13 - 17\AA$. 
Results for curved model: $D_{n^*}$ vs sequence length

Curves: numerics on straight model (same as before).

Open symbols: experimental data (same as before).

Crosses, pluses: numerics on curved model $w/r = 12, r = 18\text{Å}$.

Estimated radius: $r = 10 – 12\text{Å}$. 
Numerical method
Numerical method for $M(\Gamma, c)$

\[
\begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{hydro}} = - \begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix} \begin{bmatrix} v \\ \omega \end{bmatrix}
\]
Numerical method for $M(\Gamma, c)$

\[\begin{align*}
\mu \Delta u & = \nabla p \quad \text{in } \mathbb{R}^3 \setminus \Omega \\
\nabla \cdot u & = 0 \quad \text{in } \mathbb{R}^3 \setminus \Omega \\
u & = U[v, \omega] \quad \text{on } \Gamma \\
u, p & \rightarrow 0 \quad \text{as } |x| \rightarrow \infty
\end{align*}\]

\[
\begin{bmatrix} f \end{bmatrix}_{\text{hydro}} = - \begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix} \begin{bmatrix} v \\ \omega \end{bmatrix}
\]

The computation of $M(\Gamma, c) = L^{-1}(\Gamma, c) \in \mathbb{R}^{6 \times 6}$ requires six solutions of the exterior Stokes equations with data $U[v, \omega](x) = v + \omega \times (x - c)$. 
Boundary integral formulation

**Stokes kernels** (singular solns):

$G(x, y)$ single-layer, $H(x, y)$ double-layer.
Boundary integral formulation

**Stokes kernels** (singular solns):
$G(x, y)$ single-layer, $H(x, y)$ double-layer.

**Actual, parallel surfaces:**
$\Gamma$ actual, $\gamma$ parallel, $0 < \phi < \phi_{\Gamma}$ offset param.
Boundary integral formulation

**Stokes kernels** (singular solns):
\[ G(x, y) \text{ single-layer, } \quad H(x, y) \text{ double-layer.} \]

**Actual, parallel surfaces:**
\[ \Gamma \text{ actual, } \quad \gamma \text{ parallel, } \quad 0 < \phi < \phi_\Gamma \text{ offset param.} \]

**Mixed representation:**
\[
u(x) = \lambda \int_\gamma G(x, \xi)\psi(y(\xi)) \, da_\xi + (1 - \lambda) \int_\Gamma H(x, y)\psi(y) \, da_y\]
\[0 < \lambda < 1 \text{ interpolation param, } \quad \psi \text{ potential density.}\]
Boundary integral formulation

Stokes kernels (singular solns):
$G(x, y)$ single-layer, $H(x, y)$ double-layer.

Actual, parallel surfaces:
$\Gamma$ actual, $\gamma$ parallel, $0 < \phi < \phi_{\Gamma}$ offset param.

Mixed representation:
$u(x) = \lambda \int_{\gamma} G(x, \xi) \psi(y(\xi)) \, da_{\xi} + (1 - \lambda) \int_{\Gamma} H(x, y) \psi(y) \, da_{y}$
$0 < \lambda < 1$ interpolation param, $\psi$ potential density.

Integral equation:
Given $U$ find $\psi$ s.t.
$\lim_{x_{o} \rightarrow x} u(x_{o}) = U(x)$ for all $x \in \Gamma$. 
$x_{o} \in \mathbb{R}^3 \setminus \Omega$
Properties of formulation

\[ A^G \psi + A^H \psi + c \psi = U \]

Integral operators:

\[ (A^G \psi)(x) = \int_\Gamma G^{\lambda,\phi}(x, y) \psi(y) \, da_y \quad \text{regular} \]
\[ (A^H \psi)(x) = \int_\Gamma H^{\lambda}(x, y) \psi(y) \, da_y \quad \text{weakly singular}. \]
Properties of formulation

\[ A^G \psi + A^H \psi + c \psi = U \]

Integral operators:

\[ (A^G \psi)(x) = \int_{\Gamma} G^{\lambda,\phi}(x, y) \psi(y) \, da_y \quad \text{regular} \]
\[ (A^H \psi)(x) = \int_{\Gamma} H^{\lambda}(x, y) \psi(y) \, da_y \quad \text{weakly singular}. \]

Solvability theorem: Under mild assumptions, there exists a unique \( \psi \in C^0 \) for any \( \Gamma \in C^{1,1} \), \( \phi \in (0, \phi_{\Gamma}) \), \( \lambda \in (0, 1) \) and \( U \in C^0 \).
Properties of formulation

\[ A^G \psi + A^H \psi + c \psi = U \]

Integral operators:

\[
(A^G \psi)(x) = \int_{\Gamma} G^\lambda,\phi(x, y)\psi(y) \, da_y \quad \text{regular}
\]

\[
(A^H \psi)(x) = \int_{\Gamma} H^\lambda(x, y)\psi(y) \, da_y \quad \text{weakly singular.}
\]

Solvability theorem: Under mild assumptions, there exists a unique \( \psi \in C^0 \) for any \( \Gamma \in C^{1,1}, \phi \in (0, \phi_\Gamma), \lambda \in (0, 1) \) and \( U \in C^0 \).

