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Nonequilibrium Statistical Mechanics of Preasymptotic Dispersion

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Turbulent transport in bulk-phase fluids and transport in porous media with fractal character involve fluctuations on all space and time scales. Consequently one anticipates constitutive theories should be nonlocal in character and involve constitutive parameters with arbitrary wavevector and frequency dependence. We provide here a nonequilibrium statistical mechanical theory of transport which involves both diffusive and convective mixing (dispersion) at all scales. The theory is based on a generalization of classical approaches used in molecular hydrodynamics and on time-correlation functions defined in terms of nonequilibrium expectations. The resulting constitutive laws are nonlocal and constitutive parameters are wavevector and frequency dependent. All results reduce to their convolution-Fickian, quasi-Fickian, or Fickian counterparts in the appropriate limits.

KEY WORDS: Preasymptotic; dispersion; nonequilibrium; porous medium; heterogeneity.

1. INTRODUCTION

The evolution of a passive tracer within a velocity field exhibiting excitements on a continuum of scales typically defies representation via classical Fickian dispersion theory. This foundering is a result of randomness occurring on all length scales relative to the scale of observation.[1] Two realizations of this paradigm, fully turbulent fluid transport and transport in porous media possessing a continuum of scales of heterogeneity, are both naturally ubiquitous and environmentally important. Contamination concerns relevant to these and other natural processes continually

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reemphasize the need for an accurate general theory of dispersion. A correct description of turbulent mixing in the atmosphere is critical to prediction and control of many environmental contamination scenarios. Similarly, a clear understanding of dispersive mixing in subsurface geological environments is necessary to protect and maintain our groundwater resources. An enormous amount of effort has been directed to examination and reconstruction of dispersion theories, in both turbulent hydrodynamics and in porous-medium fluid dynamics (e.g., refs. 2–6). Yet no consequent construction is free of requisite unphysical restrictions (such as perturbation smallness) on representation of either allowable dynamics or heterogeneity, or both. Here we approach the construction of a general dispersion theory with tools of classical statistical mechanics. Within the conceptual framework of Hamiltonian dynamics, the resulting theory of dispersive mixing in environments with continuously evolving heterogeneity is fully rigorous and obtained without approximation.

2. BACKGROUND

All subsequent analysis will be directed toward flows in porous media, as bulk-phase flows can be considered special cases wherein the specific surface area of the porous medium goes to zero. A fluid in a porous medium may be distinguished from its bulk-phase counterpart by two aspects: the presence of regions of excluded volume, and the adsorption of the fluid/solute onto the surface of the excluded volume. We will concern ourselves only with conservative tracers so that the latter distinction is of no consequence. The term "excluded volume" means simply the subset of position coordinates within the domain of the media that is inaccessible to connected fluid flow, including both the bulk solid matrix and inaccessible pore spaces.

Historically for such systems,[6] Fickian constitutive theory has been enlisted to represent diffusion, and, more importantly in convective systems, conscribed as a model for dispersion. Discontinuities in mathematical (pointwise) definitions of both field and constitutive properties arise naturally from the existence of the spatially complex excluded volume. To circumvent this complication, constitutive relations are ascribed to volume averages of these properties, upon which continuum mechanical manipulations are executed to obtain models of the dynamics of the volume averages.[7] The appropriate averaging volume for operational definitions of properties is known as the "representative elementary volume" (REV). The principal weakness in this approach is that rigorous proof of the existence of satisfactory averaging volumes (obeying certain ergodic and invariance requirements) exists only for idealized porous media. In fact, porous media exhibiting heterogeneity on a continuum of scales have no REV.[1]

More generally, multiscale heterogeneity in the structure of the excluded volume leads to the so-called "scale effect" of dispersive transport in natural porous media.[8] In essence, the scale effect means the mixing length for dispersion is a function of time or travel distance and it implies dispersion is non-Markovian. Over scales of time and space on which the structure of the excluded volume is continuously evolving, classical Fickian diffusive notions and the derivative dispersive theories break down and must be replaced by more general constitutive relations.[9] It is this latter point that leads to the "scale" effect.

