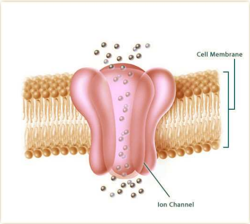
Finite-size effects in diffusion

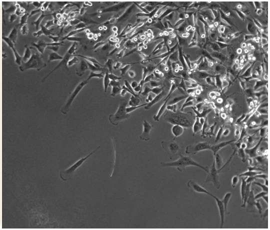
Maria Bruna and Jon Chapman

University of Oxford

Bath Spring School, 12 May 2014

Systems of interacting particles/agents





Particle-based approach

Track position of each agent $\mathbf{X}_i$. For each time step $\mathrm{d}t$, for example,

$$\mathrm{d}\mathbf{X}_i = \mathbf{f}(\mathbf{X}_1, \ldots, \mathbf{X}_N)\,\mathrm{d}t + \sqrt{2D}\,\mathrm{d}\mathbf{B}_i(t)$$

Each agent moves according to its surroundings, and the position of some/all of the other agents, with maybe some additional randomness.

Particle-based approach

Track position of each agent $\mathbf{X}_i$. For each time step $\mathrm{d}t$, for example,

$$\mathrm{d}\mathbf{X}_i = \mathbf{f}(\mathbf{X}_1, \ldots, \mathbf{X}_N)\,\mathrm{d}t + \sqrt{2D}\,\mathrm{d}\mathbf{B}_i(t)$$

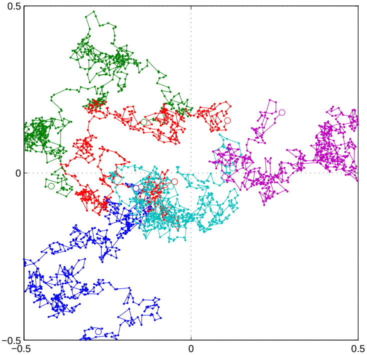
Each agent moves according to its surroundings, and the position of some/all of the other agents, with maybe some additional randomness.

Or we might track position and velocity:

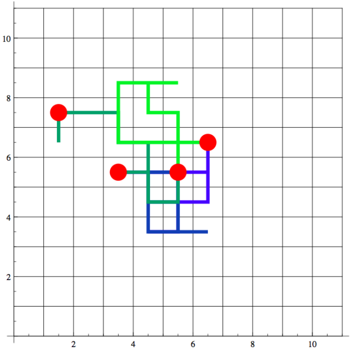
$$\begin{aligned}
\mathrm{d}\mathbf{X}_i &= \mathbf{V}_i\,\mathrm{d}t, \\
\mathrm{d}\mathbf{V}_i &= \mathbf{f}(\mathbf{X}_1, \ldots, \mathbf{X}_N)\,\mathrm{d}t + \sqrt{2D}\,\mathrm{d}\mathbf{B}_i(t).
\end{aligned}$$

Examples of individual-level diffusion processes

Continuous diffusion



Agents on a lattice



Continuum (population level) description

Diffusion

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c),$$

where c is the particle concentration

Continuum (population level) description

Diffusion

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c),$$

where c is the particle concentration

Poisson-Nernst-Planck

$$\begin{aligned} \frac{\partial n}{\partial t} &= \nabla \cdot (D \nabla n - n \nabla \phi), \\ \frac{\partial p}{\partial t} &= \nabla \cdot (D \nabla p + p \nabla \phi), \\ \lambda^2 \nabla^2 \phi &= n - p, \end{aligned}$$

n, p concentration of negative/positive particles, ϕ electric potential.

Individual to continuum

Care need to be taken when passing from individual to continuum models.

Individual to continuum

Care need to be taken when passing from individual to continuum models.

The following argument is common but fallacious. As the concentration of individuals increases, so the available space to diffuse decreases, so the diffusion coefficient should be reduced:

$$D(c) \propto 1 - c.$$

Individual to continuum

Care need to be taken when passing from individual to continuum models.

The following argument is common but fallacious. As the concentration of individuals increases, so the available space to diffuse decreases, so the diffusion coefficient should be reduced:

$$D(c) \propto 1 - c.$$

Using the (experimentally measured) root mean square displacement to estimate the (collective) diffusion coefficient can also be trouble.

Paradigm problem

System of N interacting Brownian particles in $\Omega \subset \mathbb{R}^3$.

Paradigm problem

System of N interacting Brownian particles in $\Omega \subset \mathbb{R}^3$.

Particle-level description (high-dim.)

$$\mathrm{d}\mathbf{X}_i = \sqrt{2D}\,\mathrm{d}\mathbf{B}_i(t) + \mathbf{f}_i(\mathbf{X})\,\mathrm{d}t, \quad 1 \le i \le N$$

Fokker–Planck PDE for *joint* probability density $P(\mathbf{x}_1, \ldots, \mathbf{x}_N, t)$:

$$\frac{\partial P}{\partial t}(\vec{x}, t) = \vec{\nabla}_{\vec{x}} \cdot \left[D \vec{\nabla}_{\vec{x}} P - \vec{F}(\vec{x})\, P \right] \quad \text{in} \quad \Omega^N,$$

where $\vec{x} = (\mathbf{x}_1, \ldots, \mathbf{x}_N), \quad \vec{F} = (\mathbf{f}_1, \ldots, \mathbf{f}_N)$.

Paradigm problem

System of N interacting Brownian particles in $\Omega \subset \mathbb{R}^3$.