Mobility tensor: Solutions for six independent sets of data are required to determine \( M \).

\[
(v, \omega) \rightarrow U \rightarrow \psi \rightarrow (f_{\text{hyd}}, \tau_{\text{hyd}}) \rightarrow L \rightarrow M.
\]

6 times
Locally-corrected Nystrom discretization

**Arbitrary quadrature rule:**
\( y_b \) nodes, \( W_b \) weights, \( h > 0 \) mesh size, \( \ell \geq 1 \) order.
Locally-corrected Nystrom discretization

**Arbitrary quadrature rule:**

\( y_b \) nodes, \( W_b \) weights, \( h > 0 \) mesh size, \( \ell \geq 1 \) order.

**Partition of unity functions:**

\[ \zeta_b(x), \quad \hat{\zeta}_b(x), \quad \zeta_b + \hat{\zeta}_b = 1. \]
Locally-corrected Nystrom discretization

**Arbitrary quadrature rule:**
y\(_b\) nodes, \(W_b\) weights, \(h > 0\) mesh size, \(\ell \geq 1\) order.

**Partition of unity functions:**
\[ \zeta_b(x) \mid_{y_b} \quad \hat{\zeta}_b(x) \mid_{y_b} \quad \zeta_b + \hat{\zeta}_b = 1. \]

**Discretized operators:**
\[ (A_h^G \psi)(x) = \sum_b G^{\lambda,\phi}(x, y_b) \psi(y_b) W_b \]
\[ (A_h^H \psi)(x) = \sum_b \zeta_b(x) H^{\lambda}(x, y_b) \psi(y_b) W_b + \hat{\zeta}_b(x) R_x(y_b) \psi(y_b) \]
\(R_x\) local poly correction at \(x\), \(p \geq 0\) degree of correction.
Locally-corrected Nystrom discretization

**Arbitrary quadrature rule:**

\( y_b \) nodes, \( W_b \) weights, \( h > 0 \) mesh size, \( \ell \geq 1 \) order.

**Partition of unity functions:**

\[ \zeta_b(x), \quad \hat{\zeta}_b(x) \quad y_b, \quad \zeta_b + \hat{\zeta}_b = 1. \]

**Discretized operators:**

\[
(A^G_h \psi)(x) = \sum_b G^{\lambda,\phi}(x, y_b) \psi(y_b) W_b
\]

\[
(A^H_h \psi)(x) = \sum_b \zeta_b(x) H^{\lambda}(x, y_b) \psi(y_b) W_b + \hat{\zeta}_b(x) R_x(y_b) \psi(y_b)
\]

\( R_x \) local poly correction at \( x \), \( p \geq 0 \) degree of correction.

**Moment conditions:**

\( R_x \) chosen s.t. \( A^H_h g = A^H g \) for all local polys \( g \) at \( x \) up to degree \( p \).
Properties of discretization

\[ A^G \psi + A^H \psi + c \psi = U \]
\[ A_h^G \psi_h + A_h^H \psi_h + c \psi_h = U \]

**Solvability theorem:** Under mild assumptions, there exists a unique \( \psi_h \in C^0 \) for any \( \Gamma \in C^{1,1} \), \( \phi \in (0, \phi_\Gamma) \), \( \lambda \in (0, 1) \) and \( U \in C^0 \).
Properties of discretization

\[ A^G \psi + A^H \psi + c \psi = U \]
\[ A_h^G \psi_h + A_h^H \psi_h + c \psi_h = U \]

**Solvability theorem:** Under mild assumptions, there exists a unique \( \psi_h \in C^0 \) for any \( \Gamma \in C^{1,1} \), \( \phi \in (0, \phi_{\Gamma}) \), \( \lambda \in (0, 1) \) and \( U \in C^0 \).

**Convergence theorem:** Under mild assumptions, if \( \Gamma \in C^{m+1,1} \) and \( \psi \in C^{m,1} \), then as \( h \to 0 \)

\[ \| \psi - \psi_h \|_{\infty} \to 0 \quad \forall \ell \geq 1, \ p \geq 0, \ m \geq 0 \]
\[ \| \psi - \psi_h \|_{\infty} \leq Ch \quad \forall \ell \geq 1, \ p = 0, \ m \geq 1 \]
\[ \| \psi - \psi_h \|_{\infty} \leq Ch^{\min(\ell, p, m)} \quad \forall \ell \geq 1, \ p \geq 1, \ m \geq 1. \]
Conditioning: singular values $\sigma$ vs parameters $\lambda, \phi$

Results for method with $p = 0$ and $\ell = 1$.

$\phi/\phi_\Gamma = \frac{1}{8}$ (dots), $\frac{2}{8}$ (crosses), $\frac{3}{8}$ (pluses), ..., $\frac{7}{8}$ (triangles).

Condition number $\frac{\sigma_{\text{max}}}{\sigma_{\text{min}}} \leq 10^{1.5}$ for $(\lambda, \phi/\phi_\Gamma)$ near $(\frac{1}{2}, \frac{1}{2})$. 
Accuracy: computed load $f^{\text{hyd}}$ vs mesh size $h$

Results for method with $p = 0$ and various $\ell$, $\lambda$, $\phi$.

Convergence is visible; limited by iterative solver.