Force-Induced Dispersion in Heterogeneous Media

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The effect of a constant applied external force, induced for instance by an electric or gravitational field, on the dispersion of Brownian particles in periodic media with spatially varying diffusivity, and thus mobility, is studied. We show that external forces can greatly enhance dispersion in the direction of the applied force and also modify, to a lesser extent and in some cases nonmonotonically, dispersion perpendicular to the applied force. Our results thus open up the intriguing possibility of modulating the dispersive properties of heterogeneous media by using externally applied force fields. These results are obtained via a Kubo formula that can be applied to any periodic advection diffusion system in any spatial dimension.

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In diverse systems ranging from fluid mechanics, hydrology, and soft matter to solid state physics, at mesoscopic length and time scales, the dynamics of tracer particles is described by stochastic differential equations (SDEs) and their associated Fokker-Planck equations [1–3]. In heterogeneous media, the local transport coefficients such as the diffusivity and the mobility can vary in space depending on the local material properties. In a locally isotropic material where a uniform force $\mathbf{F}$ acts on a tracer particle, the probability density function (PDF) $p(\mathbf{x}, t)$ for the tracer position at time t obeys

$$\partial_t p(\mathbf{x}, t) = \nabla \cdot [\kappa(\mathbf{x})\nabla p - \beta\kappa(\mathbf{x})\mathbf{F}p]. \quad (1)$$

The first term on the right-hand side of Eq. (1) above corresponds to diffusion with a spatially varying diffusion constant. The second term represents the drift due to a constant applied external force and the term $\beta\kappa(\mathbf{x}) = \mu(\mathbf{x})$ is the local mobility. The factor of the inverse temperature β results from the local Einstein relation between mobility and diffusivity. Physical examples include charge carriers in heterogeneous media, where $\mu(\mathbf{x})$ is proportional to the local electrical conductivity, in the presence of an external electric field, as well as colloidal diffusion in porous media, with local diffusivity $\kappa(\mathbf{x})$, with an external field induced by gravitational or buoyancy forces. Here, we study the effect that a constant external applied field has on the late time dispersion as characterized by the effective drift of a cloud of tracer particles

$$V_i = \lim_{t\to\infty} \frac{\langle X_i(t) - X_i(0)\rangle}{t} \quad (2)$$

[where $\mathbf{X}(t)$ denotes the position of a tracer particle and $\langle \cdots \rangle$ denotes ensemble averaging] and the effective diffusivity

$$D_{ii} = \lim_{t\to\infty} \frac{\langle [X_i(t) - X_i(0)]^2 \rangle_c}{2t} \quad (3)$$

[c denotes the connected part, thus the variance of the displacement $X_i(t) - X_i(0)$] characterizing the dispersion of the cloud about its mean position. Effective transport coefficients are important for estimating the spread of pollutants and chemical reaction times [4].

When $\mathbf{F} = \mathbf{0}$, the problem of determining D_{ii} and V_i dates back to Maxwell [5], where the equivalent problem of determining the dielectric constant of heterogeneous media was addressed. The Wiener bounds [6] state that $(\overline{\kappa^{-1}})^{-1} \le D \le \bar{\kappa}$, where the overbar indicates spatial averaging. In higher dimensions there are few exact results [7] but numerous approximations schemes exist [8–12]. However, the case where there is a finite external force appears not to have been studied and in this Letter we will address the force's effect on the dispersion of tracer particles.

To gain a flavor for the phenomenology of this problem we consider diffusion in a two-dimensional medium, where $\kappa(x, y)$ is shown in Fig. 1(a), with an applied force $\mathbf{F}$ oriented in the x direction. We show in Fig. 1(c) the results of numerical simulations of the corresponding SDE for the quantities D_{xx}, D_{yy}, and $V_x/\beta F$. At zero force, all the quantities shown are equal; this is a result of the Stokes-Einstein relation $D_{xx} = \beta\partial_F V_x$, which holds only when $F = 0$ (see the Supplemental Material [13]). At small F upon increasing F, we see that both D_{xx} and V_x/F decrease while D_{yy} increases. As F increases further, V_x/F continues to decrease monotonically; however, D_{xx} and D_{yy} attain minimal and maximal values, respectively, and eventually cross. This remarkable behavior shows that the fast and slow directions of dispersion can be interchanged by an applied force and that $D_{yy}(F)$ is a nonmonotonic function. In Fig. 1(d), we see that D_{xx} grows as F^2 at large forces and can thus be made arbitrarily large