Particle-level description (high-dim.)

$$\mathrm{d}\mathbf{X}_i = \sqrt{2D}\,\mathrm{d}\mathbf{B}_i(t) + \mathbf{f}_i(\mathbf{X})\,\mathrm{d}t, \quad 1 \le i \le N$$

Fokker–Planck PDE for *joint* probability density $P(\mathbf{x}_1, \dots, \mathbf{x}_N, t)$:

$$\frac{\partial P}{\partial t}(\vec{x}, t) = \vec{\nabla}_{\vec{x}} \cdot \left[D \vec{\nabla}_{\vec{x}} P - \vec{F}(\vec{x})\, P \right] \quad \text{in} \quad \Omega^N,$$

Population-level description (low-dim.)

PDE for marginal density $p(\mathrm{x}, t) = \int P(\vec{x}, t)\, \delta(\mathbf{x} - \mathbf{x}_1) \mathrm{d}\vec{x}$:

$$\frac{\partial p}{\partial t}(\mathrm{x}, t) = \boldsymbol{\nabla}_{\mathbf{x}} \cdot \left[\bar{D}(p) \nabla_{\mathbf{x}}\, p - \bar{\mathbf{f}}(\mathrm{x}, p)\, p \right] \quad \text{in} \quad \Omega$$

Diffusion of pairwise interacting particles

Suppose each particle exerts a force on the others which depends only on their separation. Then the interaction potential of the system is

$$U(\vec{x}) = \sum_{1 \leq i < j \leq N} V(\|\mathbf{x}_i - \mathbf{x}_j\|)$$

and

$$\mathbf{f}_i(\vec{x}) = -\nabla_{\mathbf{x}_i} U(\vec{x}) = -\sum_{j \neq i} \nabla_{\mathbf{x}_i} V(\|\mathbf{x}_i - \mathbf{x}_j\|).$$

Diffusion of pairwise interacting particles

Suppose each particle exerts a force on the others which depends only on their separation. Then the interaction potential of the system is

$$U(\vec{x}) = \sum_{1 \le i < j \le N} V(\|\mathbf{x}_i - \mathbf{x}_j\|)$$

and
$$\mathbf{f}_i(\vec{x}) = -\nabla_{\mathbf{x}_i} U(\vec{x}) = -\sum_{j \neq i} \nabla_{\mathbf{x}_i} V(\|\mathbf{x}_i - \mathbf{x}_j\|).$$

Integrating the Fokker–Planck eqn over $\mathbf{x}_2, \ldots, \mathbf{x}_N$ gives

$$\frac{\partial p}{\partial t} = \nabla_{\mathbf{x}_1} \cdot \left[\nabla_{\mathbf{x}_1} p - \mathbf{B}(\mathbf{x}_1) \right],$$

where the function $\mathbf{B}$ is given by

$$\mathbf{B}(\mathbf{x}_1) = -\int_{\Omega^{N-1}} \sum_{j=2}^{N} \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_j\|) \, P(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N, t) \, \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N.$$

Diffusion of pairwise interacting particles

Suppose each particle exerts a force on the others which depends only on their separation. Then the interaction potential of the system is

$$U(\vec{x}) = \sum_{1 \le i < j \le N} V(\|\mathbf{x}_i - \mathbf{x}_j\|)$$

and

$$\mathbf{f}_i(\vec{x}) = -\nabla_{\mathbf{x}_i} U(\vec{x}) = -\sum_{j \neq i} \nabla_{\mathbf{x}_i} V(\|\mathbf{x}_i - \mathbf{x}_j\|).$$

Integrating the Fokker–Planck eqn over $\mathbf{x}_2, \ldots, \mathbf{x}_N$ gives

$$\frac{\partial p}{\partial t} = \nabla_{\mathbf{x}_1} \cdot [\nabla_{\mathbf{x}_1} p - \mathbf{B}(\mathbf{x}_1)],$$

where the function $\mathbf{B}$ is given by

$$\mathbf{B}(\mathbf{x}_1) = -(N-1) \int_\Omega \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_2\|)\, P_2(\mathbf{x}_1, \mathbf{x}_2, t)\, \mathrm{d}\mathbf{x}_2,$$

where the two-particle density function

$$P_2(\mathbf{x}_1, \mathbf{x}_2, t) := \int P(\vec{x}, t)\, \mathrm{d}\mathbf{x}_3 \ldots \mathrm{d}\mathbf{x}_N.$$

Closure

Suppose $P_2(\mathbf{x}_1, \mathbf{x}_2, t) = p(\mathbf{x}_1, t)p(\mathbf{x}_2, t)$. Then

$$\mathbf{B}_c(\mathbf{x}_1) = -(N-1)\, p(\mathbf{x}_1, t) \int_\Omega \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_2\|)\, p(\mathbf{x}_2, t)\, \mathrm{d}\mathbf{x}_2.$$

Very natural. Often done implicitly.

Closure

Suppose $P_2(\mathbf{x}_1, \mathbf{x}_2, t) = p(\mathbf{x}_1, t)p(\mathbf{x}_2, t)$. Then

$$\mathbf{B}_c(\mathbf{x}_1) = -(N-1)\, p(\mathbf{x}_1, t) \int_\Omega \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_2\|)\, p(\mathbf{x}_2, t)\, \mathrm{d}\mathbf{x}_2.$$

Very natural. Often done implicitly.