Here we develop a nonequilibrium statistical mechanical theory of transport which involves both diffusive and convective mixing (dispersion) at all scales. The results are based on a generalization of classical approaches used in molecular hydrodynamics and on time-correlation functions defined in terms of nonequilibrium expectations. We begin by finishing this background section with the complement of statistical mechanical concepts necessary for the subsequent constructions.

The setting is that of both classical equilibrium and nonequilibrium statistical mechanics. Consider a fluid mixture consisting of N constituent particles residing in a bath of M fluid particles with position coordinates given by $\boldsymbol{x} = \{\mathbf{x}_1(t),..., \mathbf{x}_{N+M}(t)\}$ and conjugate momenta given by $\boldsymbol{p}(t) = \{\mathbf{p}_1(t),..., \mathbf{p}_{N+M}(t)\}$. Because of the excluded volume V_s associated with the solid matrix within which the fluid resides, the probability of finding the ith particle in an element of volume $d\mathbf{x}_i = dx_i^1 \times dx_i^2 \times dx_i^3$ (here the superscript indicates Cartesian coordinate and the subscript identifies the particle) is nonzero only when $d\mathbf{x}_i$ coincides with the complement of V_s; that is, when $d\mathbf{x}_i \cap V_s^c$ is nonzero. The phase space for the $N + M = J$ particles consists of

$$\Omega = (V_s^c)^J \times R^{3J} \tag{1}$$

Here, the solid is treated as an external force field acting on the fluid plus constituent mixture. Let $f(\boldsymbol{x}, \boldsymbol{p}; t)$ be the nonequilibrium probability per unit hypervolume of phase space that each particle i is respectively located in $d\mathbf{x}_i$ at $(\mathbf{x}_i; t)$ with momentum in $d\mathbf{p}_i$ at $(\mathbf{p}_i, t)$. We will assume the system is Hamiltonian, so that[10]

$$\frac{\partial f}{\partial t} = -iLf \tag{2}$$

where the Liouville operator represents the phase space convective derivative

$$iL = \sum_{j=1}^{J} \left[\frac{\mathbf{p}_j}{m_j} \cdot \nabla_{\mathbf{x}_j} + \mathbf{F}_j \cdot \nabla_{\mathbf{p}_j}\right] \equiv \mathbf{V} \cdot \nabla \tag{3}$$

with

$$\mathbf{V} = \left(\frac{\mathbf{p}_1}{m_1}, \ldots, \frac{\mathbf{p}_J}{m_J}, \mathbf{F}_1, \ldots, \mathbf{F}_J\right) \tag{4}$$

and

$$\nabla = (\nabla_{\mathbf{x}_1}, \ldots, \nabla_{\mathbf{x}_J}, \nabla_{\mathbf{p}_1}, \ldots, \nabla_{\mathbf{p}_J}) \tag{5}$$

and $\mathbf{F}_k$ is the total force on the kth particle (i.e., the fluid–fluid and fluid–solid contribution). Equilibrium is said to exist if f does not explicitly depend on time, in which case we label it as f_0, and

$$Lf_0 = 0 \tag{6}$$

The expected value of any dynamic variable $\alpha(t) = \alpha(\boldsymbol{x}(t), \boldsymbol{p}(t))$ is given by

$$\langle \alpha(t) \rangle = \int_\Omega \alpha(\boldsymbol{x}(t), \boldsymbol{p}(t))\, f(\boldsymbol{x}, \boldsymbol{p}; t)\, d\boldsymbol{x}\, d\boldsymbol{p} \tag{7}$$

The equilibrium expected value is given by

$$\langle \alpha(t) \rangle_0 = \int_\Omega \alpha(\boldsymbol{x}(t), \boldsymbol{p}(t))\, f_0(\boldsymbol{x}, \boldsymbol{p})\, d\boldsymbol{x}\, d\boldsymbol{p} \tag{8}$$

It is well known that

$$\frac{d}{dt} \langle \alpha(t) \rangle_0 = 0 \tag{9}$$

and that

$$\frac{d}{dt} \langle \alpha(t) \rangle = \langle \dot{\alpha}(t) \rangle \tag{10}$$

