Force induced dispersion in heterogeneous materials

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Plan of talk

•Revisting a very old problem – diffusion with spatially varying diffusivity

•General Kubo formulae for diffusion constants and drifts in periodic systems

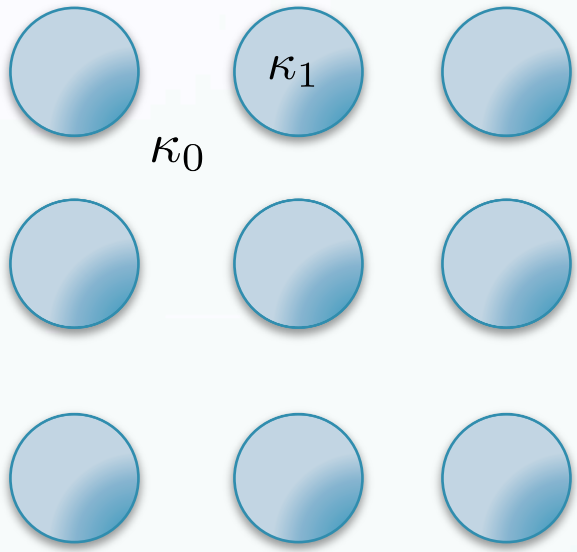
•Spatially varying diffusivity in the presence of an external force – force enhanced dispersion

• Perspectives and conclusions

Diffusion with variable diffusivity

$$\frac{\partial p(\mathbf{x};t)}{\partial t} = \nabla \cdot \kappa(\mathbf{x}) \nabla p(\mathbf{x};t)$$

Fokker Planck equation on medium with variable isotropic diffusivity



$$d\mathbf{X}_t = \sqrt{2\kappa(\mathbf{X}_t)}d\mathbf{B}_t + \nabla\kappa(\mathbf{X}_t)dt$$

Corresponding Ito SDE

$$\langle(\mathbf{X}_t - \mathbf{X}_0)^2\rangle = 2dD(t)t$$

Mean squared displacement

$$D_e = \lim_{t\to\infty} D(t)$$

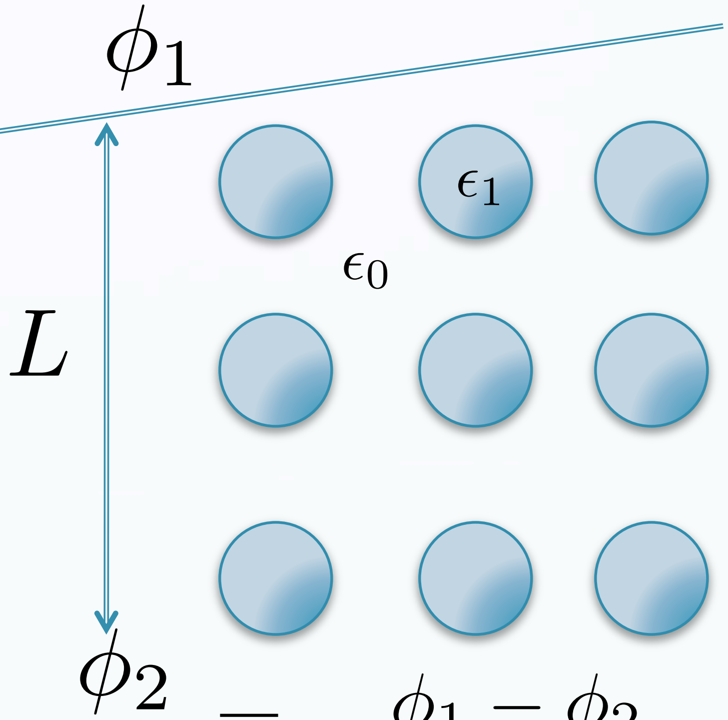
Effective diffusion constant- important for reaction rates, mean first passage times ..