Assume a short range potential: $V(r) = \tilde{V}(r/\epsilon)$. For $\epsilon \ll 1$ we find

$$\mathbf{B}_c(\mathbf{x}_1) = -2\pi\, \epsilon^3 (N-1)\, \nabla_{\mathbf{x}_1} p^2(\mathbf{x}_1, t) \int_0^\infty \tilde{V}(r) r^2\, \mathrm{d}r.$$

Nonlinear diffusion equation

$$\frac{\partial p}{\partial t}(\mathbf{x}, t) = \nabla \cdot \left(\bar{D}(p) \nabla p \right),$$

where

$$\bar{D}(p) = D\left[1 + 2(N-1)\epsilon^3 \overline{\beta}_V p\right], \qquad \overline{\beta}_V = 2\pi \int_0^\infty \tilde{V}(r) r^2\, \mathrm{d}r.$$

Matched asymptotic expansions

Can we approximate $P_2(\mathbf{x}_1, \mathbf{x}_2, t)$ using asymptotic expansions?

Matched asymptotic expansions

Can we approximate $P_2(\mathbf{x}_1, \mathbf{x}_2, t)$ using asymptotic expansions?

Outer region away from the collision surface: $\|\mathbf{x}_1 - \mathbf{x}_2\| \gg \epsilon$

- Particles are independent

$$P_{outer}(\mathbf{x}_1, \mathbf{x}_2, t) \sim p(\mathbf{x}_1, t)p(\mathbf{x}_2, t) + \mathcal{O}(\epsilon^d).$$

Matched asymptotic expansions

Can we approximate $P_2(\mathbf{x}_1, \mathbf{x}_2, t)$ using asymptotic expansions?

Outer region away from the collision surface: $\|\mathbf{x}_1 - \mathbf{x}_2\| \gg \epsilon$

- Particles are independent

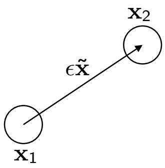
$$P_{outer}(\mathbf{x}_1, \mathbf{x}_2, t) \sim p(\mathbf{x}_1, t)p(\mathbf{x}_2, t) + \mathcal{O}(\epsilon^d).$$

Inner region near the collision surface: $\|\mathbf{x}_1 - \mathbf{x}_2\| \sim \epsilon$

- Particles are correlated
- Change of variables to inner variables:

$$\mathbf{x}_1 = \tilde{\mathbf{x}}_1, \qquad \mathbf{x}_2 = \tilde{\mathbf{x}}_1 + \epsilon\tilde{\mathbf{x}}$$

- Solve for the inner function $\tilde{P}(\tilde{\mathbf{x}}_1, \tilde{\mathbf{x}}, t) = P(\mathbf{x}_1, \mathbf{x}_2, t)$ (asymptotic expansion in ϵ).



Inner problem

The leading order inner problem is

$$2\nabla_{\tilde{\mathbf{x}}} \cdot \left[\nabla_{\tilde{\mathbf{x}}} \tilde{P}^{(0)} + \nabla_{\tilde{\mathbf{x}}} \tilde{V}(\tilde{\mathbf{x}}) \tilde{P}^{(0)} \right] = 0,$$

$$\tilde{P}^{(0)} \sim p^2(\tilde{\mathbf{x}}_1, t) \quad \text{as} \quad \|\tilde{\mathbf{x}}\| \to \infty,$$

with solution

$$\tilde{P}^{(0)}(\tilde{\mathbf{x}}_1, \tilde{\mathbf{x}}, t) = p^2(\tilde{\mathbf{x}}_1, t)\, e^{-\tilde{V}(\tilde{\mathbf{x}})}.$$

Inner problem

The leading order inner problem is

$$2\nabla_{\tilde{\mathbf{x}}}\cdot\left[\nabla_{\tilde{\mathbf{x}}}\tilde{P}^{(0)}+\nabla_{\tilde{\mathbf{x}}}\tilde{V}(\tilde{\mathbf{x}})\tilde{P}^{(0)}\right]=0,$$

$$\tilde{P}^{(0)}\sim p^2(\tilde{\mathbf{x}}_1,t)\quad\text{as}\quad\|\tilde{\mathbf{x}}\|\to\infty,$$

with solution

$$\tilde{P}^{(0)}(\tilde{\mathbf{x}}_1,\tilde{\mathbf{x}},t)=p^2(\tilde{\mathbf{x}}_1,t)\,e^{-\tilde{V}(\tilde{\mathbf{x}})}.$$

The $\mathcal{O}(\epsilon)$ inner problem is

$$2\nabla_{\tilde{\mathbf{x}}}\cdot\left[\nabla_{\tilde{\mathbf{x}}}\tilde{P}^{(1)}+\nabla_{\tilde{\mathbf{x}}}\tilde{V}(\tilde{\mathbf{x}})\tilde{P}^{(1)}\right]-\nabla_{\tilde{\mathbf{x}}_1}\cdot\left[2\nabla_{\tilde{\mathbf{x}}}\tilde{P}^{(0)}+\nabla_{\tilde{\mathbf{x}}}\tilde{V}(\tilde{\mathbf{x}})\tilde{P}^{(0)}\right]=0,$$

$$\tilde{P}^{(1)}\sim p(\tilde{\mathbf{x}}_1)\,\tilde{\mathbf{x}}\cdot\nabla_{\tilde{\mathbf{x}}_1}p(\tilde{\mathbf{x}}_1)\qquad\text{as}\qquad\|\tilde{\mathbf{x}}\|\to\infty,$$

with solution

$$\tilde{P}^{(1)}(\tilde{\mathbf{x}}_1,\tilde{\mathbf{x}},t)=p(\tilde{\mathbf{x}}_1,t)\tilde{\mathbf{x}}\cdot\nabla_{\tilde{\mathbf{x}}_1}p(\tilde{\mathbf{x}}_1,t)\,e^{-\tilde{V}(\tilde{\mathbf{x}})}.$$