3. MEMORY FUNCTION FORMALISM FOR EQUILIBRIUM TIME CORRELATION FUNCTION

As motivation for subsequent sections we briefly review the Mori–Zwanzig theory of equilibrium time correlation functions.[11,12] Let $\Psi(t)$ be a normalized equilibrium time correlation function of the dynamic variable $\alpha(t)$; that is,

$$\Psi(t) = \langle \alpha(t)\, \alpha^*(0) \rangle_0 = (\alpha(t), \alpha(0))_0 \tag{11}$$

where the asterisk indicates complex conjugate, $(\cdot, \cdot)$ indicates complex inner product, and without loss of generality it is assumed $\Psi(0)=1$ and $\dot{\Psi}(0)=0$. It is known[12] that

$$\dot{\Psi}(t) = -\int_0^t k(\tau)\, \Psi(t-\tau)\, d\tau \tag{12}$$

where the memory function $k(\tau)$ is given by

$$k(\tau) = (\exp(itQ_\alpha L)\, \dot{\alpha}(0), \dot{\alpha}(0))_0 \tag{13}$$

and the action of the complementary projection operator Q_α on the function $\gamma(t)$ is

$$Q_\alpha \gamma(t) = \gamma(t) - \alpha(0)(\gamma(t), \alpha(0))_0 \tag{14}$$

and finally where $\exp(itQ_\alpha L)$ is defined by its Neumann expansion. All the physics of the dynamic process is wound up in the memory function, which in turn defines all transport coefficients.

Motivation for Eqs. (9)–(12) is provided by an expansion on the following canonical example. A Brownian diffusive process for a massive particle bathed in a continuum fluid of lighter particles obeys the momentum balance

$$m\mathbf{a}(t) = -\xi \mathbf{v}(t) + \mathbf{b}(t) \tag{15}$$

where m is the particle mass, $\mathbf{a}(t)$ is its acceleration, ξ the friction constant, $\mathbf{v}(t)$ its velocity, and $\mathbf{b}(t)$ is a Brownian fluctuating force assumed uncorrelated with the initial velocity. If this equation is dotted with $\mathbf{v}(0)$ and equilibrium averages are taken, we get

$$\dot{C}_V(t) = -\frac{\xi}{m} C_V(t) \tag{16}$$

which has the solution

$$C_V(t) = \exp(-\xi t/m)\, C_V(0) \tag{17}$$

Thus (16) is an asymptotic result in that it is valid for processes that show exponential decay in the velocity correlation. It is a Markovian result, resulting from the independence assumption: the time rate of change of the correlation is independent of the process history. To distill (16) from the general result (12), apply the Markovian approximation

$$k(\tau) = \delta(\tau)\, \xi/m \tag{18}$$

to render a closure of (12),

$$\dot{\Psi}(t) = -\frac{\xi}{m}\int_0^{\tau} d\tau\, \delta(\tau)\, \Psi(t-\tau) \tag{19}$$

This is solved by

$$\Psi(t) = \exp(-t\xi/m)\, \Psi(0) \tag{20}$$

If $\Psi(t) = (\mathbf{v}(t), \mathbf{v}(0))_0/(\mathbf{v}(0), \mathbf{v}(0))_0$, then the Markovian simplification, (17), results. Thus the velocity correlation in (16) is a specialization of the more general non-Markovian (12). In this latter case, correlations often exhibit persistent tails, such as is commonly observed for porous formations with evolving heterogeneity.