Link with dielectric problem

Flat spatial average

$$\overline{\epsilon \mathbf{E}} = \epsilon_e \overline{\mathbf{E}}$$

Effective dielectric constant:
Maxwell 1873, Rayleigh 1892,
Maxwell-Garnett 1904, Bruggeman
1935 –old problem



$$\nabla \cdot \epsilon(\mathbf{x}) \nabla \phi = 0$$

Laplace's equation in dielectric medium

$$\overline{\mathbf{E}} = \frac{\phi_1 - \phi_2}{L} \mathbf{e}_z$$

$$\kappa(\mathbf{x}) \equiv \epsilon(\mathbf{x}) \Rightarrow D_e = \epsilon_e$$

Correspondance between effective diffusivity and effective dielectric constant

What we know

$$(\overline{\kappa^{-1}})^{-1} \le D_e \le \overline{\kappa}$$

Wiener variational bounds 1910 (improved bounds by Hashin and Shtrikman 1962)

What you might naively expect as equilibrium density is uniform

In one dimension $D_e = (\overline{\kappa^{-1}})^{-1}$ **harmonic mean**

Duality result in two dimensions if $\kappa(\mathbf{x}) \equiv \dfrac{\kappa_0^2}{\kappa(\mathbf{x})}$

then $D_e = \exp(\overline{\ln \kappa})$ **geometric mean (Dykhne 1971, Keller 1960s)**

A part from these exact results there is a huge literature on approximative methods – effective medium, perturbation theory, renormalization, homogenization

The influence of applied force

$$\partial_t p(\mathbf{x},t) = \nabla \cdot [\kappa(\mathbf{x})\nabla p - \beta\ \kappa(\mathbf{x})\ \mathbf{F}\ p\ ]$$

$$\beta\kappa(\mathbf{x}) = \mu(\mathbf{x})$$

Local Einstein relation

mobility/conductivity

External applied, force e.g. gravity, electric field

Effective drift

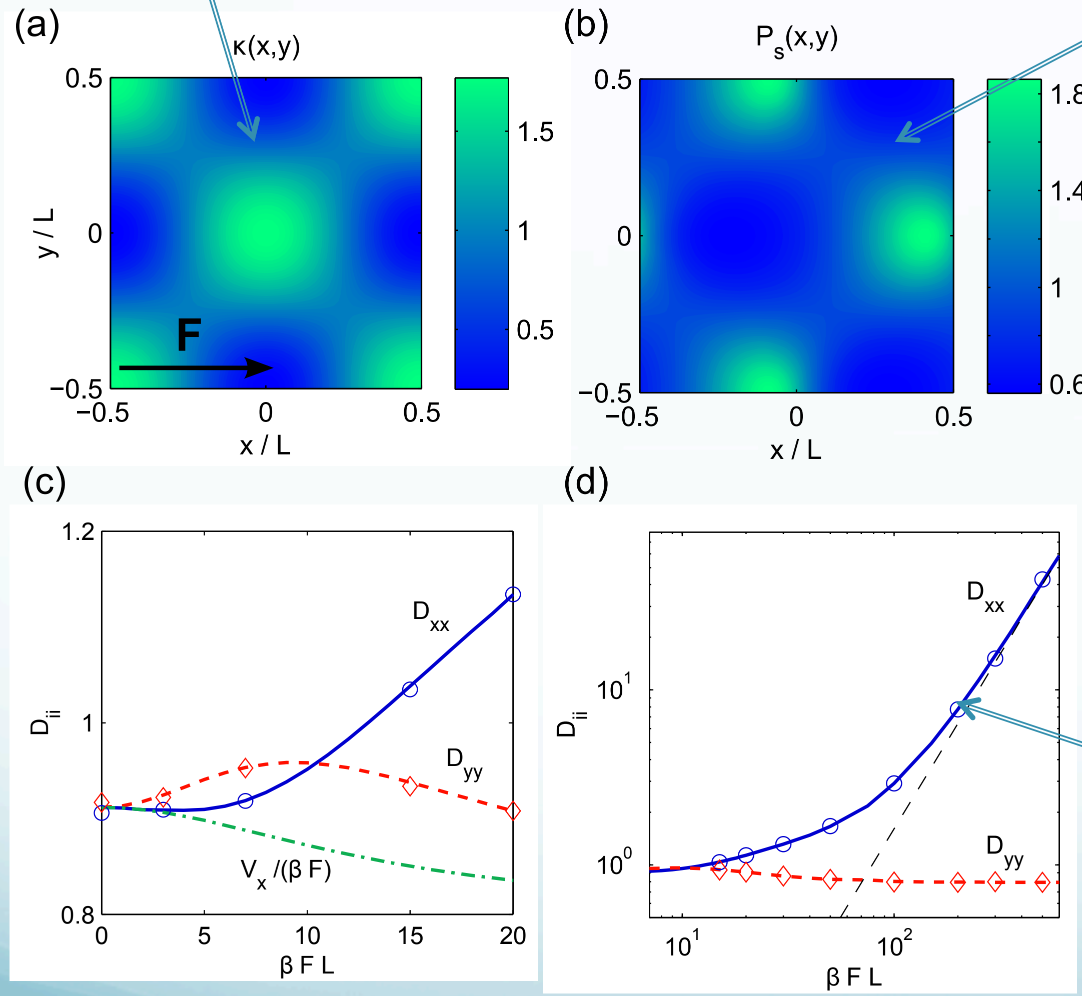
$$V_i = \lim_{t\to\infty} \frac{\langle X_i(t) - X_i(0)\rangle}{t}$$

