Dynamics vs. Kinematics: Comparison of the mean velocities computed from the Langevin equation and macrotransport theory for spatially periodic media

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Abstract

Both dynamical Langevin formalism and kinematical macrotransport theory are employed to calculate the long-time, average velocity of a Brownian sphere moving under the influence of an external force through an otherwise quiescent fluid. The Brownian particle is assumed to possess a spatially periodic hydrodynamic mobility dyadic, which arises from either the presence of solid obstacles or a viscosity gradient. Risken's techniques for non-linear Langevin equations are invoked to compute the ensemble average velocity at a given point in space from the Langevin equation, and the ergodic hypothesis furnishes a formal connection between the latter velocity and the mean velocity arising in macrotransport theory. Numerical simulations of the Langevin equation for a variable viscosity fluid provide reasonable agreement between the ensemble averaged mean velocity and the macrotransport mean velocity.

I. INTRODUCTION

This project attempts the reconciliation of two different methods of characterizing the stochastic trajectory of a Brownian particle in spatially periodic media, namely the dynamical Langevin formulation and the kinematical macrotransport formulation. In the former method, the trajectory of a particle is tracked, with the motion being governed by Newton's laws, supplemented by the addition of a stochastic, Gaussian distributed force to model random collisions of the solute molecule with the fluid molecules through which it traverses. In contrast, the macrotransport description is kinematical, concerning itself with the flux of particle probability through the bounding surface of a repetative unit cell. In spite of the disparate differences between the viewpoint adopted by either method, they must be equivalent, since their phenomenological underpinnings are identical. Indeed, the equivalence of dynamical and kinematical methods are well known throughout classical physics, for example in the derivation of the Navier-Stokes equation [1], and the equivalence of the Langevin methods and macrotransport theory for continuous processes (i.e. processes which consist of local and global coordinates, such as Taylor's original analysis [2]) has been established previously [3].

Macrotransport theory [4] constitutes a method to compute both the mean trajectory and dispersivity of a Brownian particle in a vast variety of physical situations, including spatially periodic media, chemically reactive systems, and adsorptive systems. The theory is based upon a generalization of Taylor dispersion theory, and is asymptotic in nature. Explicitly, this requires that the time for the process be much longer than the diffusional time scale, $t \gg l^2/|\mathbf{D}|$, where l is a characteristic scale for the process (in the present circumstances the characterisitc length of a unit cell comprising the periodic media) and $|\mathbf{D}|$ is a suitable norm of the molecular diffusivity dyadic. For the purposes of this project, attention will be focused solely upon the mean velocity, which is conceptually more straightforward than the dispersivity. In this context, spatially periodic macrotransport theory has been successfully employed in a number of contexts, including predicting the mean seepage velocity on the Darcy scale for porous media [4], as well as predicting the mean direction of motion of biomolecules in continuous separation devices [5]. However, given the relative simplicity (and familiarity) of a Langevin approach, it will be useful to demonstrate the equivalence of both approaches.

II. LANGEVIN FORMULATION

When analyzing the dynamics of the particle trajectory, it proves convenient to imagine the spatially periodic array to be mathematically subdivided [4] into identical contiguous unit cells, as in Figure 1. Define the global position vector $\mathbf{R}_n$ as the locator point (of, say of the centroid) of the n^{th} unit cell within the effectively infinite global space $\mathbf{R}_\infty$ of the device. In the case of a three-dimensional device, we write

$$\mathbf{R}_n = n_1\mathbf{l}_1 + n_2\mathbf{l}_2 + n_3\mathbf{l}_3 \tag{2.1}$$

in which $n_i = 0, \pm 1, \pm 2, \ldots$ $(i = 1, 2, 3)$, and wherein $(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$ are a pair of basic lattice vectors characterizing a unit cell, whose superficial area $\tau_0 = (\mathbf{l}_1 \times \mathbf{l}_2) \cdot \mathbf{l}_3$. The dynamics of an inertialess spherical particle moving through a spatially periodic media can be modeled at any point $\mathbf{R} = \mathbf{R}_n + \mathbf{r}$ within the fluid interstices $(\mathbf{R} \in \mathbf{R}_\infty)$ by an overdamped Langevin equation:

