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 non-monotonically, 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 which 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, 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) \( p(x, t) \) for the tracer position at time \( t \) obeys

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

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 \( \beta \kappa(x) = \mu(x) \) is the local mobility. The factor of the inverse temperature \( \beta \) results from the local Einstein relation between mobility and diffusivity. Physical examples include charge carriers in heterogeneous media, where \( \mu(x) \) 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 \( \kappa(x) \), 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

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

(where \( X(t) \) denotes the position of a tracer particle and \( \langle \cdot \rangle \) denotes ensemble averaging) and the effective diffusivity

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

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

When \( \mathbf{F} = 0 \), 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 \( (\kappa^{-1})^{-1} \leq D \leq \kappa \), where \( \kappa \) 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 \( D_{xx} = \beta \rho F V_x \) which holds only [13] when \( F = 0 \). 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 non-monotonic function. In Fig. 1(d), we see that \( D_{xx} \) grows as \( F^2 \) at large forces and can thus be made arbitrarily large (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 non-trivial 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 [13], the excellent agreement between this calculation and the simulations is shown in Figs. 1(c–d).

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

$$\partial_t p = \sum_{i,j=1}^d \partial_{x_i} \{ -u_i(x)p + \partial_{x_j} [\kappa_{ij}(x)p] \} \equiv \mathcal{L}_x p,$$  

where $\kappa_{ij}(x)$ is a local (symmetric) diffusion tensor, $u(x)$ is the drift field, and $\mathcal{L}_x$ is the transport operator. Our only assumption in the following is that the fields $u_i(x)$ and $\kappa_{ij}(x)$ are periodic in space. Let $\Omega$ denote the fundamental unit cell of the periodic structure. We call $p(x,t|y)$ the propagator of the stochastic process in infinite space, defined as the solution of Eq. (1) in infinite space with initial condition $p(x,0|y) = \delta(x-y)$. We distinguish this infinite space propagator $p(x,t|y)$ from the propagator calculated with periodic boundary conditions on the boundaries of $\Omega$, denoted $P(x,t|y)$, and representing the probability density to observe a particle at time $t$ at a position $x$ modulo an integer number of translations along the lattice vectors of the periodic structure. Finally, we define $P_s(x) = \lim_{t \rightarrow \infty} P(x,t|y)$ the stationary PDF of the particles with periodic boundary conditions.

In the Ito prescription, the SDE corresponding to the Fokker-Planck equation (1) in the direction $i$ [2] is

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

where $\kappa^{1/2}$ represents the square-root matrix of the positive symmetric matrix $\kappa$. The noise increments $dW_i$ are Gaussian, independent, 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]

$$V_i = \int_\Omega dx \, P_s(x) \, u_i(x).$$  

To calculate the effective diffusivity we first subtract $u_i dt$ from both sides of Eq. (4), integrate over time, square both sides of the resulting equation and then average to find

$$\langle [X_i(t) - X_i(0)]^2 \rangle + \int_0^t dt \int_0^t dt' \langle u_i(X(t)) u_i(X(t')) \rangle$$

$$-2 \int_0^t dt' \langle \{X_i(t) - X_i(t') + X_i(t') - X_i(0)\} u_i(X(t')) \rangle$$

$$= 2t \int_\Omega dx \, P_s(x) \kappa_{ii}(x).$$  

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 $u(x)$, we can evaluate the second term of Eq. (7) for $t_1 < t_2$ as

$$\langle u_i(X(t_1)) u_i(X(t_2)) \rangle =$$

$$\int_\Omega dX_1 dX_2 u_i(X_1) u_i(X_2) P(x_2, t_2 - t_1 | x_1) P_s(x_1).$$  

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 $\kappa_0$ 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 $\beta F L = 10$. (c) Components $D_{xx}$ and $D_{yy}$ of the effective diffusion tensor predicted by Eqs. (18, 19) and the normalized propagator calculated with periodic boundary conditions. (d) Same as (c) with different scales. The dashed line represents the behavior $D_{xx} \approx c F^2$ with the coefficient $c$ predicted by Eq. (23).
The second line of Eq. (7) contains the term \[ \langle [X_i(t) - X_i(0)]u_i(X(0)) \rangle = \int_{\mathbb{R}^d} d\mathbf{x} \int_{\Omega} d\mathbf{y} p(x, \tau | y) P_s(y)(x_i - y_i)u_i(y). \] (9)