A non-Markovian diffusive process generalizing (16) is found by setting α in (11) to

$$\alpha_k(t) = \exp[i\mathbf{k}\cdot\mathbf{x}(t)] \tag{21}$$

and

$$\Psi_k(t) = \hat{G}(\mathbf{k}, t) = (\alpha_k(t), \alpha_k(0))_0 \tag{22}$$

with

$$G(\mathbf{x}, t) = \langle \delta[\mathbf{x} - (\mathbf{x}_j(t) - \mathbf{x}_j(0))] \rangle_0 \tag{23}$$

where the caret denotes spatial Fourier transform. The function G is recognized as the self-part of the intermediate scattering function[12] and reports for given space-time point $(\mathbf{x}, t)$ the ensemble probability of finding a tagged particle there, given that originally it was elsewhere. As $\hat{G}$, being an equilibrium correlation function, satisfies (12), we have

$$\begin{aligned}\frac{\partial \hat{G}}{\partial t} &= -\int_0^t (\exp[iQ_{\exp[i\mathbf{k}\cdot\mathbf{x}(\tau)]}L\tau]\, i\mathbf{k}\cdot\mathbf{v}(0)\, e^{i\mathbf{k}\cdot\mathbf{x}(0)}, i\mathbf{k}\cdot\mathbf{v}(0)\, e^{i\mathbf{k}\cdot\mathbf{x}(0)})_0 \\ &\quad \times \hat{G}(\mathbf{k}, t-\tau)\, d\tau \\ &= i\mathbf{k}\cdot\int_0^t (\exp[iQ_{\exp[i\mathbf{k}\cdot\mathbf{x}(\tau)]}L\tau]\, \mathbf{v}(0)\, e^{i\mathbf{k}\cdot\mathbf{x}(0)}, \mathbf{v}(0)\, e^{i\mathbf{k}\cdot\mathbf{x}(0)})_0 \\ &\quad \cdot [i\mathbf{k}\hat{G}(\mathbf{k}, t-\tau)]\, d\tau \\ &\equiv i\mathbf{k}\cdot\int_0^t \hat{\mathbf{D}}(\mathbf{k}, \tau)\cdot[i\mathbf{k}G(\mathbf{k}, t-\tau)]\, d\tau\end{aligned} \tag{24}$$

Inverse Fourier transform, using the dualities

$$-i\mathbf{k} \leftrightarrow \nabla_x$$

and

$$\hat{f}(\mathbf{k})\,\hat{g}(\mathbf{k}) \leftrightarrow f(\mathbf{x})^*\,g(\mathbf{x}) = \int_{R^3} f(\mathbf{y})\,g(\mathbf{x}-\mathbf{y})\,d\mathbf{y}$$

yields from (24),[10]

$$\frac{\partial G}{\partial t} = \nabla_{\mathbf{x}} \cdot \int_0^t \int_{R^3} \mathbf{D}(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y}, t-\tau)\,d\mathbf{y}\,d\tau \tag{25}$$

where $\mathbf{D}(\mathbf{y}, \tau)$ is the inverse Fourier transform of $\hat{\mathbf{D}}(\mathbf{k}, \tau)$, which is a generalized wavevector- and frequency-dependent diffusion tensor.[11] This diffusion equation is valid for media with evolving heterogeneity such as structures with fractal character.

4. MEMORY FUNCTION FORMALISM FOR NONEQUILIBRIUM TIME CORRELATION FUNCTIONS

The standard projection operator methodology[13] for obtaining the memory function equation for equilibrium correlation functions does not work for nonequilibrium correlation functions. However, the following analysis is valid. Let $\Psi(t)$ be a nonequilibrium correlation function for the dynamic variable $\alpha(t)$,

$$\Psi(t) = \langle \alpha(t)\,\alpha^*(0) \rangle \equiv (\alpha(t), \alpha(0))_t \tag{26}$$

such that

$$\Psi(0) = \langle \alpha(0)\,\alpha^*(0) \rangle = 1 \tag{27}$$

We have

$$\begin{aligned} \varphi(t) \equiv \dot{\Psi}(t) &= \int_\Omega \alpha(t)\,\alpha^*(0)\,\dot{f}(x, p; t)\,dx\,dp \\ &\quad + \int_\Omega \dot{\alpha}(t)\,\alpha^*(0)\,f(x, p; t)\,dx\,dp \\ &= \langle \dot{\alpha}(t)\,\alpha^*(0) \rangle \end{aligned} \tag{28}$$

where we have used $\dot{f} = 0$. Similarly

$$\Phi(t) = -\ddot{\Psi}(t) = -\langle \ddot{\alpha}(t)\,\alpha^*(0) \rangle \tag{29}$$

Introducing the Laplace transform denoted by the tilde, we have

$$\tilde{\varphi}(s) = s\tilde{\Psi}(s) - 1 \tag{30}$$

$$\tilde{\Phi}(s) = -s^2\tilde{\Psi}(s) + s + \varphi(0) \tag{31}$$

where s is dual to t.