Recall we need to calculate

$$\mathbf{B}(\mathbf{x}_1) = -(N-1)\int_\Omega \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_2\|)\, P_2(\mathbf{x}_1, \mathbf{x}_2, t)\, \mathrm{d}\mathbf{x}_2.$$

Recall we need to calculate

$$\mathbf{B}(\mathbf{x}_1) = -(N-1)\int_\Omega \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_2\|)\, P_2(\mathbf{x}_1, \mathbf{x}_2, t)\,\mathrm{d}\mathbf{x}_2.$$

Using our inner expression for $P_2(\mathbf{x}_1, \mathbf{x}_2, t)$ we find

$$\mathbf{B}(\mathbf{x_1}) = -2\beta_V\,\epsilon^3\,p(\mathrm{x}_1, t)\nabla_{\mathbf{x}_1} p(\mathbf{x}_1),$$

where

$$\beta_V = 2\pi\int_0^\infty \left(1 - \mathrm{e}^{-\tilde{V}(r)}\right) r^2\,\mathrm{d}r.$$

Recall we need to calculate

$$\mathbf{B}(\mathbf{x}_1) = -(N-1)\int_\Omega \nabla_{\mathbf{x}_1} V(\|\mathbf{x}_1 - \mathbf{x}_2\|)\, P_2(\mathbf{x}_1, \mathbf{x}_2, t)\,\mathrm{d}\mathbf{x}_2.$$

Using our inner expression for $P_2(\mathbf{x}_1, \mathbf{x}_2, t)$ we find

$$\mathbf{B}(\mathbf{x_1}) = -2\beta_V\,\epsilon^3\, p(\mathrm{x}_1, t)\nabla_{\mathbf{x}_1} p(\mathbf{x}_1),$$

where

$$\beta_V = 2\pi \int_0^\infty \left(1 - \mathrm{e}^{-\tilde{V}(r)}\right) r^2\,\mathrm{d}r.$$

Same form, different coefficient.

$$\overline{\beta}_V = 2\pi \int_0^\infty \tilde{V}(r) r^2\,\mathrm{d}r.$$

Method can be modified to deal with hard spheres, where closure fails.

Diffusion with size-exclusion: hard-spheres

Suppose system consists of N hard spheres of diameter ϵ under an external potential W. Then the interaction potential is

$$V_{\mathrm{HS}}(r) = \begin{cases} \infty, & r < \epsilon \\ 0, & r > \epsilon \end{cases} \quad \text{and } \beta_{\mathrm{HS}} := \alpha = 2\pi/3.$$

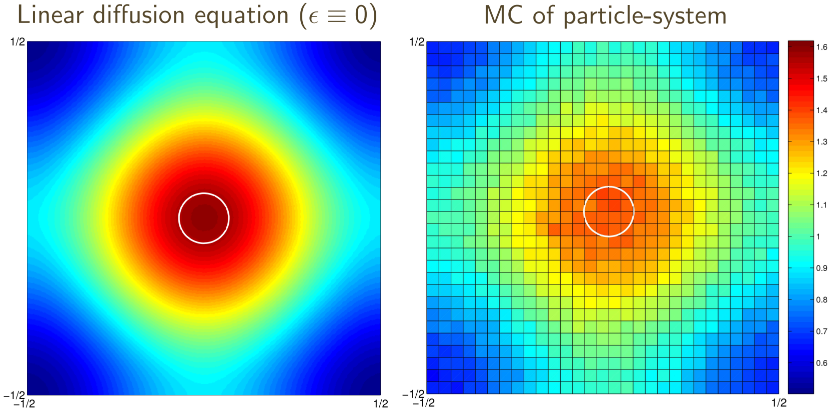
So p evolves according to the nonlinear PDE:

$$\frac{\partial p}{\partial t} = \nabla_{\mathbf{x}} \cdot \left[\overline{D}(p) \nabla_{\mathbf{x}} p + \nabla_{\mathbf{x}} W\, p\right], \quad \overline{D}(p) = 1 + 2\alpha(N-1)\epsilon^3 p.$$

- Excluded-volume interactions → increased collective diffusion:
- It preserves gradient-flow structure of original Fokker-Planck (s.s. are minimizers of energy functional):

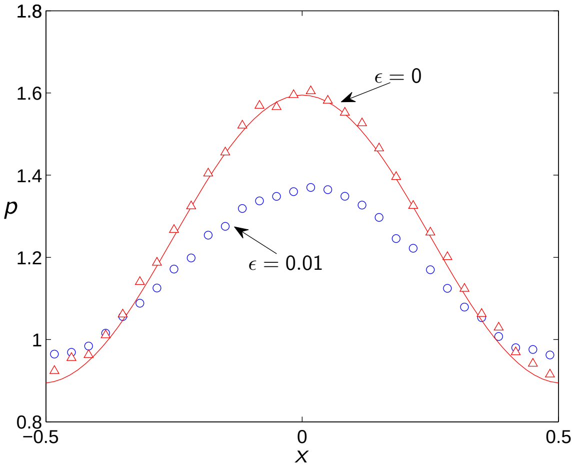
$$\mathcal{F}(p) = \int_\Omega \left[p \log p + \alpha(N-1)\epsilon^3 p^2\right] + pW(\mathbf{x})\mathrm{d}\mathbf{x}.$$