Differentiating with respect to \( \tau \), using Eq. (4) and integrating by parts over \( x \), we obtain

\[
\partial_t \langle [X_i(t) - X_i(0)]u_i(X(0)) \rangle = \int_{\mathbb{R}^d} d\mathbf{x} \int_{\Omega} d\mathbf{y} \left[ u_i(x)p(x, \tau | y) - \sum_{j=1}^d \partial_x \kappa_{ij}(x)p(x, \tau | y) \right].
\] (10)

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

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

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

\[
\langle [X_i(t) - X_i(0)]u_i(X(t)) \rangle = \int_{\mathbb{R}^d} d\mathbf{x} \int_{\Omega} d\mathbf{y} \left[ \mathcal{L}^p \mathcal{L}^t P_s(y)(x_i - y_i)u_i(x) \right].
\] (12)

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

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

Using the definition of the adjoint operator, we write

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

Again exploiting the periodicity of \( u \) and explicitly calculating \( \mathcal{L}^p \mathcal{L}^t P_s(y)(x_i - y_i) \) gives

\[
\partial_t \langle [X_i(t) - X_i(0)]u_i(X(t)) \rangle = \int_{\Omega} d\mathbf{x} \left[ u_i(x)p(x, t | y) - \sum_{j=1}^d \partial_y \kappa_{ij}(y) P_s(y) \right],
\] (15)

where \( J_{s,i}(y) \) the local current in the stationary state at position \( y \), given by

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

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

\[
D_{ii} = \int_{\Omega} d\mathbf{y} P_s(y) \kappa_{ii}(y) + \int_{\mathbb{R}^d} dx dy u_i(x)G(x | y)[2J_{s,i}(y) - u_i(y)P_s(y)],
\] (17)

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

\[
\mathcal{L}^t f_{s,i}(x) = -2J_{s,i}(x) + u_i(x)P_s(x)
\]

\[
+ P_s(x) \int_{\Omega} d\mathbf{y} [2J_{s,i}(y) - u_i(y)P_s(y)],
\] (18)

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

\[
D_{ii} = \int_{\Omega} d\mathbf{x} \left[ P_s(x) \kappa_{ii}(x) + u_i(x) f_{s,i}(x) \right].
\] (19)

Non-equilibrium 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, \( P_s(x) \) is uniform, \( J_s \) is equal to the flow \( \mathbf{u} \) and one recovers the equations describing dispersion in incompressible hydrodynamic flows (compare for example Eqs. (18,19) to Eqs. (35,48) 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

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

The effective dispersion tensor \( D_{ii} \) can be obtained by solving numerically the partial differential equations (18,19), 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. 2a), \( \mathbf{f} \) depends only on \( x \) and can be calculated analytically (13). For vanishing forces, the diffusivity tensor reads

\[
D_{xx} = 1/\kappa - \tau, \quad D_{yy} = \kappa, \quad D_{xy} = 0 \quad (|\mathbf{F}| \to 0).
\] (21)

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

\[
D_{ij} = (\kappa^{-1})^{-1} \left\{ \delta_{ij} + \frac{\tau F_i F_j}{|\mathbf{F} \cdot \mathbf{e}_j|^2} \left[ \frac{\kappa^{-2}}{(\kappa^{-1})^2} - 1 \right] \right\},
\] (22)
so the dispersion becomes larger in the direction parallel to the force than in the perpendicular direction [12]. 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 \( \kappa_0 \) on the fundamental rectangular unit cell. (b) and (c): Cloud of particles diffusing in the local diffusivity field shown in (a) in the presence of external force at a time \( t = 10L^2/\kappa_0 \). In (b) no external force and in (c) the force has magnitude given by \( \beta F L = 100 \), 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. [21,22].

**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 quasi-static approximation \( P(x,y,t) \approx \pi(y,t)P_x(x|y) \), where \( P_x(x|y) \sim \kappa^{-1}(x,y) \) 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. [18,19], to obtain [13]

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

(23)

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

\[
R(y) = \int_0^y du \ e^{\ln \kappa(u)}; W(y) = \int_0^y du \ \kappa^{-1}(u)e^{\ln \kappa(u)}.
\]

(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) give a coefficient of \( F^2 \) which is in agreement with the simulations, as seen in Fig. 1(d).

**Conclusion.** Taylor dispersion [10] 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/diffusivity. We have also seen that an external force can non-monotonically 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 non-uniform 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 [33,34] 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.
SUPPLEMENTAL MATERIAL

Appendix A: The Generalized Stokes-Einstein Relation

The Stokes-Einstein relation is a relationship between effective diffusivity and effective drift or mobility which applies in equilibrium systems, and is often used to deduce diffusivity from mobility (for a recent example see [14]). Here we show how, beyond the regime of linear response, the Stokes-Einstein relation breaks down due to the presence of currents associated with the stationary distribution.