Effective dispersion/ diffusion

$$D_{ii} = \lim_{t\to\infty} \frac{\langle [X_i(t) - X_i(0)]^2\rangle_c}{2t}$$

Example in 2d

$$\kappa(x, y) = \kappa_0[1 + 0.8\cos(2\pi x/L)\cos(2\pi y/L)]$$



Steady state pdf in periodic cell

Non monotonic behavior of both diffusion constants with F

Huge increase in dispersion in direction of force at large F

$$D_{xx} \simeq cF^2$$

Kubo formula for dispersion in periodic systems

Find explicit expressions for dispersion coefficients for Fokker-Planck equations with arbitrary periodic diffusivities and drifts

Generalize and extend know results for diffusion with applied force plus periodic potentials in one dimensions (based on first passage time arguments Riemann et al 2000 and Lindner and Schimansky-Geier 2002) to higher dimensions.

Recover results from homogenization theory for stationnary incompressible flows (Brenner 1980, Schraiman 1987 Majda and Kramer 1999)

Kubo formula from SDE

General method from FP in 1d by Derrida 1983 – extension to higher d Dean et al 1996

$$\frac{\partial p}{\partial t} = -Hp \qquad Hf = -\frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_j}(\kappa_{ij}(\mathbf{x})f(\mathbf{x})) - A_i(\mathbf{x})f(\mathbf{x})\right)$$