Results: hard spheres



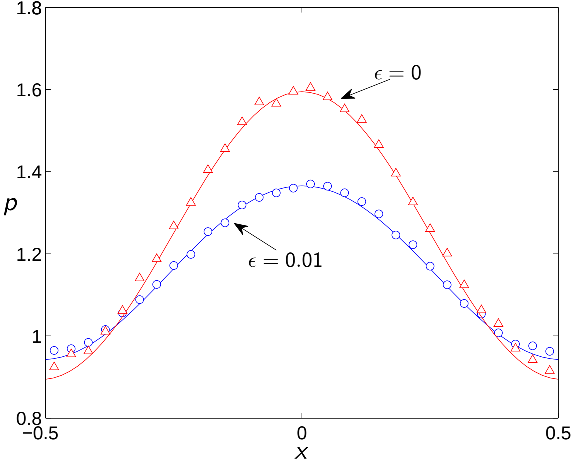
Marginal density $p(\mathbf{x}, t)$ at time $t = 0.05$ with normally distributed initial data ($\sigma = 0.05$), $N = 400$ and $\mathbf{f} = 0$. Histogram made with 10^4 runs.

Results: hard spheres



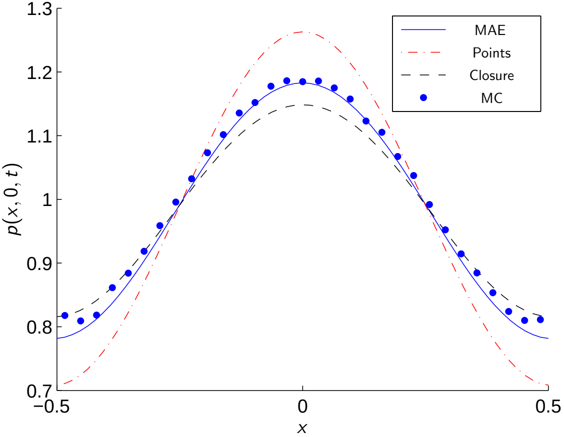
Slice through $y = 0$ of the marginal density $p(\mathbf{x}, t)$ at time $t = 0.05$.

Results: hard spheres

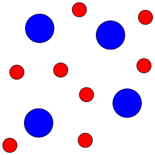


Results: soft spheres

Particles interacting with $U(r) = (\epsilon/r)e^{-r/\epsilon}$



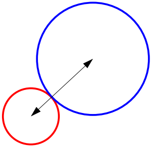
Multiple Species



Blues and Reds

Blues and reds

Take a mixture of two types of hard-spheres particles with different **numbers** (N_b, N_r), **sizes** (ϵ_b, ϵ_r), **diffusivities** (D_b, D_r) and external **drifts** $(\mathbf{f}_b, \mathbf{f}_r)$.

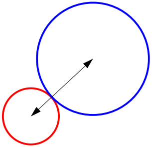


N_b blues at $\vec{x}_b = (\mathbf{x}_1, \dots, \mathbf{x}_{N_b})$ $\qquad$ N_r reds at $\vec{x}_r = (\mathbf{x}_{N_b+1}, \dots, \mathbf{x}_N)$

Joint probability density: $P(\mathbf{x}_1, \dots, \mathbf{x}_{N_b}, \mathbf{x}_{N_b+1}, \dots, \mathbf{x}_N, t)$

Blues and reds

Take a mixture of two types of hard-spheres particles with different **numbers** (N_b, N_r), **sizes** (ϵ_b, ϵ_r), **diffusivities** (D_b, D_r) and external **drifts** $(\mathbf{f}_b, \mathbf{f}_r)$.



N_b blues at $\vec{x}_b = (\mathbf{x}_1, \ldots, \mathbf{x}_{N_b})$ N_r reds at $\vec{x}_r = (\mathbf{x}_{N_b+1}, \ldots, \mathbf{x}_N)$

Joint probability density: $P(\mathbf{x}_1, \ldots, \mathbf{x}_{N_b}, \mathbf{x}_{N_b+1}, \ldots, \mathbf{x}_N, t)$

Configuration space: $\Omega_\epsilon^N = \Omega^N \setminus \mathcal{B}_\epsilon$ with

$$\mathcal{B}_\epsilon = \left\{ \vec{x} \in \Omega^N : \exists i \neq j \text{ s.t. } \|\mathbf{x}_i - \mathbf{x}_j\| \leq \tfrac{1}{2}(\epsilon_i + \epsilon_j) \right\}.$$

Population-level densities:

$$b(\mathbf{x}, t) = \int P(\vec{x}, t)\, \delta(\mathbf{x} - \mathbf{x}_1) \mathrm{d}\vec{x}, \qquad r(\mathbf{x}, t) = \int P(\vec{x}, t)\, \delta(\mathbf{x} - \mathbf{x}_N) \mathrm{d}\vec{x}.$$

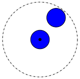
- $b(\mathbf{x}, t)$: probability of one of the N_b blue particles to be at $\mathbf{x}$ at time t.

Blue's population-level equation

Pick the first blue particle at $\mathbf{x}_1$ and integrate FP eq. over slice $\Omega_\epsilon^N(\mathbf{x}_1)$.