The effective drift is given by the Stratonovich formula \[ V_i = \int_{\Omega} dx \, P_s(x) \, u_i(x), \tag{A1} \]
where \( P_s \) is the stationary distribution on the unit cell \( \Omega \). Now consider a system where the local drift \( u_i \) is perturbed by a small external force \( F \) so that the local drift \( u_i \) changes to
\[ u'_i(x) = u_i(x) + \beta \sum_{j=1}^{d} \kappa_{ij}(x) F_j. \tag{A2} \]
The induced local drift due to the force \( F \) takes this form as the local mobility tensor is given, using the local Stokes-Einstein formula or detailed balance, by \( \mu_{ij} = \beta \kappa_{ij} \), where \( \beta = 1/k_B T \) is the inverse of the thermal energy and \( \kappa_{ij} \) is the local diffusivity tensor. From the above formulas we then see that
\[ \frac{\partial V_i}{\partial F_i} = \beta \int_{\Omega} dx \, P_s(x) \kappa_{ii}(x) + \int_{\Omega} dx \frac{\partial P_s(x)}{\partial F_i} u_i(x). \tag{A3} \]
Differentiating the stationary Fokker-Planck equation \( \mathcal{L}_x P_s = 0 \) with respect to \( F_i \) then yields
\[ \mathcal{L}_x \frac{\partial P_s(x)}{\partial F_i} - \beta \sum_{j=1}^{d} \frac{\partial}{\partial x_j} \left[ \kappa_{ij}(x) P_s(x) \right] = 0. \tag{A4} \]
The boundary conditions for \( \frac{\partial P_s(x)}{\partial F_i} \) are clearly that it is periodic on the boundaries of \( \Omega \), but also we must have, by conservation of probability, that
\[ \int_{\Omega} dx \frac{\partial P_s(x)}{\partial F_i} = 0. \tag{A5} \]
By definition (see e.g. Ref. [41]), the pseudo-Green’s function \( G(x|y) \) for \( \mathcal{L}_x \) on \( \Omega \) obeys
\[ \mathcal{L}_x G(x|y) = -\delta(x-y) + P_s(x). \tag{A6} \]
We can use this pseudo-Green’s function \( G(x|y) \) to construct the solution of Eq. \( (A4) \) as
\[ \frac{\partial P_s(x)}{\partial F_i} = -\int_{\Omega} dy \, G(x|y) \beta \sum_{j=1}^{d} \frac{\partial}{\partial y_j} \left[ \kappa_{ij}(y) P_s(y) \right], \tag{A7} \]
which clearly satisfies the integral condition Eq. \( (A5) \). Substituting this solution into Eq. \( (A3) \) then yields
\[ \frac{\partial V_i}{\partial F_i} = \beta \left\{ \int_{\Omega} dx \, P_s(x) \kappa_{ii}(x) \right. \]
\[ \left. - \int_{\Omega} dx dy \, u_i(x)G(x|y) \sum_{j=1}^{d} \frac{\partial}{\partial y_j} \left[ \kappa_{ji}(y) P_s(y) \right] \right\}. \tag{A8} \]
Now, using Eq. \( (17) \) of the main text and the definition Eq. \( (16) \) of the current \( J_s, i \) we can write
\[ \frac{\partial V_i}{\partial F_i} = \beta D_{ii} - \beta \int_{\Omega} dx dy \, u_i(x)G(x|y)J_s, i(y). \tag{A9} \]

The Stokes Einstein relation \( \partial V_i/\partial F_i = \beta D_{ii} \) between the effective drift and diffusivity thus in general holds only when the current of the stationary state \( J_s \) vanishes. We also note that the first term of Eq. \( (A9) \), being the diffusion constant, it clearly positive. However, the sign of the second term is not obvious. In Ref. [15], it was found that a particle with constant applied force in a two dimensional periodic, ratchet-like, potential can exhibit absolute negative mobility - it would be interesting to see if the formalism developed here could be used to better understand this phenomenon.