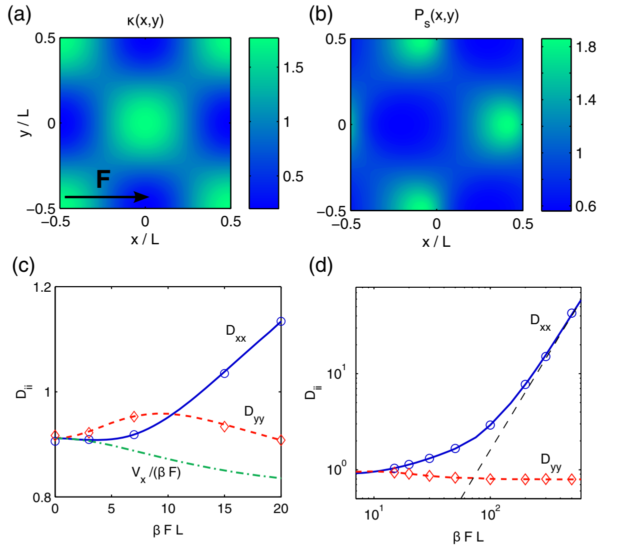

FIG. 1 (color online). (a) The 2D periodic diffusivity field $\kappa(x,y) = \kappa_0[1 + 0.8\cos(2\pi x/L)\cos(2\pi y/L)]$, in units of κ_0 on the fundamental rectangular unit cell. The arrow indicates the direction of the external force. (b) Stationary PDF in the diffusivity field shown in (a) with an external force of magnitude $\beta FL = 10$. (c) Components D_{xx} and D_{yy} of the effective diffusion tensor predicted by Eqs. (18) and (19) and the normalized effective drift $V_x/\beta F$ from Eq. (6) (lines) along with simulations results for the SDE (5) (symbols). (d) Same as (c) with different scales. The dashed line represents the behavior $D_{xx} \simeq cF^2$ with the coefficient c predicted by Eq. (23).

(thus exceeding the upper Wiener bound for the forceless case), giving rise to force-induced dispersion enhancement. The key difference between systems with and without an external force is that in the latter case the steady state probability distribution $P_s(x,y)$ on the periodic unit cell of the system is constant, whereas in the presence of the field it becomes nontrivial as shown in Fig. 1(b).

To explain these results we will derive a Kubo-type formula for the transport coefficients for general Fokker-Planck equations with arbitrary periodic diffusion tensors and advection fields. This formula generalizes a number of existing results for convection by incompressible velocity fields with constant molecular diffusivity as in the case of Taylor dispersion [16]. Examples include diffusion in Rayleigh-Bénard convection cells [17–19], diffusion in frozen turbulent flows [20], and transport by a fluid in porous media [21–24]. Our formula also encapsulates results for diffusion in periodic potentials [25–29]. In one dimension, results on diffusion in periodic potentials plus constant forces have been derived [30–34], as well as the more general case where the noise amplitude is a periodic function of position [35–37].

The Kubo formula we derive here is valid in any dimension. The terms in the Kubo formula can be analytically evaluated when the diffusivity varies only in one direction, and we give analytical results for such stratified systems. We also solve the generic problem analytically in the limit of large forces, proving that the coefficient of D_{ii}, where i is the direction of the force, is generically proportional to F^2. Finally, the Kubo formula can be evaluated by solving a set of associated partial differential equations numerically (see the Supplemental Material [13]); the excellent agreement between this calculation and the simulations is shown in Figs. 1(c) and 1(d).