Only pairwise interactions with $N_b - 1$ blues ...

$$\frac{\partial b}{\partial t}(\mathbf{x}_1, t) = \nabla_{\mathbf{x}_1} \cdot \left[D_b \nabla_{\mathbf{x}_1} b - \mathbf{f}_b(\mathbf{x}_1)\, b \right] + (N_b - 1)\, \nabla_{\mathbf{x}_1} \cdot \left[\alpha \epsilon_b^3\, D_b \nabla_{\mathbf{x}_1} b^2 \right]$$

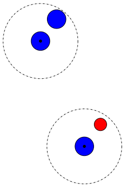


Blue's population-level equation

Pick the first blue particle at $\mathbf{x}_1$ and integrate FP eq. over slice $\Omega_\epsilon^N(\mathbf{x}_1)$.

Only pairwise interactions with $N_b - 1$ blues plus N_r reds ...

$$\frac{\partial b}{\partial t}(\mathbf{x}_1, t) = \nabla_{\mathbf{x}_1} \cdot \left[D_b \nabla_{\mathbf{x}_1} b - \mathbf{f}_b(\mathbf{x}_1)\, b \right]$$
$$+ (N_b - 1)\, \nabla_{\mathbf{x}_1} \cdot \left[\alpha \epsilon_b^3\, D_b \nabla_{\mathbf{x}_1} b^2 \right]$$
$$+ N_r\, \mathcal{I}_{br}$$



$\mathcal{I}_{br}$: contribution of an inner region involving one blue and one red.
Obtain it computing a blue–red interaction via matched asymptotics.

Blue's population-level equation

We find that

$$\frac{\partial b}{\partial t}(\mathbf{x},t) = \boldsymbol{\nabla}_{\mathbf{x}} \cdot \Big[D_b \boldsymbol{\nabla}_{\mathbf{x}} b - \mathbf{f}_b(\mathbf{x}) b + (N_b - 1)\epsilon_b^3 D_b \alpha \, b \boldsymbol{\nabla}_{\mathbf{x}} b + N_r \epsilon_{br}^3 \big\{ D_b (\beta_b \, b \boldsymbol{\nabla}_{\mathbf{x}} r - \gamma_b r \boldsymbol{\nabla}_{\mathbf{x}} b) + \gamma_b \left[\mathbf{f}_b(\mathbf{x}) - \mathbf{f}_r(\mathbf{x}) \right] br \big\} \Big],$$

where

$$\epsilon_{br} = \frac{\epsilon_b + \epsilon_r}{2} \qquad \text{(distance at contact between red \& blue particles)}$$

$$\alpha = \frac{4\pi}{3}, \quad \beta_b = \frac{2\pi}{3} \frac{[2D_b + 3D_r]}{D_b + D_r}, \quad \gamma_b = \frac{2\pi}{3} \frac{D_b}{D_b + D_r},$$

Final model for the blues & reds

We obtain a cross-diffusion system for b and r:

$$\frac{\partial}{\partial t}\begin{pmatrix} b \\ r \end{pmatrix}(\mathbf{x}, t) = \nabla_{\mathbf{x}} \cdot \left[\mathbf{D}(b, r)\nabla_{\mathbf{x}}\begin{pmatrix} b \\ r \end{pmatrix} - \mathbf{F}(b, r)\begin{pmatrix} b \\ r \end{pmatrix}\right]$$

with

$$\mathbf{D}(b, r) = \begin{pmatrix} D_b\left[1 + (N_b - 1)\epsilon_b^3\alpha b - N_r\epsilon_{br}^3\gamma_b r\right] & D_b N_r \epsilon_{br}^3\beta_b b \\ D_r N_b \epsilon_{br}^3 \beta_r r & D_r\left[1 + (N_r - 1)\epsilon_r^3\alpha r - N_b\epsilon_{br}^3\gamma_r b\right] \end{pmatrix}$$

$$\mathbf{F}(b, r) = \begin{pmatrix} \mathbf{f}_b & N_r\epsilon_{br}^3\gamma_b(\mathbf{f}_r - \mathbf{f}_b)b \\ N_b\epsilon_{br}^3\gamma_r(\mathbf{f}_b - \mathbf{f}_r)r & \mathbf{f}_r \end{pmatrix}$$

Gradient flow structure: two species

If $\mathbf{f}_b = -\nabla_{\mathbf{x}} W_b$ and $\mathbf{f}_r = -\nabla_{\mathbf{x}} W_r$:

$$\frac{\partial}{\partial t}\begin{pmatrix} b \\ r \end{pmatrix} = \nabla \cdot \left[\mathbf{M}(b,r)\nabla \begin{pmatrix} \partial_b \mathcal{F} \\ \partial_r \mathcal{F} \end{pmatrix}\right],$$

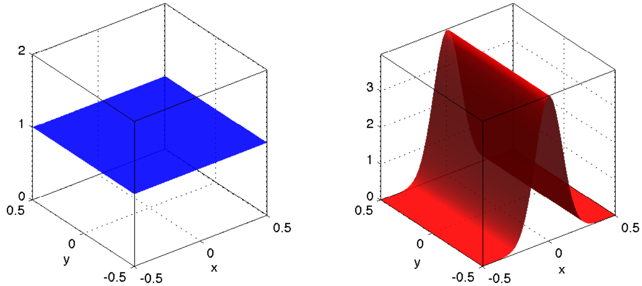
where $\mathcal{F}(b,r)$ is a entropy functional and $\mathbf{M}(b,r)$ the mobility matrix.

