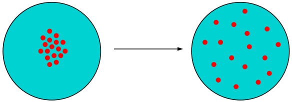
On the hydrodynamic diffusion of rigid particles

O. Gonzalez

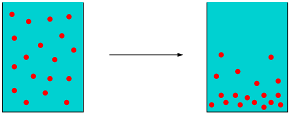
Introduction

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

Diffusion:



Sedimentation:



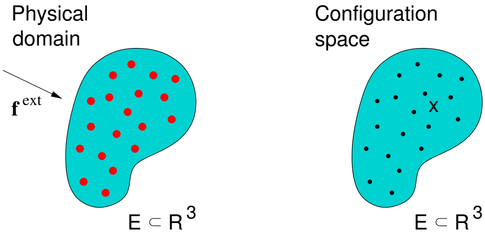
Applications. Molecular separation techniques, structure determination; particle transport, mixing in microfluidic devices.

Outline

Spherical bodies

Classic model for spherical bodies

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

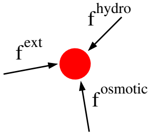


$\rho(x,t)$	# spheres per unit volume of E.
$f^{\rm ext}(x,t)$	external body force.
μ, T	fluid viscosity, temperature.

Modeling assumptions

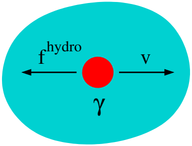
Consider locally time-averaged forces and motion for each particle and assume:

1. Net force balance.



$$f^{\mathrm{ext}} + f^{\mathrm{hydro}} + f^{\mathrm{osmotic}} = 0.$$

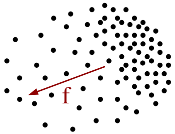
2. Hydrodynamic force model.



$$f^{\mathrm{hydro}} = -6\pi\gamma\mu v, \quad \gamma \text{ radius.}$$

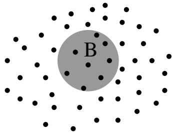
Modeling assumptions

3. Osmotic force model.



$$f^{\mathrm{osmotic}} = -\nabla\psi, \quad \psi = kT\ln\rho.$$

4. Conservation of mass.



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

Resulting model on E

Equations. Combining 1-3 and localizing 4 we get

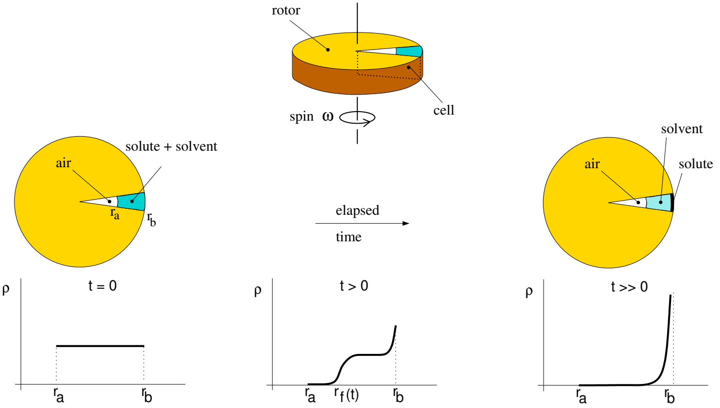
$$f^{\text{ext}} - 6\pi\gamma\mu v - \frac{kT}{\rho}\nabla\rho = 0, \qquad \frac{\partial\rho}{\partial t} + \nabla\cdot[\rho v] = 0.$$

Eliminating v gives

$$\boxed{\begin{gathered}\frac{\partial\rho}{\partial t} = \nabla\cdot[D\nabla\rho - C\rho f^{\text{ext}}] \\ D = \frac{kT}{6\pi\mu\gamma}, \qquad C = \frac{1}{6\pi\mu\gamma}.\end{gathered}}$$

Remark. Various experiments can measure D or C and hence γ.