Kubo formula for the dispersion.—Consider the general Fokker-Planck equation

$$\partial_t p = \sum_{i=1}^{d} \partial_{x_i}\left\{-u_i(\mathbf{x})p + \sum_{j=1}^{d}[\kappa_{ij}(\mathbf{x})p]\right\} = \mathcal{L}_{\mathbf{x}}p, \quad (4)$$

where $\kappa_{ij}(\mathbf{x})$ is a local (symmetric) diffusion tensor, $\mathbf{u}(\mathbf{x})$ is the drift field, and $\mathcal{L}_{\mathbf{x}}$ is the transport operator. Our only assumption in the following is that the fields $u_i(\mathbf{x})$ and $\kappa_{ij}(\mathbf{x})$ are periodic in space. Let Ω denote the fundamental unit cell of the periodic structure. We call $p(\mathbf{x},t|\mathbf{y})$ the propagator of the stochastic process in infinite space, defined as the solution of Eq. (4) in infinite space with the initial condition $p(\mathbf{x},0|\mathbf{y}) = \delta(\mathbf{x}-\mathbf{y})$. We distinguish this infinite space propagator $p(\mathbf{x},t|\mathbf{y})$ from the propagator calculated with periodic boundary conditions on the boundaries of Ω, denoted $P(\mathbf{x},t|\mathbf{y})$, and representing the probability density to observe a particle at time t at a position $\mathbf{x}$ modulo an integer number of translations along the lattice vectors of the periodic structure. Finally, we define $P_s(\mathbf{x}) = \lim_{t\to\infty} P(\mathbf{x},t,|\mathbf{y})$ as the stationary PDF of the particles with periodic boundary conditions.

In the Ito prescription, the SDE corresponding to the Fokker-Planck equation (4) in the direction i [2,3] is

$$dX_i = u_i(\mathbf{X}(t))dt + \sum_{j=1}^{d}[\kappa^{1/2}(\mathbf{X}(t))]_{ij}dW_j, \quad (5)$$

where $\kappa^{1/2}$ represents the square-root matrix of the positive symmetric matrix κ. The noise increments dW_i are Gaussian, independent, and of zero mean and are only correlated at equal times as $\langle dW_i dW_j\rangle = 2\delta_{ij}dt$. Ensemble averaging Eq. (5) yields the Stratonovich result [38]

$$V_i = \int_\Omega d\mathbf{x} P_s(\mathbf{x})u_i(\mathbf{x}). \quad (6)$$

To calculate the effective diffusivity we first substract $u_i dt$ from both sides of Eq. (5), integrate over time, square both sides of the resulting equation, and then average to find

$$\langle[X_i(t)-X_i(0)]^2\rangle + \int_0^t dt_1 \int_0^t dt_2 \langle u_i(\mathbf{X}(t_1))u_i(\mathbf{X}(t_2))\rangle$$
$$-2\int_0^t dt'\langle\{X_i(t)-X_i(t')+X_i(t')-X_i(0)\}u_i(\mathbf{X}(t'))\rangle$$
$$= 2t\int_\Omega d\mathbf{x} P_s(\mathbf{x})\kappa_{ii}(\mathbf{x}). \quad (7)$$

The average of the right-hand side of Eq. (7) follows from the independence of the dW_i at different time steps. Exploiting the periodicity of the field $\mathbf{u}(\mathbf{x})$, we can evaluate the second term of Eq. (7) for $t_1 < t_2$ as

$$\langle u_i(\mathbf{X}(t_1))u_i(\mathbf{X}(t_2))\rangle = \iint_\Omega d\mathbf{x}_1 d\mathbf{x}_2 u_i(\mathbf{x}_2)u_i(\mathbf{x}_1) \times P(\mathbf{x}_2, t_2 - t_1|\mathbf{x}_1)P_s(\mathbf{x}_1). \quad (8)$$

The second line of Eq. (7) contains the term [39]

$$\langle [X_i(\tau) - X_i(0)]u_i(\mathbf{X}(0))\rangle = \int_{\mathbb{R}^d} d\mathbf{x} \int_\Omega d\mathbf{y}\, p(\mathbf{x}, \tau|\mathbf{y})P_s(\mathbf{y})(x_i - y_i)u_i(\mathbf{y}). \quad (9)$$