Example for large num. of particles: Define $\tilde{b} = N_b b$ and $\tilde{r} = N_r r$ and set $D_b = D_r = 1$.

$$\mathcal{F} = \int_\Omega \left[\tilde{b}\log\tilde{b} + \tilde{r}\log\tilde{r} + \tilde{b}W_b + \tilde{r}W_r + \tfrac{2\pi}{3}\left(\epsilon_b^3\,\tilde{b}^2 + 2\epsilon_{br}^3\,\tilde{b}\tilde{r} + \epsilon_r^3\,\tilde{r}^2\right)\right]\mathrm{d}\mathbf{x}$$

$$\mathbf{M}(\tilde{b},\tilde{r}) = \begin{pmatrix} \tilde{b}(1-\frac{\pi}{3}\epsilon_{br}^3\tilde{r}) & \frac{\pi}{3}\epsilon_{br}^3\tilde{b}\tilde{r} \\ \frac{\pi}{3}\epsilon_{br}^3\tilde{b}\tilde{r} & \tilde{r}(1-\frac{\pi}{3}\epsilon_{br}^3\tilde{b}) \end{pmatrix}$$

Numerical example: Initial distributions

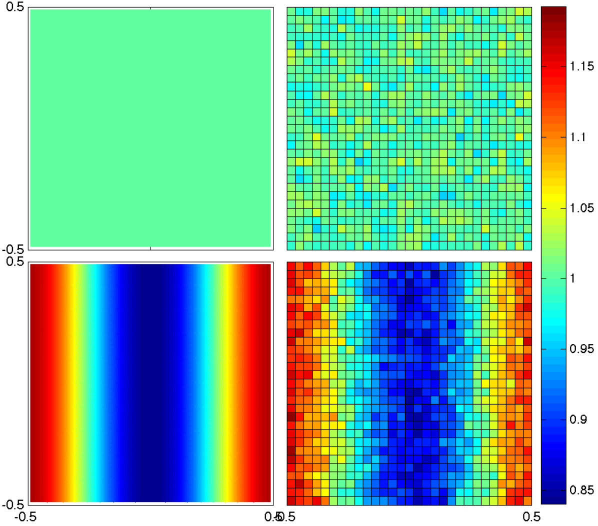


- $N_b = 100$, $\epsilon_b = 0.01$, $\mathbf{f}_b(\mathbf{x}_1) = 0$, $D_b = 1$.
- $N_r = 300$, $\epsilon_r = 0.02$, $\mathbf{f}_r(\mathbf{x}_1) = 0$, $D_r = 1$.
- Volume fraction: 10.2%.

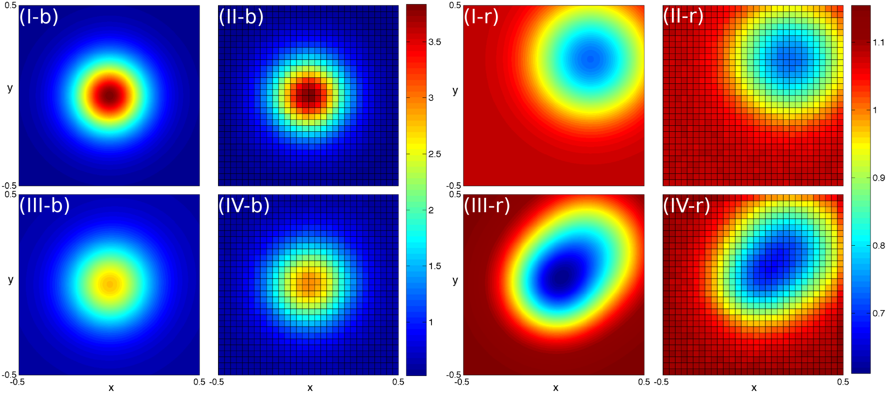
Numerical example: blues at T_f

Point particles ($\epsilon_b = 0$)

Finite-sized particles ($\epsilon_b = 0.01$)



Stationary example



Stationary densities of blues (left) and reds (right) under an external potential, $D_b = D_r = 1$ and $N_b = N_r = 400$.
Top row Point particles ($\epsilon_b = \epsilon_r = 0$), $b_s \propto e^{-V_b}$ and $r_s \propto e^{-V_r}$.
Bottom row Finite-size particles ($\epsilon_b = \epsilon_r = 0.02$).

Self and collective diffusion

Suppose particles are identical, but we label one red and N blue.
No applied force.

$$\begin{aligned}\partial_t b &= D\nabla\cdot[\nabla b + (N-1)\epsilon^3\alpha b\nabla b + \epsilon^3\beta\, b\nabla r - \epsilon^3\gamma r\nabla b],\\ \partial_t r &= D\nabla\cdot[\nabla r + N\epsilon^3\beta\, r\nabla b - N\epsilon^3\gamma b\nabla r]\end{aligned}$$

where $\alpha = \frac{4\pi}{3}$, $\beta = \frac{5\pi}{3}$, $\gamma = \frac{\pi}{3}$.

Self and collective diffusion

Suppose particles are identical, but we label one red and N blue.
No applied force.

$$\begin{aligned}\partial_t b &= D\nabla\cdot[\nabla b + (N-1)\epsilon^3\alpha b\nabla b + \epsilon^3\beta\, b\nabla r - \epsilon^3\gamma r\nabla b],\\ \partial_t r &= D\nabla\cdot[\nabla r + N\epsilon^3\beta\, r\nabla b - N\epsilon^3\gamma b\nabla r]\end{aligned}$$

where $\alpha = \frac{4\pi}{3}$, $\beta = \frac{5\pi}{3}$, $\gamma = \frac{\pi}{3}$.