$$\mathbf{M}^{-1}(\mathbf{r}\left\{t\right\}) \cdot \mathbf{U}(t) = \mathbf{F}^T(\mathbf{r}\left\{t\right\}, t), \tag{2.3}$$

$$\mathbf{F}^T(\mathbf{r}\left\{t\right\}, t) = \mathbf{F}^{ext} + \Gamma(t) \tag{2.4}$$

where $\mathbf{U} \equiv d\mathbf{R}/dt$ is the instantaneous velocity of the particle. The total force $\mathbf{F}^T$ acting on the particle consists of the deterministic external force $\mathbf{F}$, as well as the fluctuating force Γ arising from the solvent molecule impacts. From a purely dynamical viewpoint, one is concerned with tracking the global position $\mathbf{R}$, or the local position $\mathbf{r}$, as a function of the process time t. Accordingly, when considering *dynamical* modeling of the process, the particle position vector $\mathbf{R}$ (or $\mathbf{r}$) will be denoted as $\mathbf{R}\left\{t\right\}$ (or $\mathbf{r}\left\{t\right\}$) to reflect the time dependence of the latter position vectors. In later *kinematical* modeling, the explicitly time dependent notation will be suppressed.

Dynamically, as a consequence of the periodic nature of the chip geometry, together with the assumed absence of inertial effects, the particle recognizes only its local interstitial position $\mathbf{r}$ within the particular unit cell that it happens to be instantaneously transversing at time t, rather than being functionally dependent upon its global position, $\mathbf{R}$, within the chip. Reflecting the global periodic structure of the device, the mobility dyadic appearing in eq. (2.3) is spatially periodic:

$$\mathbf{M}(\mathbf{R}_n\{t\} + \mathbf{r}\{t\}) = \mathbf{M}(\mathbf{r}\{t\}). \tag{2.5}$$

The present analysis is restricted to spherical particles, whose mobility in an unbounded, otherwise quiescent fluid is isotropic, and given by Stokes law.[1] However, hydrodynamic wall effects [6] alter the hydrodynamic mobility of a particle at a specified position relative to the wall. Moreover, the mobility in the vicinity of the solid obstacle is itself may be anisotropic [6]. Although not considered within the context of this analysis, the latter wall effect may be enhanced when the walls also exert an attractive force upon the particles, thereby increasing the probability density proximate to the wall. Ultimately, given the laws of hydrodynamics, the mobility of a particle within the interstices is both anisotropic and position dependent whenever the particle is sufficiently close to an obstacle.

More formally, the local linear velocity $\mathbf{U}$ (of, say, the sphere center C) and angular velocity Ω are generically related to the external force $\mathbf{F}$ and torque $\mathbf{L}$ (about C) by the resistance tensor formalism [6],

$$\mathbf{F} = \mu\left({}^t\mathbf{K}\cdot\mathbf{U} + {}^c\mathbf{K}^\dagger\cdot\Omega\right), \tag{2.6}$$

$$\mathbf{L} = \mu\left({}^c\mathbf{K}\cdot\mathbf{U} + {}^r\mathbf{K}\cdot\Omega\right), \tag{2.7}$$

with $\dagger$ the transpose operator, and ${}^t\mathbf{K}$, ${}^c\mathbf{K}$, and ${}^r\mathbf{K}$, respectively, the translational, coupling, and rotational resistance tensors for the sphere in the presence of a stationary, no-slip obstacle. For the external torque-free particle motions occurring in the systems of interest, the angular velocity induced by the wall is given by

$$\Omega = -{}^r\mathbf{K}^{-1}\cdot{}^c\mathbf{K}\cdot\mathbf{U}. \tag{2.8}$$

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[1] Were the particles nonspherical, their instantaneous orientations as they rotated as a consequence of wall effects or rotary Brownian motion would have to be incorporated into the analysis.