Differentiating with respect to τ, using Eq. (4) and integrating by parts over $\mathbf{x}$, we obtain

$$\partial_\tau\langle [X_i(\tau) - X_i(0)]u_i(\mathbf{X}(0))\rangle = \int_\Omega d\mathbf{y} P_s(\mathbf{y})u_i(\mathbf{y}) \int_{\mathbb{R}^d} d\mathbf{x}\Big\{ u_i(\mathbf{x})p(\mathbf{x}, \tau|\mathbf{y}) - \sum_{j=1}^d \partial_{x_j}[\kappa_{ij}(\mathbf{x})p(\mathbf{x}, \tau|\mathbf{y})]\Big\}. \quad (10)$$

Finally, exploiting the periodicity of the field $\mathbf{u}$, we can replace the integral over $\mathbf{x}$ over the infinite space by an integral over the unit cell Ω if one replaces the infinite space propagator p by the propagator with periodic boundary conditions P, yielding for any $t > t'$ [40]

$$\partial_t\langle [X_i(t) - X_i(t')]u_i(\mathbf{X}(t'))\rangle = \int_\Omega d\mathbf{x} \int_\Omega d\mathbf{y} u_i(\mathbf{y})u_i(\mathbf{x})P(\mathbf{x}, t - t'|\mathbf{y})P_s(\mathbf{y}). \quad (11)$$

The last term to be computed in Eq. (7) is

$$\langle [X_i(t) - X_i(0)]u_i(\mathbf{X}(t))\rangle = \int_{\mathbb{R}^d} d\mathbf{x} \int_\Omega d\mathbf{y}\, p(\mathbf{x}, t|\mathbf{y})P_s(\mathbf{y})(x_i - y_i)u_i(\mathbf{x}). \quad (12)$$

Because of the periodicity, we can exchange the integration domains of $\mathbf{y}$ and $\mathbf{x}$ in this equation. We now use the backward Fokker-Planck equation [3] $\partial_t p(\mathbf{x}, t|\mathbf{y}) = \mathcal{L}^\dagger_\mathbf{y} p$ (where $\mathcal{L}^\dagger$ is the adjoint of the transport operator $\mathcal{L}$) to find

$$\partial_t\langle [X_i(t) - X_i(0)]u_i(\mathbf{X}(t))\rangle = \int_\Omega d\mathbf{x} \int_{\mathbb{R}^d} d\mathbf{y}[\mathcal{L}^\dagger_\mathbf{y} p(\mathbf{x}, t|\mathbf{y})]P_s(\mathbf{y})(x_i - y_i)u_i(\mathbf{x}). \quad (13)$$

Using the definition of the adjoint operator, we write

$$\partial_t\langle [X_i(t) - X_i(0)]u_i(\mathbf{X}(t))\rangle = \int_{\mathbb{R}^d} d\mathbf{y} \int_\Omega d\mathbf{x} u_i(\mathbf{x})p(\mathbf{x}, t|\mathbf{y})\mathcal{L}_\mathbf{y}\{P_s(\mathbf{y})(x_i - y_i)\}. \quad (14)$$

Again exploiting the periodicity of $\mathbf{u}$ and explicitly calculating $\mathcal{L}_\mathbf{y}\{P_s(\mathbf{y})(x_i - y_i)\}$ gives

$$\partial_t\langle [X_i(t) - X_i(0)]u_i(\mathbf{X}(t))\rangle = \int_\Omega d\mathbf{x} u_i(\mathbf{x}) \int_\Omega d\mathbf{y} P(\mathbf{x}, t|\mathbf{y})\Big\{ J_{s,i}(\mathbf{y}) - \sum_{j=1}^d \partial_{y_j}[\kappa_{ij}(\mathbf{y})P_s(\mathbf{y})]\Big\}, \quad (15)$$

where $\mathbf{J}_s(\mathbf{y})$ is the local current in the stationary state at position $\mathbf{y}$, given by

$$J_{s,i}(\mathbf{y}) = u_i(\mathbf{y})P_s(\mathbf{y}) - \sum_{j=1}^d \partial_{y_j}[\kappa_{ij}(\mathbf{y})P_s(\mathbf{y})]. \quad (16)$$