- Diffusion coefficient of r in a uniform concentration of b is:

$$D_s = D(1 - N\epsilon^3\gamma b) \qquad \text{(self diffusion).}$$

Self and collective diffusion

Suppose particles are identical, but we label one red and N blue.
No applied force.

$$\begin{aligned}\partial_t b &= D\nabla\cdot[\nabla b + (N-1)\epsilon^3\alpha b\nabla b + \epsilon^3\beta\, b\nabla r - \epsilon^3\gamma r\nabla b],\\ \partial_t r &= D\nabla\cdot[\nabla r + N\epsilon^3\beta\, r\nabla b - N\epsilon^3\gamma b\nabla r]\end{aligned}$$

where $\alpha = \frac{4\pi}{3}$, $\beta = \frac{5\pi}{3}$, $\gamma = \frac{\pi}{3}$.

- Diffusion coefficient of r in a uniform concentration of b is:

$$D_s = D(1 - N\epsilon^3\gamma b) \qquad \text{(self diffusion)}.$$

- But if $r = b$ ($= p$, say) then both equations give

$$\frac{\partial p}{\partial t} = D\nabla\cdot\left[\nabla p + N\epsilon^3\alpha p\nabla p\right], \qquad \text{since } \beta - \gamma = \alpha.$$

Thus $\qquad D_c = D(1 + N\epsilon^3\alpha p) \qquad$ (collective diffusion).

Diffusion through obstacles

Use two-species model with red particles as obstacles, setting the reds diffusion D_r and external forces $\mathbf{f}_r$, $\mathbf{f}_b$ to zero:

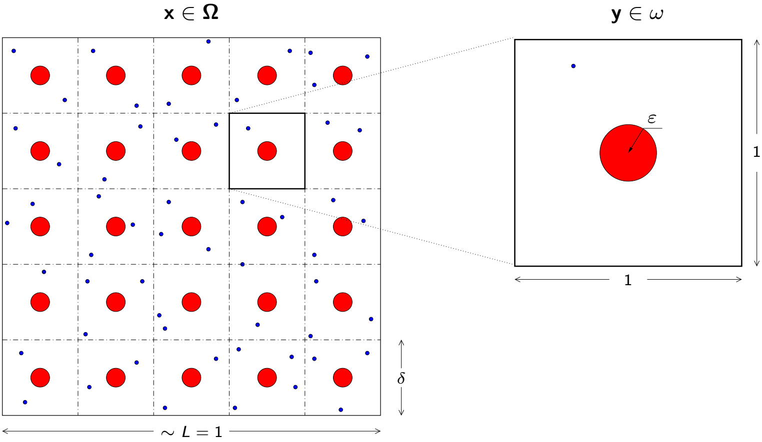
$$\frac{\partial b}{\partial t}(\mathbf{x}, t) = \nabla \cdot \Big[\big(1 + \epsilon_b^3 \alpha_b\, b - \epsilon_{br}^3 \gamma_b r\big) \nabla b + \epsilon_{br}^3 \beta_b \nabla r\; b \Big],$$

- Competition between enhanced diffusion from self-crowding and reduced diffusion due to obstacles.
- Drift due to gradient in obstacles density.
- Can prescribe any obstacles distribution with r (random).

How does this relate with a deterministic distribution? Alternative approach: multiple scale method on ordered array of obstacles.

Obstacles in ordered array (deterministic)

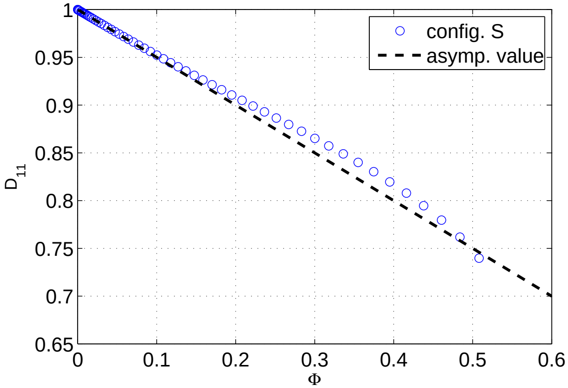
Multiple scale method: $\boxed{\mathbf{y} = \mathbf{x}/\delta}$ $\mathbf{x}$ macroscale, $\mathbf{y}$ microscale.



Take blues as points, $\epsilon_b = 0$, but red obstacles as big as we want, $\epsilon_r \lesssim 1$.

Comparison between two approaches

Blues diffusion coefficient as a function of red obstacles concentration:



Obstacles **uniformly distributed** (black line) vs. obstacles in a periodic (*deterministic*) array (dots).

Summary

Systematic method to obtain a population-level equation from a system of interacting Brownian particles.

- One-species: overall diffusion enhanced due to crowding.
- Two-species: competition between enhanced diffusion from self-crowding and reduced diffusion due to crowding of the other species.

Outlook

- Combination of short- and long-range interactions.
- Anisotropic interactions.
- Away from Brownian motion.

Funding

- St John's College, Oxford.
- 2020 Science programme: EPSRC Cross-Discipline Interface Programme (grant number EP/I017909/1) and Microsoft Research.