Example: centrifuge experiment

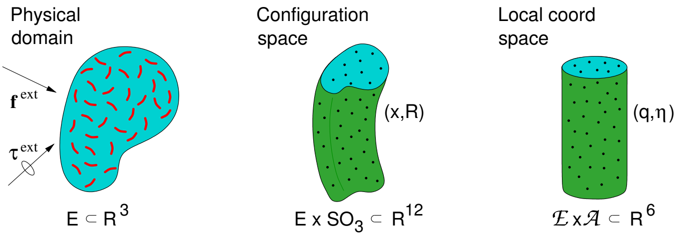


D and/or C can be determined from speed of moving front $r_f(t)$.

Arbitrary bodies

Model for arbitrary bodies

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

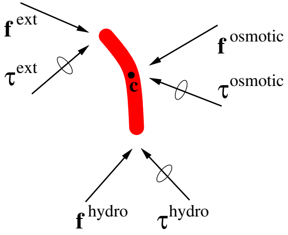


$\rho(q,\eta,t)$ — # bodies per unit volume of $E \times SO_3$.
$(f^{\text{ext}},\tau^{\text{ext}})(q,\eta,t)$, — external body force, torque.
μ, T — fluid viscosity, temperature.

Modeling assumptions

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

1. Net force and torque balance.



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

or

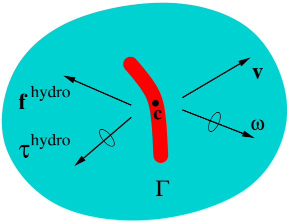
$$\mathfrak{F}^{\text{ext}} + \mathfrak{F}^{\text{hydro}} + \mathfrak{F}^{\text{osmotic}} = 0 \in \mathbb{R}^6$$

where

$$\mathfrak{F} = \Lambda^T \begin{bmatrix} f \\ \tau \end{bmatrix}$$ local basis components.

Modeling assumptions

2. Hydrodynamic force model.



$$\begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{hydro}} = -\begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix} \begin{bmatrix} v \\ \omega \end{bmatrix}$$

or

$$\begin{bmatrix} v \\ \omega \end{bmatrix} = -\begin{bmatrix} M_1 & M_3 \\ M_2 & M_4 \end{bmatrix} \begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{hydro}}$$

or

$$\mathcal{V} = -\mathcal{M}\mathcal{F}^{\text{hydro}} \in \mathbb{R}^6$$

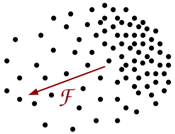
where

$$L = L(\Gamma, c), \qquad M = M(\Gamma, c) \in \mathbb{R}^{6\times 6}$$

$$\mathcal{M} = \Lambda^{-1} M \Lambda^{-T}, \qquad \mathcal{V} = \Lambda^{-1} \begin{bmatrix} v \\ \omega \end{bmatrix}.$$

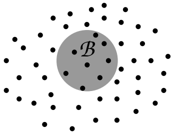
Modeling assumptions

3. Osmotic force model.



$$\mathfrak{F}^{\text{osmotic}} = -\nabla\psi$$
$$\psi = kT \ln\rho, \qquad \nabla = (\nabla_q, \nabla_\eta).$$

4. Conservation of mass.



$$\frac{\partial}{\partial t}\int_{\mathcal{B}} \rho g \, dV + \int_{\partial\mathcal{B}} \rho g \mathcal{V} \cdot \mathcal{N} \, dA = 0$$
$$\forall \mathcal{B} \subset \mathcal{E} \times \mathcal{A}.$$

Resulting model on $E \times SO_3$

Equations. Combining 1-3 and localizing 4 we get

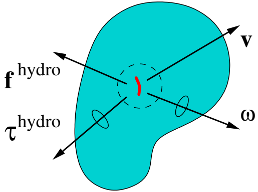
$$\mathcal{F}^{\text{ext}} - \mathcal{M}^{-1}\mathcal{V} - \frac{kT}{\rho}\nabla\rho = 0, \qquad \frac{\partial(\rho g)}{\partial t} + \nabla \cdot [\rho g \mathcal{V}] = 0.$$