Finally, all the terms in Eq. (7) can be evaluated by using Eqs. (9), (11), and (15). Taking the large time limit, we obtain the Kubo formula for the effective diffusion tensor

$$D_{ii} = \int_\Omega d\mathbf{y} P_s(\mathbf{y})\kappa_{ii}(\mathbf{y}) + \iint_\Omega d\mathbf{x} d\mathbf{y} u_i(\mathbf{x})G(\mathbf{x}|\mathbf{y})[2J_{s,i}(\mathbf{y}) - u_i(\mathbf{y})P_s(\mathbf{y})], \quad (17)$$

where $G(\mathbf{x}|\mathbf{y}) = \int_0^\infty dt\{P(\mathbf{x}, t|\mathbf{y}) - P_s(\mathbf{x})\}$ is the pseudo-Green function [41] of $\mathcal{L}$ on Ω. Equation (17) gives in an explicit way the dispersion properties in terms of quantities that are defined at the level of an individual cell Ω, with periodic boundary conditions. We may reexpress D_{ii} by introducing $\mathbf{f}(\mathbf{x})$, the solution of

$$\mathcal{L}_\mathbf{x} f_i(\mathbf{x}) = -2J_{s,i}(\mathbf{x}) + u_i(\mathbf{x})P_s(\mathbf{x}) + P_s(\mathbf{x}) \int_\Omega d\mathbf{y}[2J_{s,i}(\mathbf{y}) - u_i(\mathbf{y})P_s(\mathbf{y})], \quad (18)$$

again with periodic boundary conditions on Ω, and with the integral condition $\int_\Omega d\mathbf{x}\mathbf{f}(\mathbf{x}) = \mathbf{0}$. The diffusion tensor is then given by

$$D_{ii} = \int_\Omega d\mathbf{x}\{P_s(\mathbf{x})\kappa_{ii}(\mathbf{x}) + u_i(\mathbf{x})f_i(\mathbf{x})\}. \quad (19)$$

Nonequilibrium effects are manifested in Eq. (17) by the presence of the local currents of the stationary state, generalizing similar Kubo formulas derived for equilibrium problems. In the case of transport by incompressible fluid flows, $P_s(\mathbf{x})$ is uniform, $\mathbf{J}_s$ is proportional to the flow $\mathbf{u}$, and one recovers the equations describing dispersion in incompressible hydrodynamic flows [compare, for example, Eqs. (18) and (19) to Eqs. (35) and (48) of Ref. [24]].

Periodic diffusivity with an external uniform force.—We now focus on advection-diffusion systems described by Eq. (1), which fall in the class of the general equation (4) with

$$\kappa_{ij}(\mathbf{x}) = \delta_{ij}\kappa(\mathbf{x}), \qquad \mathbf{u}(\mathbf{x}) = \kappa(\mathbf{x})\beta\mathbf{F} + \nabla\kappa(\mathbf{x}). \quad (20)$$

The effective dispersion tensor D_{ii} can be obtained by solving numerically the partial differential equations (18) and (19), leading to the results on Fig. 1, which compare very well to numerical simulations of the SDE (5).

Stratified media.—In systems where the local diffusivity varies only in one dimension, $\kappa(x,y) = \kappa(x)$ as illustrated in Fig. 2(a); $\mathbf{f}$ depends only on x and can be calculated analytically (see the Supplemental Material [13]). For vanishing forces, the diffusivity tensor reads

$$D_{xx} = 1/\overline{\kappa^{-1}}, \qquad D_{yy} = \bar{\kappa}, \qquad D_{xy} = 0 \quad (|\mathbf{F}| \to 0). \quad (21)$$

Here, the anisotropy of the dispersion is imposed by the anisotropy of the field κ; from Jensen's inequality we see that $D_{xx} \le D_{yy}$, indicating that dispersion is faster in the direction parallel to the strata of the medium [Fig. 2(b)]. For large forces however we find that

$$D_{ij} = (\overline{\kappa^{-1}})^{-1}\left\{\delta_{ij} + \frac{F_iF_j}{|\mathbf{F}\cdot\mathbf{e}_x|^2}\left[\frac{\overline{\kappa^{-2}}}{(\overline{\kappa^{-1}})^2} - 1\right]\right\}, \quad (22)$$

so the dispersion becomes larger in the direction parallel to the force than in the perpendicular direction [42]. The dispersion is highly sensitive to the projection of the force normal to the strata [Fig. 2(c)], and the diffusion coefficients in the planes of the strata diverge when $\mathbf{F}$ is in the plane of the strata (in fact, they grow as $|\mathbf{F}|^2$).