Substitution of (2.8) into (2.6), followed by inversion, furnishes the definition of the hydrodynamic mobility,

$$\mathbf{U} = \mathbf{M} \cdot \mathbf{F}, \tag{2.9}$$

with the mobility dyadic

$$\mathbf{M} = \mu^{-1} \left[{}^t\mathbf{K} - {}^c\mathbf{K}^\dagger \cdot {}^r \mathbf{K}^{-1} \cdot {}^c\mathbf{K} \right]^{-1}. \tag{2.10}$$

It is noted for future reference the mobility dyadic is symmetric [6],

$$\mathbf{M} = \mathbf{M}^\dagger. \tag{2.11}$$

Numerical values for these resistance tensors are available elsewhere (see, for example, [6]), but for the present circumstances it suffices to note that the values of these tensors depend upon the relative distance between the particle and the wall.

The stochastic force vector $\Gamma(\mathbf{r},t)$ is defined by its Gaussian white-noise statistical properties:

$$\langle \Gamma(t) \rangle = \mathbf{0}, \tag{2.12}$$

$$\langle \Gamma(t)\Gamma(t') \rangle = 2kT \left\langle \mathbf{M}^{-1}(\mathbf{r}\,\{t\}\,) \right\rangle \delta(t - t'), \tag{2.13}$$

with δ the Dirac delta function, kT the Boltzmann factor, and $\langle \mathbf{Y} \rangle$ the ensemble average of the stochastic variable $\mathbf{Y}$.

The fundamental importance of the position dependence of the mobility dyadic is immediately apparent from the Langevin equation. Application of the ensemble averaging operator to eq. (2.3) furnishes the ensemble average of the instantaneous particle velocity vector at the time t,

$$\langle \mathbf{U} \rangle = \left\langle \mathbf{M}(\mathbf{r}\,\{t\}\,) \cdot \mathbf{F}^T(t) \right\rangle. \tag{2.14}$$

Essential to the analysis of the separation mechanism is the concept of the instantaneous interstitial particle position $\mathbf{r}\,\{t\}$, which is directly coupled to the global position $\mathbf{R}\,\{t\}$, as a stochastic variable. The instantaneous particle position (quantifying the particle trajectory) evolves stochastically in time owing to the presence of the Gaussian white noise, giving rise to the kinematical notion of diffusion relative to the mean particle motion, the latter arising from the *steady* portion of the applied force.

III. MACROTRANSPORT DESCRIPTION

The macrotranport formalism presented herein may be derived formally from a method of moments analysis [4], the latter technique providing a set of partial differential equations for computing both the long-time mean velocity $\mathbf{U}^*$, as well as the dispersivity $\mathbf{D}^*$. For the present circumstances, we will focus our attention solely upon the mean velocity of the Brownian particle in the limit that the process time is much greater than the characterstic diffusive time [7]. In essence, the formulae for computing the mean velocity can be envisioned as representing a stationary solution to the local-space ($\mathbf{r}$) Fokker-Planck equation [3].

Macrotransport theory constitutes, *inter alia*, a scheme for computing the macrotransport field $P_0^\infty(\mathbf{r})$, the unconditional probability density of the particle being situated at the interstitial position $\mathbf{r}$ within a given unit cell. This field may be computed by the solution of the steady-state, unit-cell boundary value problem [4]:

$$\nabla \cdot \mathbf{J}_0^\infty = 0, \tag{3.1}$$

with

$$\mathbf{J}_0^\infty(\mathbf{r}) = \mathbf{M}(\mathbf{r}) \cdot (\mathbf{F} - kT\nabla)\, P_0^\infty(\mathbf{r}), \quad (\mathbf{r} \in \tau_0)\,, \tag{3.2}$$

subject to the following periodicity conditions,

$$P_0^\infty(\mathbf{r} + \mathbf{l}_\alpha) = P_0^\infty(\mathbf{r}), \quad (\alpha = 1, 2, 3)\,, \tag{3.3}$$

$$\nabla P_0^\infty(\mathbf{r} + \mathbf{l}_\alpha) = \nabla P_0^\infty(\mathbf{r}), \quad (\alpha = 1, 2, 3)\,, \tag{3.4}$$

and normalization condition,

$$\int_{\tau_0} d^3\mathbf{r}\, P_0^\infty(\mathbf{r}) = 1. \tag{3.5}$$

The no flux boundary condition on the surface(s) s_p of the solid obstacles within a unit cell requires that

$$\upsilon \cdot \mathbf{J}_0^\infty = 0 \quad \text{on} \quad s_p, \tag{3.6}$$

with υ the normal unit vector. From macrotransport theory, the mean velocity $\overline{\mathbf{U}}^*$ is calculated by the unit cell quadrature,

$$\overline{\mathbf{U}}^* = \int_{\tau_0} d^3\mathbf{r}\, \mathbf{J}_0^\infty(\mathbf{r}). \tag{3.7}$$