Appendix B: Results in one dimension

In more than one dimension the resolution of the partial differential equation Eq. \( (18) \) to evaluate the Kubo formula for the diffusion equation is not possible analytically. However, in one dimension the corresponding differential equation can be evaluated analytically and we give the general result for any diffusion advection in one dimension and then specialize the result to the case of diffusion in a medium of varying diffusivity subject to an external field. Refs [29, 30, 31, 33, 34, 37] are landmark papers in the study of diffusion in non-equilibrium systems, as the problem of diffusion in a periodic potential plus a constant force was first studied in Refs. [30, 31] and the result generalized to arbitrary advection diffusion was obtained in Refs. [35, 37] (although in Ref. [35] a Stratonovich prescription for the Langevin equation was used and in Ref. [36, 37] a specific problem related to Fick-Jacobs diffusion was studied, the results given are in fact the most general possible in one dimension). The approach of Refs. [29, 30, 31, 33, 34, 37] was based on an expression for the diffusion constant in one dimension deduced from moments of first passage times, we will show here how the general result can be rederived via the Kubo formula Eq. \( (17) \).

In what follows, we compute the dispersion properties for the model described by Eq. \( (4) \) of the main text in one dimension, and we show how to use these formulas to derive the effective diffusion tensor in stratified media. We use notation based on the aforementioned references
to aid the reader who wished to compare the results. In
one dimension, the stationary probability distribution is
given by

\[ P_s(x) = J_s I_+(x), \]  
(B1)

where \( J_s \) is the (constant) current in one dimension and

\[ I_+(x) = \frac{\exp(\Gamma(x))}{\kappa(x)} \int_{-\infty}^{x} dz' \exp(-\Gamma(z')), \]  
(B2)

\[ \Gamma(x) = \int_{-\infty}^{x} dz' \frac{u(z')}{\kappa(z')} . \]  
(B3)

Due to the periodicity of \( u \) and \( \kappa \) the function \( \Gamma \) obeys
the relation

\[ \Gamma(x + L) = \Gamma(x) + \Gamma(L). \]  
(B4)

When \( \Gamma(L) = 0 \) the system clearly has a steady state
equilibrium distribution with no current. In writing Eq. (B2) we have assumed, without loss of generality, that
\( \Gamma(L) > 0 \) so that the integral on the right hand side
converges. The steady state current is then obtained from
the condition of normalization of \( P_s \) and is thus given by

\[ J_s = \frac{1}{\int_{-L}^{L} dx I_+(x)} . \]  
(B5)

and thus the effective drift is given by \( V = J_s L \). The
Eq. (18) of the main text can be solved in terms of
the function \( I_+ \) and the function \( I_- \) defined as

\[ I_-(x) = \exp(-\Gamma(x)) \int_{-\infty}^{x} dz' \frac{\exp(\Gamma(z'))}{\kappa(z')} . \]  
(B6)

After some algebra we obtain the general compact expres-
sion for the effective large scale diffusivity

\[ D = \frac{L^2}{\int_{-L}^{L} dx \kappa(x) I_+(x)^2 I_+(x)} \]  
(B7)

where \( \pm \) indicates that one may (consistently) take the
sign \(+\) or \(-\) in the above. The formula Eq. (B7) agrees
with those given in Refs. [29, 31, 34, 37].

In the case of the diffusion in a periodic diffusivity field
with constant applied force we find

\[ I_+(x) = \exp(\beta F x) \int_{-\infty}^{x} dx' \frac{\exp(-\beta F x')}{\kappa(x')} , \]  
(B8)

\[ I_-(x) = \frac{\exp(\beta F)}{\beta F \kappa(x)} . \]  
(B9)

Now, we write the inverse of \( \kappa(x) \) as a Fourier series, \( i.e. \)

\[ \kappa(x) = \frac{1}{\kappa^{-1}} \sum_{k} a_k \exp\left(\frac{2\pi ikx}{L}\right) \]  
(B10)

where \( a_0 = 1 \) and \( a_{-k} = a_k \). This then gives

\[ I_+(x) = \frac{1}{\kappa^{-1}} \sum_{k} \frac{a_k \exp(\frac{2\pi ikx}{L})}{\beta F - \frac{2\pi ik}{L}} , \]  
(B11)

which yields the following expression for the effective diffusivity

\[ D(F) = \frac{1}{\kappa^{-1}} \left[ 1 + 2\beta^2 F^2 \sum_{k>0} \frac{|a_k|^2}{\beta^2 F^2 + \frac{4\pi^2 k^2}{L^2}} \right] . \]  
(B12)