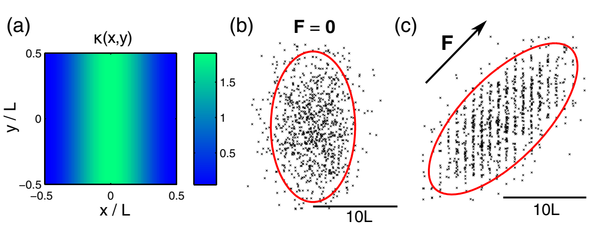

FIG. 2 (color online). (a) The 2D periodic diffusivity field for our example of stratified medium, $\kappa(x,y) = \kappa_0[1 + 0.95\cos(2\pi x/L)]$, shown in units of κ_0 on the fundamental rectangular unit cell. (b),(c) Cloud of particles diffusing in the local diffusivity field shown in (a) at a time $t = 10L^2/\kappa_0$. In (b) there is no external force and in (c) the force has a magnitude given by $\beta FL = 100$ and acts in the direction indicated by the arrow. The ellipses represent the region in which 95% of the points should fall and are determined from Eqs. (21) and (22).

Force induced dispersion enhancement in 2D.—Consider the general 2D problem in the case of large forces. For large forces, it is natural to suppose that the equilibration time in the direction (here x) of the force is much shorter than in the other direction. We thus make the quasistatic approximation $P(x,y,t) \simeq \pi(y,t)P_s(x|y)$, where $P_s(x|y) \sim \kappa^{-1}(x,y)$ is the stationary probability to observe x given the value of y. An effective Fokker-Planck equation can then be derived for the PDF $\pi(y,t)$ by integrating over x, and using Eqs. (18) and (19), to obtain (see the Supplemental Material [13])

$$D_{xx} = \frac{[\beta FR(L)]^2}{W(L)}\int_0^L dy\left[\frac{W(y)}{W(L)} - \frac{R(y)}{R(L)}\right]^2 e^{-\overline{\ln\kappa}(y)}, \quad (23)$$

where L is the length of the period in the direction y, the notation $\bar{g}(y)$ representing uniform spatial averaging over x for any function $g(x,y)$, and where

$$R(y) = \int_0^y du e^{\overline{\ln\kappa}(u)}, \qquad W(y) = \int_0^y du \overline{\kappa^{-1}}(u)e^{\overline{\ln\kappa}(u)}. \quad (24)$$

Equation (23) shows that local heterogeneities generically give rise to diffusion coefficients scaling as the square of the force for large forces, implying that the force-induced diffusivity can be much larger than the microscopic diffusion coefficients. Quadrature of the integrals in Eq. (23) gives a coefficient of F^2 that is in agreement with the simulations, as seen in Fig. 1(d).

Conclusion.—Taylor dispersion [16] is a textbook example of a phenomenon where spatial variations of a time-independent compressible velocity field, along with locally constant molecular diffusivity, lead to enhanced dispersion. Here, external uniform forces lead to increased dispersion in the direction of the force. The mechanism is similar to that behind Taylor dispersion in that particles with different trajectories experience very different advection by the applied force due to its coupling to the local mobility or diffusivity. We have also seen that an external force can nonmonotonically modify the dispersion in the direction perpendicular to the applied force. This surprising effect is due to the fact that an applied force yields a nonuniform stationary distribution over the fundamental periodic cell. It is possible that one may construct experimental systems where the effects predicted here could be observed. Periodic optical potentials, in which colloidal particles can be tracked, can be generated by lasers [43,44] and it would be interesting to see if experimental realizations of media with spatially modulated diffusivities could be similarly produced in order to observe the effects predicted in this Letter. Finally, we stress that the results here can be applied to any periodic advection-diffusion system and thus have a wide range of applicability. For instance, one can use the formulas to study the dispersion in periodic potentials in any dimension in the presence of an external force [30,31] (even with varying local mobility) as well as in systems with no local detailed balance, such as active particle systems.

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