Eliminating $\mathcal{V}$ gives

$$\boxed{\begin{array}{c} \dfrac{\partial \rho}{\partial t} = g^{-1}\nabla \cdot [g\mathcal{D}\nabla\rho - g\rho\mathcal{C}\mathcal{F}^{\text{ext}}] \\ \mathcal{D} = kT\mathcal{M}(\Gamma, c), \qquad \mathcal{C} = \mathcal{M}(\Gamma, c). \end{array}}$$

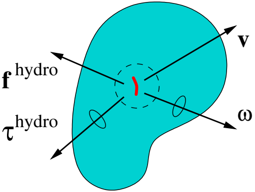
Remark. Model is fully coupled b/w translations and rotations.

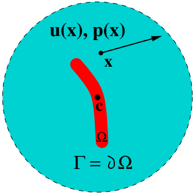
Detail on hydrodynamic model



$$\begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{hydro}} = - \begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix} \begin{bmatrix} v \\ \omega \end{bmatrix}$$

Detail on hydrodynamic model





$$\begin{array}{rcll} \mu\Delta u & = & \nabla p & \text{in } \mathbb{R}^3 \backslash \Omega \\ \nabla \cdot u & = & 0 & \text{in } \mathbb{R}^3 \backslash \Omega \\ u & = & v + \omega \times (x - c) & \text{on } \Gamma \\ u, p & \to & 0 & \text{as } |x| \to \infty \end{array} \quad \Rightarrow \quad \begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{hydro}} = - \begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix} \begin{bmatrix} v \\ \omega \end{bmatrix}$$

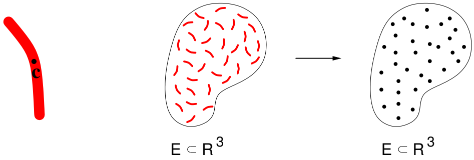
$M(\Gamma, c) = L(\Gamma, c)^{-1} \in \mathbb{R}^{6\times 6}$, where $L(\Gamma, c)$ is a Dirichlet-to-Neumann map.

Asymptotic analysis

Basic question

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

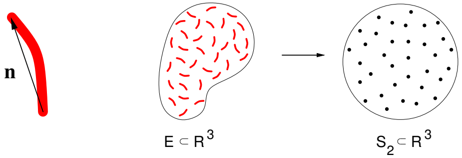
$$\frac{\partial \rho_c}{\partial t} = ? \quad \text{where } \rho_c \text{ is } \# \text{ of ref points } c \text{ per unit volume of } E.$$



Basic question

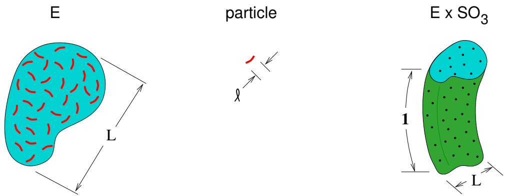
Question. What does the coupled model imply about various observable densities of interest?

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



Scale separation

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



$$\left.\begin{array}{ll}\text{Translations:} & t_E = \text{time to diffuse across } E \\ \text{Rotations:} & t_S = \text{time to diffuse across } SO_3\end{array}\right\} \quad \frac{t_S}{t_E} \sim \left(\frac{\ell}{L}\right)^2$$

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

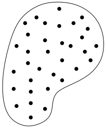
Limiting model on E

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

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

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

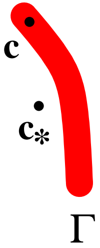
$$\rho_c = \# \text{ of ref points } c \text{ per unit volume of } E.$$



Property of model on E

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

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



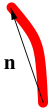
Limiting model on S_2

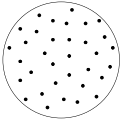
Result. For particles whose shape Γ and mobility tensor $M(\Gamma, c)$ satisfy an elongation condition wrt the body axis n, the leading-order equation on S_2 on the scale t_S is

$$\frac{\partial \rho_n}{\partial t} = D_n \Delta \rho_n$$

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

$$\rho_n = \# \text{ of ref points } n \text{ per unit area of } S_2.$$

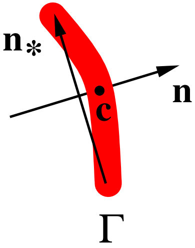




Property of model on S_2

Result. The diffusivity D_n depends on body shape Γ and ref vector n, but not ref point c. For each Γ, there is at least one $n_* \in S_2$ such that