IV. EQUIVALENCE OF THE MEAN VELOCITY

The subsequent derivation is based upon an extension of the techniques employed by Risken [8] to compute Kramers-Moyal coefficients from nonlinear, multi-dimensional Langevin equations. Essentially, the demonstration of equivalence consists of two parts. First, the ensemble average velocity at a given time t, $\langle \mathbf{U} \rangle (t)$, is computed directly from the Langevin equation by considering the ensemble averaged instantaneous displacement of the particle. Secondly, the ergodic hypothesis is invoked to provided a probabilistic definition of the mean velocity. The periodicity of the process provides the link between the Langevin equation and the macrotransport mean velocity. In what follows, the mobility dyadic of the particle will be denoted, for clarity, by its global position, $\mathbf{M}(\mathbf{R})$, which is equivalent to the value of the mobility at a local position $\mathbf{r}$, $\mathbf{M}(\mathbf{r})$, by periodicity (2.5). In the final result, the mobility will again be expressed solely as a function of the local position to facilitate subsequent manipulations [cf. eq. (4.18)].

A. Instantaneous Mean Velocity

So as to compute the value of the correlation function (2.14) between the mobility dyadic and the force experienced by the Brownian particle at a time t, express the ensemble average mean velocity $\langle \mathbf{U} \rangle$ in its Lagrangian form as the displacement of the particle's global position

$\mathbf{R}(t)$ over a short time interval τ,

$$\langle \mathbf{U} \rangle = \lim_{\tau \to 0} \tau^{-1} \langle \mathbf{R}(t+\tau) - \mathbf{R}(t) \rangle . \tag{4.1}$$

Integrating eq. (2.3) over the time period τ,

$$\langle \mathbf{U} \rangle = \lim_{\tau \to 0} \tau^{-1} \left\langle \int_t^{t+\tau} dt' \, \mathbf{M}(\mathbf{R}\{t'\}) \cdot \mathbf{F} + \mathbf{M}(\mathbf{R}\{t'\}) \cdot \Gamma(t') \right\rangle . \tag{4.2}$$

Given the brevity of the latter time interval, it is reasonable to expand the mobility dyadic in a Taylor series for small changes in time,

$$\mathbf{M}(t') = \mathbf{M}(\mathbf{R}\{t\}) + (\mathbf{R}(t') - \mathbf{R}(t)) \cdot \nabla \mathbf{M}(\mathbf{R}\{t\}) + \cdots . \tag{4.3}$$

Substituting the latter two expansions into (4.2),

$$\langle \mathbf{U} \rangle = \lim_{\tau \to 0} \tau^{-1} \begin{pmatrix} \left\langle \int_t^{t+\tau} dt' \, \mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F} \right\rangle + \\ + \left\langle \int_t^{t+\tau} dt' \, (\mathbf{R}(t') - \mathbf{R}(t)) \cdot \nabla \mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F} \right\rangle + \cdots \\ + \left\langle \int_t^{t+\tau} dt' \, \mathbf{M}(\mathbf{R}\{t\}) \cdot \Gamma(t') \right\rangle + \\ + \left\langle \int_t^{t+\tau} dt' \, (\mathbf{R}(t') - \mathbf{R}(t)) \cdot \nabla \mathbf{M}(\mathbf{R}\{t\}) \cdot \Gamma(t') \right\rangle + \cdots \end{pmatrix} \tag{4.4}$$

For terms which involve $(\mathbf{R}(t') - \mathbf{R}(t))$, this procedure can be performed recursively.