periodic

Here start with SDE – also allows computation of finite time corrections

Ito SDE

$$dX_i(t) = dW_i(t) + A_i(\mathbf{X}(t))dt$$

$$\langle dW_i(t)dW_j(t)\rangle = 2\kappa_{ij}(\mathbf{X}(t))dt$$

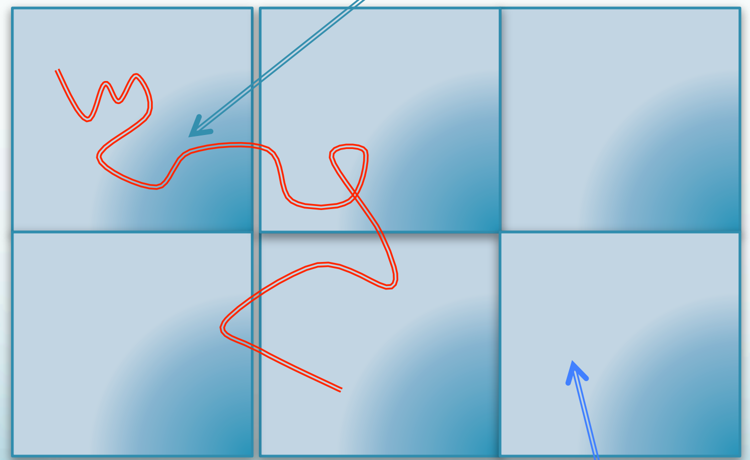
Formula for MSD

$$X_i(t) - X_i(0) - \int_0^t dt' A_i(\mathbf{X}(t')) = \int_0^t dW_i(t'),$$

Square and average –important to do it this way!

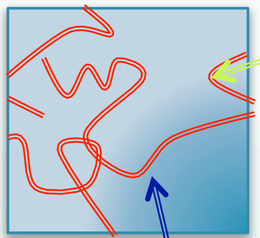
$$\langle (X_i(t) - X_i(0))^2 \rangle - \langle 2(X_i(t) - X_i(0)) \int_0^t dt' A_i(\mathbf{X}(t')) \rangle + \langle \left(\int_0^t dt' A_i(\mathbf{X}(t')) \right)^2 \rangle = 2 \langle \int_0^t dt' \kappa_{ii}(\mathbf{X}(t')) \rangle$$

Diffusion in infinite periodic cell $X(t)$



Unit cell Ω

$X(t)\ mod(\Omega)$



In steady state this is in equilibrium

Unit cell with Ω
Periodic boundaries

$X(t)\ mod(\Omega)$ **Has PDF obeying FP equation** $\dfrac{\partial P}{\partial t} = -HP$

$P_s(\mathbf{x})$ **steady state distribution** $HP_s(\mathbf{x}) = 0$

Steady state current $J_{si}(\mathbf{x}) = -\dfrac{\partial}{\partial x_j}(\kappa_{ij}(\mathbf{x})P_s(\mathbf{x})) + A_i(\mathbf{x})P_s(\mathbf{x})$

Effective drift $V_i = \int_\Omega d\mathbf{x} J_{si}(\mathbf{x}) = \int_\Omega d\mathbf{x}\ P_s(\mathbf{x})A_i(\mathbf{x})$

Stratonovich 1953

Diffusion coefficient

$$D^e_{ii} = \int_\Omega d\mathbf{x}\ \kappa_{ii}(\mathbf{x})P_s(\mathbf{x}) + \int_\Omega\int_\Omega d\mathbf{x}d\mathbf{y}\ \tilde{P}'(\mathbf{x},\mathbf{y},0)A_i(\mathbf{x})[J_{si}(\mathbf{y}) - \frac{\partial}{\partial y_j}(\kappa_{ij}(\mathbf{y})P_s(\mathbf{y}))]$$

$H\tilde{P}'(\mathbf{x},\mathbf{y},0) = \delta(\mathbf{x}-\mathbf{y}) - P_s(\mathbf{x})$ **Pseudo Green's function of H on** Ω

$P'(\mathbf{x},\mathbf{y}) = \sum_{\lambda>0} \dfrac{1}{\lambda}\psi_{R\lambda}(\mathbf{x})\psi_{L\lambda}(\mathbf{y})$ **Expansion in terms of left and right eigenfunctions**

Compact form for diffusion coefficients

Define
$$f_i(\mathbf{x}) = \int_\Omega d\mathbf{y}\ \tilde{P}'(\mathbf{x},\mathbf{y},0)[A_i(\mathbf{y})P_s(\mathbf{y}) - 2\frac{\partial}{\partial y_j}(\kappa_{ij}(\mathbf{y})P_s(\mathbf{y}))]$$