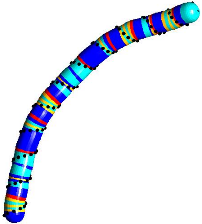
$$D_{n_*} = \min_{n \in S_2} D_n.$$



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.

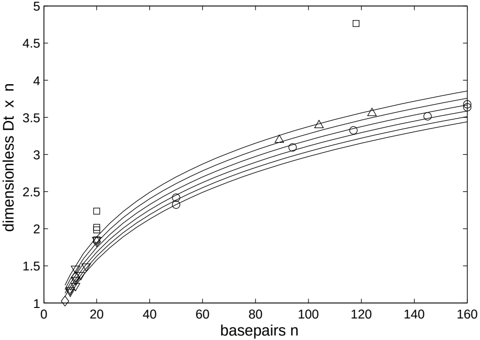


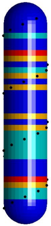
$\Gamma(S, r)$, S = DNA sequence.

$r = ?$

$$D_c = \frac{kT}{3}\,\mathrm{tr}[M_1(\Gamma(S, r), c)], \quad D_n = \frac{kT}{2}\,\mathrm{tr}[P_n M_4(\Gamma(S, r), c) P_n].$$

Results for straight model: D_{c_*} vs sequence length



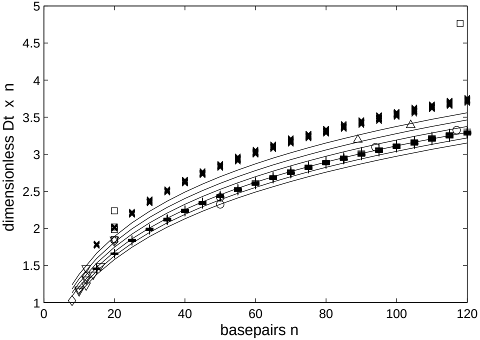


Curves: numerics w/$r = 10, 11, \ldots, 15$Å (top to bottom).

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

Estimated radius: $r = 10 - 15$Å.

Results for curved model: D_{c_*} vs sequence length



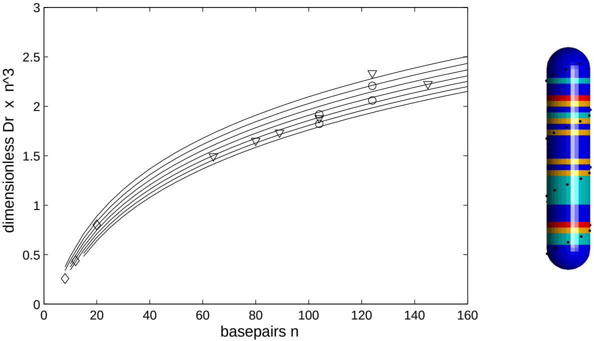
Curves: numerics on straight model (same as before).

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

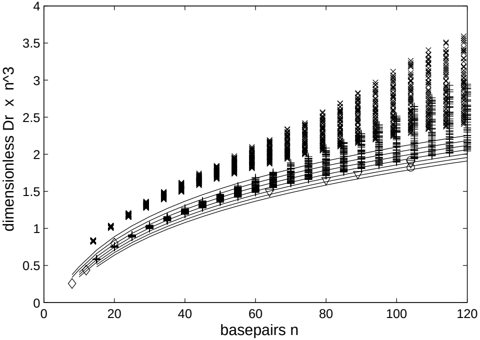


Curves: numerics w/$r = 12, 11, \ldots, 18\mathring{A}$ (top to bottom).

Symbols: experiments (birefringence, light scattering).

Estimated radius: $r = 13 - 17$Å.