The infinite expansion can be vastly simplified. Any integral which involves multiples of more than two Langevin forces will vanish in the limit $\tau \to 0$. This may be shown explicitly by referring to the higher order correlations of the Gaussian distributed noise [8],

$$\langle \Gamma(t_1)\Gamma(t_2) \cdots \Gamma(t_{2n-1}) \rangle = \mathbf{0}, \tag{4.5}$$

$$\begin{aligned} \langle \Gamma(t_1)\Gamma(t_2) \cdots \Gamma(t_{2n}) \rangle = {} & \left[2kT \left\langle \mathbf{M}^{-1}(\mathbf{r}\{t\}) \right\rangle \right]^n \times \\ & \times \left[\sum_{P_d} \delta(t_{i_1} - t_{i_2}) \delta(t_{i_3} - t_{i_4}) \cdots \delta(t_{i_{2n-1}} - t_{i_{2n-2}}) \right], \end{aligned} \tag{4.6}$$

where the summation index P_d refers to the $(2n)!/(2^n n!)$ permutations which give different expressions for the terms in the summation. Accordingly, integrals of averages of odd numbers of Langevin forces in (4.4) vanish identically, while integrals of averages of even powers of Langevin forces in (4.4) will contribute, at most, factors of τ^2, which vanish in the limit $\tau \to 0$. Terms involving n powers of the deterministic velocity, $\mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F}$, will contribute factors of τ^n upon integration. Accordingly, the only terms which survive in the limit are

$$\langle \mathbf{U} \rangle = \lim_{\tau \to 0} \tau^{-1} \left\langle \int_t^{t+\tau} dt'\, \mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F} \right\rangle + \lim_{\tau \to 0} \tau^{-1} \left\langle \int_t^{t+\tau} dt'\, \mathbf{M}(\mathbf{R}\{t\}\,) \cdot \Gamma(t') \right\rangle + \\ + \lim_{\tau \to 0} \tau^{-1} \left\langle \int_t^{t+\tau} dt' \mathbf{M}(\mathbf{R}\{t'\}) \cdot \left(\int_t^{t'} dt'' \Gamma(t'') \right) \cdot \nabla \mathbf{M}(\mathbf{R}\{t\}) \cdot \Gamma(t') \right\rangle. \tag{4.7}$$

The remaining three terms may be evaluated individually. The ensemble averaging operator does not effect the value of a phenomenological parameter at a fixed position $\mathbf{R}\{t\}$, whereby

$$\lim_{\tau \to 0} \tau^{-1} \left\langle \int_t^{t+\tau} dt'\, \mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F} \right\rangle = \mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F}. \tag{4.8}$$

From the zero mean of the Langevin force (2.12),

$$\lim_{\tau \to 0} \tau^{-1} \left\langle \int_t^{t+\tau} dt'\, \mathbf{M}(\mathbf{R}\{t\}\,) \cdot \Gamma(t') \right\rangle = \mathbf{0}. \tag{4.9}$$

Rearranging the final integral,

$$\int_t^{t+\tau} dt' \mathbf{M}(\mathbf{R}\{t'\}) \cdot \left(\int_t^{t'} dt'' \Gamma(t'') \right) \cdot \nabla \mathbf{M}(\mathbf{R}\{t\}) \cdot \Gamma(t') = \\ \int_t^{t+\tau} dt' \mathbf{M}(\mathbf{R}\{t'\}) \cdot \left(\int_t^{t'} dt'' \Gamma(t'') \Gamma(t') \right) : \nabla \mathbf{M}(\mathbf{R}\{t\}), \tag{4.10}$$

where we have made use of the symmetry of the mobility dyadic (2.11), as well as the double dot product convention,

$$\mathbf{ab} : \mathbf{cd} = (\mathbf{a} \cdot \mathbf{c})\,(\mathbf{b} \cdot \mathbf{d})\,. \tag{4.11}$$