When \( F = 0 \) we recover the classic result (Eq. (21))
\( D(0) = \kappa^{-1} \), that is to say that \( D(0) \) only depends
on the mean value of the inverse diffusivity. We see that for
finite \( F \) the diffusivity depends on all the Fourier co-
efficients of the inverse diffusivity, this means that in prin-
ciple that measurements of the effective diffusion constant
with applied external forces could be used to reconstruct the
diffusivity field in one dimension. For large \( F \), \( D(F) \)
saturates at the value

\[ D(\infty) = \frac{1}{\kappa^{-1}} \left[ 1 + 2 \sum_{k>0} |a_k|^2 \right] = \frac{\kappa^{-2}}{\kappa^{-1}} . \]  
(B13)

The above formula recovers Eq. (22) for \( D_{xx} \) when the
force is directed in the \( x \) direction (here the diffusion in the
\( y \) direction has no effect on that in the \( x \)). Note that
this saturation is specific to the case of one dimension or
for diffusion in stratified media in the direction parallel to the
force when there are no variations of the diffusivity in the
direction perpendicular to the applied force.

**Appendix C: Details on numerical calculations and
simulations.**

**Numerical solution of Eqs (18,19) of the main
text.** The numerical resolution of Eq. (18) of the main
text was carried out with the finite element software Flex-
PDE (www.pdesolutions.com). In the examples consid-
ered the unit cell \( \Omega \) was a square, with periodic boundary
conditions. First the equation for the steady state distribu-
tion \( P_s(x) \) was solved, either directly or by relaxing an
initially uniform probability solution to its steady state
fixed point by numerically integrating the time depen-
dent Fokker-Planck equation (in cases where there were
convergence problems with the direct solution). This
solution was then used to solve Eq. (18) for the two com-
ponents of \( f \). Finally the diffusion coefficients \( D_{xx} \) and
\( D_{yy} \) were obtained by numerical evaluation of the two
integrals in Eq. (19) within the same software.

**Numerical simulations.** Numerical simulation of the
stochastic differential equation for particles in a
medium of varying diffusivity with applied external force
were based upon integrating the simple discrete version of
the Ito stochastic differential equation

\[ X_i(t + \Delta t) = X_i(t) + \left[ \partial_{x_i} \kappa(X(t)) + \beta F \kappa(X(t)) \right] \Delta t \]
\[ + \sigma_i \sqrt{2\kappa(X(t))} \Delta t . \]  
(C1)

Here \( \sigma_i \) are independent Gaussian random variables of
zero mean and unit variance. Performing several runs
enables the measurement of \( X_i(t) - X_i(0) \) and therefore
to evaluate the effective drift and diffusivities defined in
Eq. (2,3) of the main text. For the simulations shown
in Fig. 1. and Fig. 2. of the main text, the time step
was chosen to be \( \Delta t = 10^{-5}L^2/\kappa_0 \), where \( L \) is the
size of the square unit cell and \( \kappa_0 \) is the diffusivity averaged
over the unit cell. The effective diffusivity was obtained by
estimating the variance of \( [X_i(t) - X_i(0)]/\sqrt{2\pi t} \)
and a time \( t \) large enough to be in the diffusive regime (we
took \( t = 10L^2/\kappa_0 \)). Averages were taken over more than
150,000 runs, and controls were made to ensure that the
simulation results do not depend on the time step.

Appendix D: Effective diffusivity at large forces in 2D

In this section, we derive Eq. (23) of the main text,
giving the effective diffusivity of particles submitted to
a large force in a varying periodic two-dimensional diffusivity
field. Here, we assume that the force is oriented in the
direction \( x \), and we call \( h = \beta F \) the external field,
and for simplicity, we assume that the fundamental unit
cell of the structure is a rectangle of sides \( L_x, L_y \).
The Fokker-Planck equation is Eq. (1) of the main text:
\[
\partial_t p(x,y,t) = \partial_x [\kappa(x,y)\partial_x p - h \kappa(x,y)p] + \partial_y [\kappa(x,y)\partial_y p].
\]  

\[\text{(D1)}\]