Results for curved model: D_{n_*} vs sequence length



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

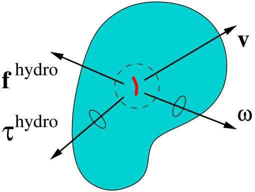
Open symbols: experimental data (same as before).

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

Estimated radius: $r = 10 - 12$Å.

Numerical method

Numerical method for $M(\Gamma, c)$



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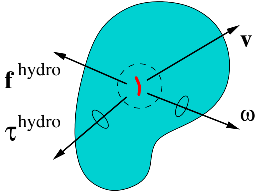
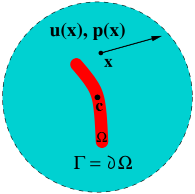
Numerical method for $M(\Gamma, c)$





$$
\begin{aligned}
\mu\Delta u &= \nabla p && \text{in } \mathbb{R}^3\backslash\Omega \\
\nabla\cdot u &= 0 && \text{in } \mathbb{R}^3\backslash\Omega \\
u &= U[v,\omega] && \text{on } \Gamma \\
u, p &\to 0 && \text{as } |x|\to\infty
\end{aligned}
\quad\Rightarrow\quad
\begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{hydro}} = -\begin{bmatrix} L_1 & L_3 \\ L_2 & L_4 \end{bmatrix}\begin{bmatrix} v \\ \omega \end{bmatrix}
$$

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.

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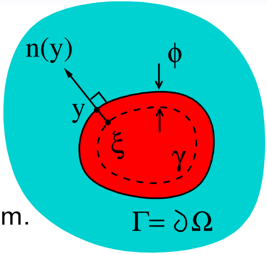
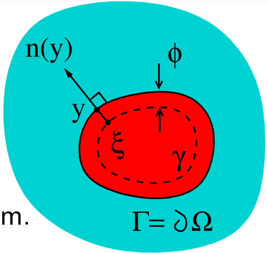


Actual, parallel surfaces:
Γ actual, γ parallel, $0 < \phi < \phi_\Gamma$ offset param.

Boundary integral formulation



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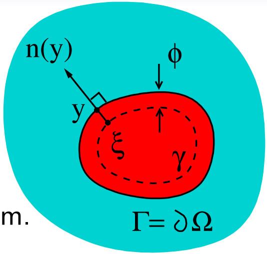
Actual, parallel surfaces:
Γ actual, γ parallel, $0 < \phi < \phi_\Gamma$ offset param.

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, ψ potential density.

Boundary integral formulation



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$0 < \lambda < 1$ interpolation param, ψ potential density.

Integral equation:
Given U find ψ s.t. $\lim_{\substack{x_o \to x \\ x_o \in \mathbb{R}^3 \setminus \Omega}} u(x_o) = U(x)$ for all $x \in \Gamma$.

Properties of formulation

$$A^G\psi + A^H\psi + c\psi = U$$

Integral operators:

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

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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 $U \in C^0$.

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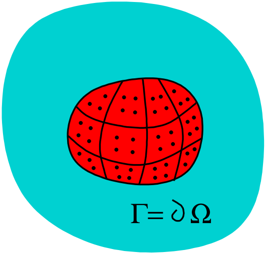
Mobility tensor: Solutions for six independent sets of data are required to determine M.

$$\underbrace{(v,\omega) \longrightarrow U \longrightarrow \psi \longrightarrow (f^{\mathrm{hyd}}, \tau^{\mathrm{hyd}})}_{\text{6 times}} \longrightarrow L \longrightarrow M.$$

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

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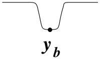
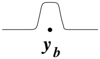
Partition of unity functions:

$\zeta_b(x)$ 

, $\widehat{\zeta}_b(x)$ 

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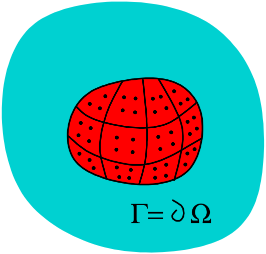