Again, the ensemble average does not effect the phenomenological parameters,

$$\left\langle \int_t^{t+\tau} dt' \mathbf{M}(\mathbf{R}\{t'\}) \cdot \left(\int_t^{t'} dt'' \Gamma(t'') \Gamma(t') \right) : \nabla \mathbf{M}(\mathbf{R}\{t\}) \right\rangle = \\ \int_t^{t+\tau} dt' \mathbf{M}(\mathbf{R}\{t'\}) \cdot \left(\int_t^{t'} dt''\, \langle \Gamma(t'') \Gamma(t') \rangle \right) : \nabla \mathbf{M}(\mathbf{R}\{t\}). \tag{4.12}$$

Employing the average correlation (2.13),

$$\int_t^{t'} dt'' \langle \Gamma(t'')\Gamma(t') \rangle = \int_t^{t'} dt'' 2kT \left\langle \mathbf{M}^{-1} \right\rangle \delta(t'' - t'). \tag{4.13}$$

We use the Stratonovich rule [8] to evaluate the integral,

$$\int_t^{t'} dt'' 2kT \left\langle \mathbf{M}^{-1} \right\rangle \delta(t'' - t') = kT\mathbf{M}^{-1}(\mathbf{R}\{t'\}), \tag{4.14}$$

which leads to the result

$$\left\langle kT \int_t^{t+\tau} dt' \mathbf{M}(\mathbf{R}\{t'\}) \cdot \mathbf{M}^{-1}(\mathbf{R}\{t'\}){:}\nabla\mathbf{M}(\mathbf{R}\{t\}) \right\rangle = \nabla \cdot \mathbf{D}(\mathbf{R}\{t\}), \tag{4.15}$$

where the mobility dyadic has been replaced with the diffusivity dyadic by the Nernst-Planck-Einstein relationship,[2]

$$\mathbf{D}(\mathbf{R}) = kT\mathbf{M}(\mathbf{R}). \tag{4.16}$$

Accordingly, the ensemble average velocity is

$$\langle \mathbf{U} \rangle = \mathbf{M}(\mathbf{R}\{t\}) \cdot \mathbf{F} + \nabla \cdot \mathbf{D}(\mathbf{R}\{t\}), \tag{4.17}$$

which, upon noting the periodicity of the mobility (2.5), and the implied periodicity of the diffusivity (4.16), can be rewritten in the form

$$\langle \mathbf{U} \rangle = \mathbf{M}(\mathbf{r}\{t\}) \cdot \mathbf{F} + \nabla \cdot \mathbf{D}(\mathbf{r}\{t\}). \tag{4.18}$$

B. Long-Time Mean Velocity

As the particle moves along its Lagrangian trajectory through the device, at each instant in time it possesses the velocity given by eq. (4.18). The total of this translational motion

[2]It follows then that the diffusivity dyadic is both spatially periodic (2.5) and symmetric (2.11).

through the device is what gives rise to a sensible mean Lagrangian velocity, $\overline{\mathbf{U}}^*$. Ergodically, after sufficient time has elapsed such that the particle has had opportunity to sample all points within the unit cell numerous times, the latter mean velocity is equivalent to the instantaneous velocity (4.18) weighted by the long-time limited probability density within the unit cell. Explicitly, this mean velocity $\overline{\mathbf{U}}^*$ possesses the form

$$\overline{\mathbf{U}}^* = \int_{\tau_0} d^3\mathbf{r}\ [\mathbf{M}(\mathbf{r}) \cdot \mathbf{F}]\, P_0^\infty(\mathbf{r}) + P_0^\infty(\mathbf{r})\nabla\cdot\mathbf{D}(\mathbf{r}). \tag{4.19}$$

To demonstrate the equivalence between the mean velocity derived via macrotransport theory (3.7) and the ergodic mean velocity from the Langevin equations (4.19), rewrite the second term of (4.19) using the product rule,

$$P_0^\infty(\mathbf{r})\nabla \cdot \mathbf{D}(\mathbf{r}) = \nabla\cdot [P_0^\infty(\mathbf{r})\mathbf{D}(\mathbf{r})] - \mathbf{D}(\mathbf{r}) \cdot \nabla P_0^\infty(\mathbf{r}). \tag{4.20}$$