Gives
$$D_{ii} = \int_\Omega d\mathbf{x}\ \kappa_{ii}(\mathbf{x})P_s(\mathbf{x}) + \int_\Omega d\mathbf{x} A_i(\mathbf{x})f_i(\mathbf{x}).$$

Action of H on f
$$Hf_i(\mathbf{x}) = \left[\left(A_i(\mathbf{x}) - \int_\Omega d\mathbf{y} A_i(\mathbf{y})P_s(\mathbf{y})\right)P_s(\mathbf{x}) - 2\frac{\partial}{\partial x_j}(\kappa_{ij}(\mathbf{x})P_s(\mathbf{x}))\right]$$

Orthogonality from right/left eigenfunction expansion of P'
$$\int_\Omega d\mathbf{x}\ f_i(\mathbf{x}) = 0$$

Recovers results from homogenization theory for incompressible flows

$$\kappa_{ij}(\mathbf{x}) = \kappa_0\delta_{ij} \qquad A_i(\mathbf{x}) = u_i(\mathbf{x}) \quad \nabla\cdot\mathbf{u} = 0 \Rightarrow P_s(\mathbf{x}) = \frac{1}{|\Omega|}$$

Alternative adjoint representation

$$D_{ii} = \int_\Omega d\mathbf{x}\ \kappa_{ii}(\mathbf{x}) P_s(\mathbf{x}) + \int_\Omega d\mathbf{x} g_i(\mathbf{x})[A_i(\mathbf{x})P_s(\mathbf{x}) - 2\frac{\partial}{\partial x_j}(\kappa_{ij}(\mathbf{x})P_s(\mathbf{x}))]$$

Define

$$g_i(\mathbf{x}) = \int_\Omega d\mathbf{y}\ \ A_i(\mathbf{y})\tilde{P}'(\mathbf{y},\mathbf{x};0)$$

Action with adjoint of H

$$H^\dagger g_i(\mathbf{x}) = A_i(\mathbf{x}) - \int_\Omega d\mathbf{y} P_s(\mathbf{y})A_i(\mathbf{y})$$

Orthogonality condtion

$$\int_\Omega d\mathbf{y} P_s(\mathbf{y}) g_i(\mathbf{y}) = 0$$

Useful to check numerical methods, compare results with f and g

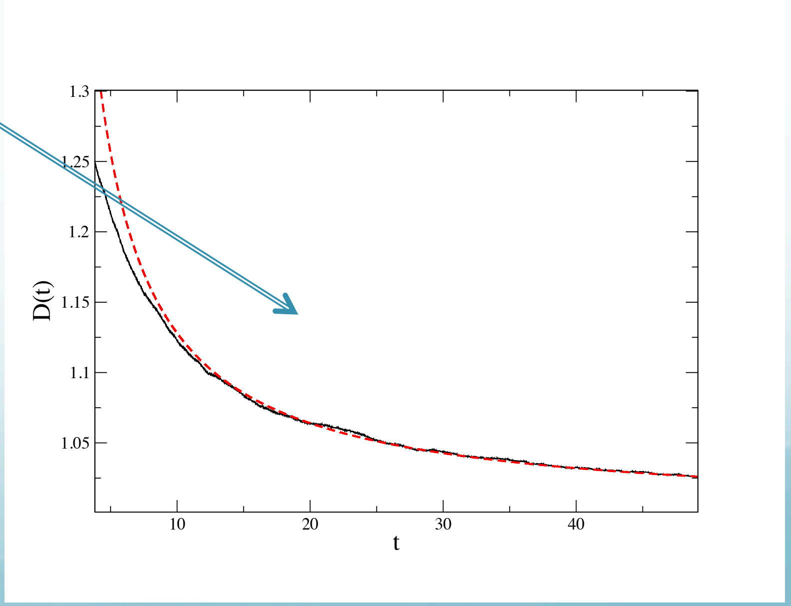
Finte time corrections

$$D_{ii}(t) \sim D_{ii}^{(e)} + \frac{C_{ii}}{t},$$

Leading finite time correction – next order decays as $\exp(-\lambda_1 t)/t$

$$C_{ii} = -\int_\Omega d\mathbf{x}\ g_i(\mathbf{x}) f_i(\mathbf{x})$$

Generalizes DD and G. Oshanin (2014) (periodic potentials) and DD and T. Guerin 2014 (diffusivity) – cases with no current