At high fields, \( h \to \infty \), the stationary distribution \( P_s \)
satisfies
\[
0 = \partial_x [h \kappa(x,y) P_s(x,y)].
\]

\[\text{(D2)}\]

so that the leading order term in \( h \) vanishes. Therefore,
the stationary distribution \( P_s \) takes the following general
form:
\[
P_s(x,y) \approx C(y)\kappa^{-1}(x,y),
\]

\[\text{(D3)}\]

where \( C(y) \) is a still unknown function of \( y \). At high
forces, it is natural to assume that the equilibration time
in the direction \( x \) is much shorter than the one in the
direction \( y \). Therefore, we approximate the propagator of
the process by
\[
p(x,y,t) \approx \pi(y,t)P_s(x|y),
\]

\[\text{(D4)}\]

where \( P_s(x|y) \) is the probability to observe a particle with
an \( x \)-coordinate of value \( x \), given that the coordinate in
the other direction is \( y \), and \( \pi(y,t) \) is the marginal
distribution of particles in the direction \( y \) at time \( t \). From
\[\text{(D3)}\]
and the normalization condition, we find that
\[
P_s(x|y) = \frac{1}{\kappa(x,y)L_x \kappa^{-1}(y)}.
\]

\[\text{(D5)}\]

where we call \( \bar{g}(y) = L_x^{-1}\int_0^{L_x} dx \ g(x,y) \) for any function
\( g \), with \( L_x \) the length of the period in the direction \( x \).

Inserting the approximation \[\text{(D4)}\] into \[\text{(D1)}\] and integrating
over \( x \) leads to an effective Fokker-Planck equation
for \( \pi(y,t) \):
\[
\partial_t \pi(y,t) \approx \int_0^{L_x} dx \ \partial_y \{\kappa(x,y)\partial_y [\pi(y,t)P_s(x|y)]\}
\]

\[\text{(D6)}\]

Performing explicitly the integral over \( x \) by using \[\text{(D5)}\],
we find
\[
\partial_t \pi(y,t) = \partial_y^2 [\kappa_e(y)\pi(y,t)] - \partial_y \{[\partial_y \ln \kappa(y)]\kappa_e(y)\pi(y,t)}
\]

\[\text{(D7)}\]

where we have posed \( \kappa_e(y) = 1/\kappa^{-1}(y) \). For large times,
the stationary distribution of the effective Fokker-Planck
equation \[\text{(D7)}\] is
\[
\pi_s(y) = \frac{e^{\ln \kappa(y)}}{\kappa(y) \int_0^{L_y} du \ e^{\ln \kappa(u)} / \kappa_e(u)}.
\]

\[\text{(D8)}\]

Now, selecting the term of order \( h^2 \) in the equation (19)
of the main text, we get:
\[
D_{xx} \approx h^2 \int_0^{L_x} dy \int_0^{L_y} dy_0 \kappa_e(y)
\times \kappa_e(y_0) \int_0^\infty dt \ [\pi(y,t|y_0) - \pi_s(y)]\pi_s(y_0),
\]

\[\text{(D9)}\]

where \( \pi(y,t|y_0) \) is the propagator for the effective
dynamics in the direction \( y \). It is useful to introduce the function \( f_c \) defined as the solution of
\[
\partial_y^2 [\kappa_e(y)f_c(y)] - \partial_y \{[\partial_y \ln \kappa(y)]\kappa_e(y)f_c(y)} =
\]

\[-\kappa_e(y)\pi_s(y) + \pi_s(y) \int_0^{L_y} du \ \kappa_e(u)\pi_s(u),
\]

\[\text{(D10)}\]

with the orthogonality condition \( \int_0^{L_y} dy f_c(y) = 0 \). From
Eqs. \[\text{(D7),(D9)}\], we deduce that the effective diffusion
coefficient can be written in terms of \( f_c \) as
\[
D_{xx} \approx h^2 \int_0^{L_y} dy \ \kappa_e(y)f_c(y).
\]

\[\text{(D11)}\]

Now, we introduce the functions \( R \) and \( W \) introduced in
Eq. (24) of the main text:
\[
R(y) = \int_0^y du \ e^{\ln \pi(u)}; W(y) = \int_0^y du \ \kappa_e^{-1}(u)e^{\ln \pi(u)}.
\]

\[\text{(D12)}\]

Rewriting the right-hand side of Eq. \[\text{(D10)}\] by using \[\text{(D8)}\]
and expressing the result in terms of these two functions
\( R \) and \( W \), we find:
\[
\partial_y^2 [\kappa_e(y)f_c(y)] - \partial_y \{[\partial_y \ln \kappa(y)]\kappa_e(y)f_c(y)} =
\]

\[-\frac{\partial_R R(y)}{W(L_y)} + \frac{\partial_W W(y)R(L_y)}{W(L_y)^2}.
\]

\[\text{(D13)}\]
Then, we can integrate once with respect to $y$. The resulting equation is a first order differential equation of a single variable function, and can be solved analytically. Taking into account the orthogonality condition $\int_0^1 dy f_x(y) = 0$, we arrive after some lines of algebra, at the expression (23) of the main text.

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