Application of the divergence theorem furnishes

$$\int_{\tau_0} d^3\mathbf{r}\, \nabla\cdot [P_0^\infty(\mathbf{r})\mathbf{D}(\mathbf{r})] = \oint_{\partial\tau_0} d\mathbf{S}\cdot P_0^\infty(r)\mathbf{D}(\mathbf{r}) = \mathbf{0}, \tag{4.21}$$

with $d\mathbf{S}$ the directed area element and $\partial\tau_0$ the surface enclosing τ_0. Since the probability density (3.3), as well as the mobility dyadic (2.5), are spatially periodic, this contour integral vanishes [4] by an elementary theorem of spatially periodic media. Therefore, the mean velocity possesses the form,

$$\overline{\mathbf{U}}^* = \int_{\tau_0} d^3\mathbf{r}\ [\mathbf{M}(\mathbf{r}) \cdot \mathbf{F}]\, P_0^\infty(\mathbf{r}) - \mathbf{D}(\mathbf{r}) \cdot \nabla P_0^\infty(r). \tag{4.22}$$

Noting that the latter integrand is exactly the flux $\mathbf{J}_0^\infty(\mathbf{r})$ contained in eq. (3.2), we conclude that the mean velocity calculated from the long-time limit of the Langevin equation is exactly equal to that derived from macrotransport theory.

V. AN EXAMPLE

The present section explores the equivalence achieved in the latter sections in the context of a specific example involving the unidirectional motion of a Brownian sphere possessing a spatially periodic diffusivity. Consider, as in Figure 2, a diffusivity of the form,

$$D(x) = \begin{cases} D_1 & (0 < x < 1/2) \\ D_2 & (1/2 < x < 1) \end{cases}, \tag{5.1}$$

where x is the dimensionless position scaled with the length of the period, l. A steady, external force of magnitude F is applied to the Brownian sphere, and it translates, on average, in the direction of the external force. The present example is a simplied version of a process employed to demonstrate the macrotransport modeling of micropatterned separation devices [5], as well as the generic macrotransport modeling of spatially periodic potential fields [9].

A. Macrotransport Solution

The macrotransport solution proceeds as follows. The scalar flux, J_0^∞, is of the form (3.2)

$$J_0^\infty = D(x)\left[\frac{F}{kT}P_0^\infty - \frac{dP_0^\infty}{dx}\right], \tag{5.2}$$

where the Stokes-Einstein equation (4.16) has been employed to relate the mobility $M(x)$ to the diffusivity $D(x)$. Application of eq. (3.1) furnishes the ordinary differential equation for P_0^∞,

$$\frac{d}{dx}\left[\frac{dP_0^\infty}{dx} - PeP_0^\infty\right] = 0, \tag{5.3}$$

where Pe is the Peclet number,

$$Pe = \frac{Fl}{kT}, \tag{5.4}$$

measuring the relative importance of convection to diffusion. The solution of (5.3), with application of the periodicity (3.3) and normalization (3.5) conditions[3], is of the form

$$P_0^\infty = C\exp(Pex)\left[1 - K\int_0^x dx' \frac{\exp(-Pex')}{D(x')}\right], \tag{5.5}$$

with the constants

$$K = \frac{1-\exp(-Pe)}{\displaystyle\int_0^1 dx \frac{\exp(-Pex)}{D(x)}}, \tag{5.6}$$

$$C^{-1} = l\int_0^1 dx\exp(Pex)\left[1 - K\int_0^x dx' \frac{\exp(-Pex')}{D(x')}\right]. \tag{5.7}$$

It is readily verified that the flux is a constant possessing the value

$$J_0^\infty = \frac{KC}{l}, \tag{5.8}$$

whereby

$$\overline{U}^* = KC. \tag{5.9}$$

B. Numerical Simulation of the Langevin Equation

The preceding macrotransport solution was compared to numerical values computed by simulating the Langevin equation. The numerical simulations followed the procedure outlined by Risken [8] and were implimented in MatLab. Based upon prior investigations [5], it is known that the (scaled) mean velocity is only dependent upon the ratio of the diffusivities, D_1/D_2, rather than the actual values of the diffusivities themselves. This implies scaling the mean velocity with the average velocity, $\langle M\rangle F$, where the average mobility $\langle M\rangle = (D_1 + D_2)/(2kT)$. The process time is scaled with the diffusional length scale,

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[3]The second periodicity condition involving the gradients of the probability density is satisfied trivially.