Stokes Einstein Relation

Great interest in generalization of Stoke's Einstein Relation for driven out of equilibrium systems – few explicit results before Riemann et al 2000 and Lindner and Schimansky-Geier 2002.

$$V_i = \int_\Omega d\mathbf{x}\ P_s(\mathbf{x}) A_i(\mathbf{x})$$

$$A_i(\mathbf{x}) = A_i^{(0)}(\mathbf{x}) + \kappa_{ij}(\mathbf{x})\beta F_j$$

differentiate wrt F_i

Perturbation of drift due to force and local Einstein relation

$$\frac{\partial V_i}{\partial F_i} = \beta \int_\Omega d\mathbf{x}\ P_s(\mathbf{x})\kappa_{ii}(\mathbf{x}) + \int_\Omega d\mathbf{x}\ \frac{\partial P_s(\mathbf{x})}{\partial F_i} A_i(\mathbf{x}).$$

Differentiate steady state FP eq. wrt F_i

$$H\frac{\partial P_s}{\partial F_i} + \frac{\partial}{\partial x_j}\left(\beta\kappa_{ji}P_s\right) = 0 \qquad \int_\Omega d\mathbf{x}\ \frac{\partial P_s(\mathbf{x})}{\partial F_i} = 0$$

$\frac{\partial P_s(\mathbf{x})}{\partial F_i}$ **has periodic bcs**

Conservation of probability

Can compute $\frac{\partial P}{\partial F_i}$ **with pseudo Green's function P'**

$$\frac{\partial V_i}{\beta\partial F_i} = \int_\Omega d\mathbf{x}\ P_s(\mathbf{x})\kappa_{ii}(\mathbf{x}) - \int_\Omega d\mathbf{x}\int_\Omega d\mathbf{y}\, A_i(\mathbf{x})\tilde{P}'(\mathbf{x},\mathbf{y};0)\frac{\partial}{\partial y_j}\left(\kappa_{ji}(\mathbf{y})P_s(\mathbf{y})\right).$$

Relation between drift and diffusion

$$D_{ii} = \frac{\partial V_i}{\beta \partial F_i} + \Delta_i$$

Stoke's Einstein recovered when$\Delta_i = 0$

$$\Delta_i = \int_\Omega \int_\Omega d\mathbf{x} d\mathbf{y} \;\tilde{P}'(\mathbf{x}, \mathbf{y}, 0) A_i(\mathbf{x}) J_{si}(\mathbf{y})$$

Violation in general when steady state has a non-zero current

General Result in 1D

Riemann et al 2002

$$\langle \dot{x} \rangle = \frac{L}{T_1(x_0 \rightarrow x_0 + L)},$$

Mean first passage time

$$D = \frac{L^2}{2} \frac{\Delta T_2(x_0 \rightarrow x_0 + L)}{[T_1(x_0 \rightarrow x_0 + L)]^3}.$$

Variance of first passage time

$$\Gamma(x) = \int_0^x dx' \frac{A(x)}{\kappa(x)}$$

$$I_+(x) = \frac{\exp(\Gamma(x))}{\kappa(x)} \int_x^\infty dx' \ \exp(-\Gamma(x'))$$

$$I_-(x) = \exp(-\Gamma(x)) \int_{-\infty}^x dx' \ \frac{\exp(\Gamma(x'))}{\kappa(x')}$$