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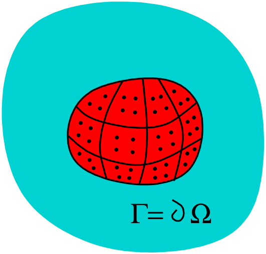

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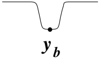
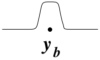
$\zeta_b(x)$ 

, $\widehat{\zeta}_b(x)$ 

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Discretized operators:

$(A_h^G \psi)(x) = \sum_b G^{\lambda,\phi}(x, y_b)\psi(y_b)W_b$

$(A_h^H \psi)(x) = \sum_b \zeta_b(x) H^{\lambda}(x, y_b)\psi(y_b)W_b + \widehat{\zeta}_b(x)R_x(y_b)\psi(y_b)$

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

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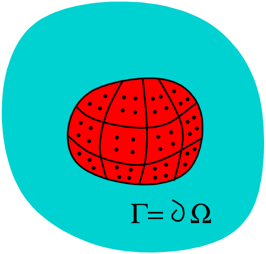

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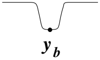
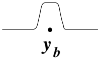
$\zeta_b(x)$ 

, $\widehat{\zeta}_b(x)$ 

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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 $U \in C^0$.

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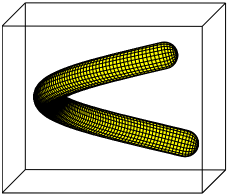
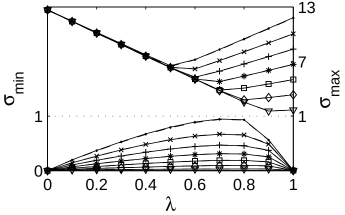
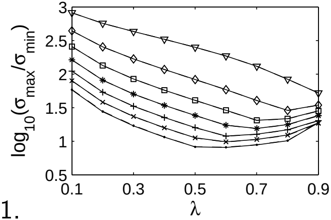
Convergence theorem: Under mild assumptions, if $\Gamma \in C^{m+1,1}$ and $\psi \in C^{m,1}$, then as $h \to 0$

$$\begin{aligned}
&||\psi - \psi_h||_\infty \to 0 && \forall \ell \geq 1, p \geq 0, m \geq 0 \\
&||\psi - \psi_h||_\infty \leq Ch && \forall \ell \geq 1, p = 0, m \geq 1 \\
&||\psi - \psi_h||_\infty \leq Ch^{\min(\ell,p,m)} && \forall \ell \geq 1, p \geq 1, m \geq 1.
\end{aligned}$$

Conditioning: singular values σ vs parameters λ, ϕ





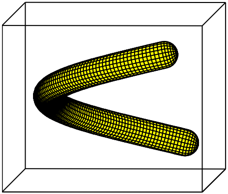


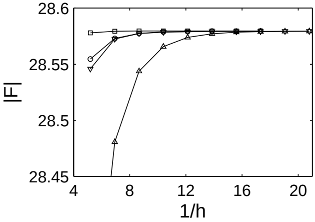
Results for method with $p = 0$ and $\ell = 1$.

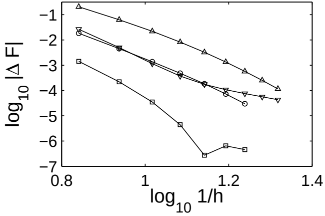
$\phi/\phi_\Gamma = \frac{1}{8}$ (dots), $\frac{2}{8}$ (crosses), $\frac{3}{8}$ (pluses), …, $\frac{7}{8}$ (triangles).

Condition number $\frac{\sigma_{\max}}{\sigma_{\min}} \leq 10^{\mathbf{1.5}}$ for $(\lambda, \phi/\phi_\Gamma)$ near $(\frac{1}{2}, \frac{1}{2})$.

Accuracy: computed load f^{hyd} vs mesh size h







Results for method with $p = 0$ and various ℓ, λ, ϕ.

Convergence is visible; limited by iterative solver.