$l^2/\langle M\rangle kT$. Since Taylor dispersion theory is known to be only an asymptotic theory, one would expect the results to converge only for values of large dimensionless time.

Simulations were undertaken for the values $D_1/D_2 = 2/3$ and $D_1/D_2 = 100$ for Peclet numbers of $Pe = 0.1$ and $Pe = 5$. Large Peclet number processes, while readily implemented in the numerical algorithm, become difficult to compute from the macrotransport problem owing to the presence of terms involving exponential of the Peclet number. Of course, in the infinite Peclet number limit, the particle moves with a scaled mean velocity equal to unity. The numerical routine was tested against the limiting cases $D_1/D_2 = 0$ and $D_1/D_2 = 1$. In both cases, the expected results were achieved, namely $\overline{U}^* = 0$ and $\overline{U}^* = 1$, when properly scaled. Each plot is the result of 100 simulations, each simulation consisting of 1000 time steps. The low number of simulations were employed to emphasize the transient results obtained at low values of the dimensionless time, while simultaneously exhibiting the asymptotic limiting behavior at high values of the dimensionless time, even with the lower sample rate. Data collected from 1000 simulations, not presented explicitly herein, significantly decreased the transients for short dimensionless times.

1. Nearly Homogeneous Media, $D_1/D_2 = 2/3$

Figures 3 and 4 present data obtained for the nearly homogeneous media with diffusivity ratio of 2/3. In both cases, the agreement between the macrotransport mean velocity and the Langevin equation is quite good. At small times, where the macrotransport mean velocity is not expected to be valid, the Langevin mean velocity exhibits large fluctuations and deviates significantly from its long-time limit. However, these fluctuations are damped by the higher Peclet number simulations, which is expected since the process is dominated under these circumstances by the deterministic convective component of the velocity. As noted previously, the use of additional simulations has the effect of reducing the short-time fluctuations, but has little effect upon the long-time result. Finally, note that approximately 5 time constants are needed to arrive at the steady-state behavior.

2. Heterogeneous Media, $D_1/D_2 = 100$

Figures 5 and 6 present data obtained for the more heterogeneous media with a diffusivity ratio of 100. Similar trends are observed as in the previous case, namely (i) higher fluctuations at short times, (ii) lower fluctuations at higher Peclet numbers, and (iii) reasonably good agreement between the numerical simulations and the theoretical answer. Results are not quite as consistent for the $Pe = 5$ case, but this behavior may be due to the large value of some parameters employed in the simulation. Overall, the local velocity field, that is the velocity in either the D_1 or D_2 phase, differs dramatically between phases. Accordingly, if the stochastic component of the Langevin equation cause the particle to move into a different phase, its velocity will be differ from a particle whos stochastic force causes it to remain in the same phase. The latter behavior not only accounts for the poor agreement in the data, but also is the fundamental mechanism of dispersion in the system, which may also be modeled using macrotransport theory [4].

VI. CONCLUDING REMARKS

The preceding has demonstrated, from both analytical methods and numerical simulations, that, in the long-time limit, the mean trajectory of a Brownian particle provided by the dynamical Langevin approach is equivalent to that provided by the kinematical macrotransport theory. That these two theories should furnish identical results is unsurprising, inasmuch as their phenomenological basis is similar, and the latter equivalence was previously shown for continuous macrotransport theory [3]. Nevertheless, it is satisfying to reconcile the two approaches, and to confirm the results through numerical simulation. It should be noted that although the preceding derivations and simulations were restricted to purely external force-driven motion, the analysis is readily extended to include flowing systems as well. The extended analysis requires the addition of a hydrodynamic force to the total force experience by the particle (2.4), and this force may be readily calculated from the prior fluid mechanical discussion. Moreover, the macrotransport description of the particle transport process was originally developed for flow through porous media [4], and the force driven flow situations considered herein constitute a special case of the general theory.

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