Effective potential – if periodic no current

$$V = \frac{L}{\int_0^L dx I_\pm(x)}$$

Effective drift

$$D = \frac{L^2 \int_0^L dx \ \kappa(x) I_\pm(x)^2 I_\mp(x)}{\int_0^L dx \ I_\pm(x)^3}$$

Effective diffusion constant

Varying diffusivity plus force in 1D

$$A(x) = \frac{dk}{dx} + \kappa(x)\beta F$$

for this case

Express inverse diffusivity as Fourier series

$$\kappa(x) = \frac{1}{\overline{\kappa^{-1}} \sum_k a_k \exp(\frac{2\pi k i x}{L})} \qquad a_0 = 1$$

Force dependent diffusion constant

$$D(F) = \frac{1}{\overline{\kappa^{-1}}} \left[1 + 2\beta^2 F^2 \sum_{k>0} \frac{|a_k|^2}{\beta^2 F^2 + \frac{4\pi^2 k^2}{L^2}} \right]$$

Becomes dependent on spatial structure of diffusivity

$$D(0) = \overline{\kappa^{-1}}^{-1}$$

zero force

$$D(\infty) = \frac{1}{\overline{\kappa^{-1}}} \left[1 + 2 \sum_{k>0} |a_k|^2 \right] = \frac{\overline{\kappa^{-2}}}{\overline{\kappa^{-1}}^3}$$

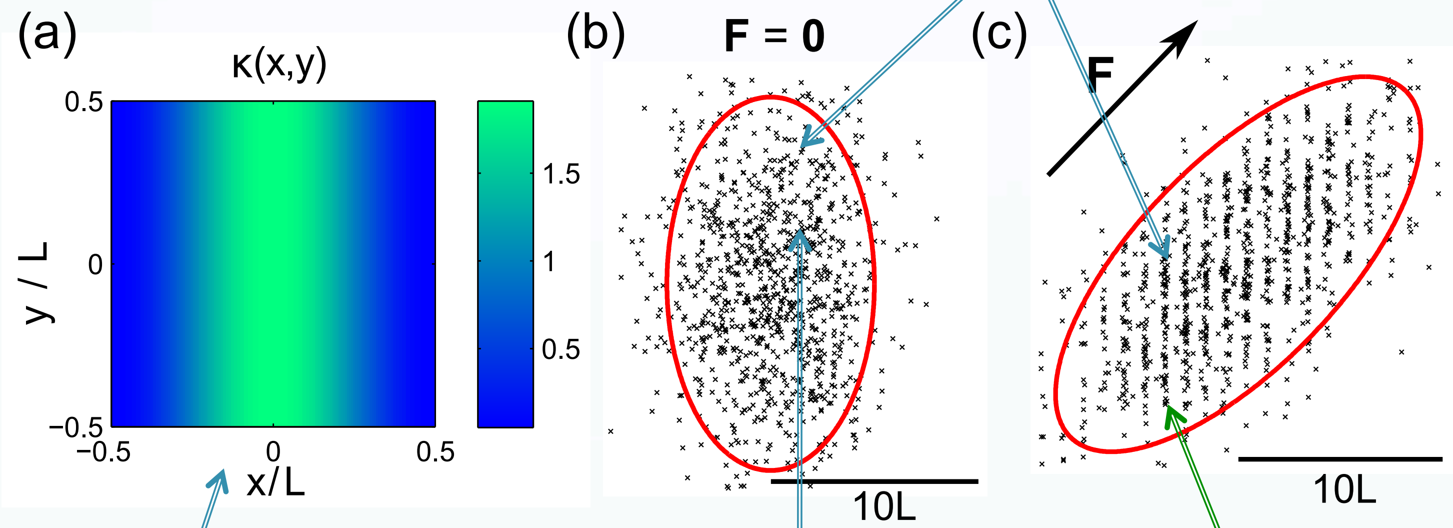
$$\frac{\partial V}{\beta \partial F} = \overline{\kappa^{-1}}^{-1}$$

Stokes Einstein only valid for F=0

Diffusion constant saturates at large force

Diffusion in stratified media

Diffusion clouds from simulations



$$\kappa(x,y) = \kappa_0[1 + 0.95\cos(2\pi x/L)]$$

$$D_{xx} < D_{yy}$$

$$D_{xx} = \overline{\kappa^{-1}}^{-1} \qquad D_{yy} = \overline{\kappa}$$

Steady state P_s is not flat for non-zero force

$$D_{xx} > D_{yy}$$

$$D_{ij} = (\overline{\kappa^{-1}})^{-1}\left\{\delta_{ij} + \frac{F_i F_j}{|\mathbf{F}\cdot\mathbf{e_x}|^2}\left[\frac{\overline{\kappa^{-2}}}{(\overline{\kappa^{-1}})^2} - 1\right]\right\},$$

At large F

Dispersion at large force

In two dimensions but for arbitrary diffusivity

$$\partial_t p(x,y,t) = \partial_x[\kappa(x,y)\partial_x p - h\ \kappa(x,y)p] + \partial_y \kappa(x,y)\partial_y p$$

with $h = \beta F_x$

At large h $\partial_x\left[h\ \kappa(x,y)\quad P_{\rm s}(x,y)\ \right] \approx 0 \quad \Rightarrow P_{\rm s}(x,y) \simeq C(y)\kappa^{-1}(x,y)$

At large forces equilibriation in the direction x is rapid

$p(x,y,t) \simeq \pi(y,t)P_{\rm s}(x|y)$ **Quasi-static applroximation for x given y**

$$P_{\rm s}(x|y) = \frac{1}{\kappa(x,y)\ L_x\ \overline{\kappa^{-1}}(y)}. \qquad \overline{g}(y) = L_x^{-1}\int_0^{L_x} dx\ g(x,y)$$

L_x **Period in x direction**

$$\partial_t \pi(y,t) \simeq \int_0^{L_x} dx\ \partial_y\{\kappa(x,y)\partial_y[\pi(y,t)P_{\rm s}(x|y)]\}$$

Effective FP for y variable

$$\partial_t \pi(y,t) = \partial_y^2[\kappa_e(y)\pi(y,t)] - \partial_y\{[\partial_y \overline{\ln\kappa}(y)]\kappa_e(y)\pi(y,t)\}$$

$$\kappa_e(y) = 1/\overline{\kappa^{-1}}(y)$$

$$\pi_{\rm s}(y) = \frac{e^{\overline{\ln\kappa}(y)}}{\kappa_e(y)\int_0^{L_y} du\ e^{\overline{\ln\kappa}(u)}/\kappa_e(u)}.$$

Order F^2 contribution to diffusion coeff in direction of force

$$D_{xx} = \frac{[\beta F R(L)]^2}{W(L)} \int_0^L dy \left[\frac{W(y)}{W(L)} - \frac{R(y)}{R(L)}\right]^2 e^{-\overline{\ln\kappa}(y)}$$

Generic quadratic enhancement

$$R(y) = \int_0^y du\ e^{\overline{\ln\kappa}(u)}; W(y) = \int_0^y du\ \kappa_e^{-1}(u) e^{\overline{\ln\kappa}(u)}$$

when $\kappa(x,y) = \kappa(x)$ **this F^2 term vanishes – saturation in 1d**

Conclusions

General points - perspectives

•General formulae for transport coefficients for periodic FP equations in any dimension.

• Further applications to incompressible flows, periodic potentials in higher dimensions.

• Explict formula for violation of Stokes-Einstein relation when a current flows.

Media with varying mobility/diffusivity

•Rich non-monotonic behavior in transport coefficients

•Force induced enhancement of diffusions

•Possible experiments – vary viscosity in liquids via temperature control ...