It follows that for s not equal to zero

$$[s^2\tilde{\Psi}(s) - s - \varphi(0)]\,\tilde{\Psi}(s) = \left[s\tilde{\Psi}(s) - 1 - \frac{\varphi(0)}{s}\right]\left[1 + \frac{\varphi(0)}{s} + \frac{s^2\tilde{\Psi}(s) - s - \varphi(0)}{s}\right] \tag{32}$$

or

$$-\tilde{\Phi}(s)\,\tilde{\Psi}(s) = \left[s\tilde{\Psi}(s) - 1 - \frac{\varphi(0)}{s}\right]\left[1 + \frac{\varphi(0)}{s} - \frac{\tilde{\Phi}(s)}{s}\right] \tag{33}$$

For $[1 + \varphi(0)/s - \tilde{\Phi}(s)/s]^{-1}$ finite it follows that

$$s\tilde{\Psi}(s) - 1 - \frac{\varphi(0)}{s} = -\left[1 + \frac{\varphi(0)}{s} - \frac{\tilde{\Phi}(s)}{s}\right]^{-1}\tilde{\Phi}(s)\,\tilde{\Psi}(s) \tag{34}$$

Setting

$$\tilde{k}(s) = \left[1 + \frac{\varphi(0)}{s} - \frac{\tilde{\Phi}(s)}{s}\right]^{-1}\tilde{\Phi}(s) \tag{35}$$

and inverting (34) gives

$$\dot{\Psi}(t) = -\int_0^t k(\tau)\,\Psi(t-\tau)\,d\tau + \varphi(0) \tag{36}$$

This equation has the same basic form as (12), but all averages are now nonequilibrium.

5. NONEQUILIBRIUM DISPERSION

Our goal in this section is to find the general nonequilibrium counterpart to (25). To this end we again define G and $\hat{G}$ as before except that averages are now nonequilibrium. The basis for the subsequent development is the additive decomposition of the Lagrangian coordinate of the tagged particle into a nonequilibrium average displacement $\langle \mathbf{x}(t) \rangle$ and a fluctuation about this average $\mathbf{x}'(t)$,

$$\mathbf{x}(t) = \langle \mathbf{x}(t) \rangle + \mathbf{x}'(t) \tag{37}$$

With this decomposition and assuming $\langle \mathbf{x}(0) \rangle = 0$ we have

$$\hat{G}(\mathbf{k}, t) = e^{i\mathbf{k} \cdot \langle \mathbf{x}(t) \rangle} \hat{G}'(\mathbf{k}, t) \tag{38}$$

where

$$\hat{G}'(\mathbf{k}, t) = \langle \exp[i\mathbf{k} \cdot \mathbf{x}'(t)] \exp[-i\mathbf{k} \cdot \mathbf{x}'(0)] \rangle \tag{39}$$

Because $\hat{G}'(\mathbf{k}, t)$ is a normalized correlation function, it satisfies

$$\frac{\partial \hat{G}'}{\partial t} = -\int_0^t \hat{\kappa}'(\mathbf{k}, \tau)\, \hat{G}'(\mathbf{k}, t-\tau)\, d\tau + \hat{\varphi}(\mathbf{k}, 0) \tag{40}$$

where

$$\begin{aligned} \hat{\varphi}(\mathbf{k}, 0) &= \left\langle \exp[-i\mathbf{k} \cdot \mathbf{x}'(0)] \left\{ \frac{d}{dt} \exp[i\mathbf{k} \cdot \mathbf{x}'(t)] \right\}_{t=0} \right\rangle \\ &= i\mathbf{k} \cdot \langle \mathbf{v}'(0) \rangle \end{aligned} \tag{41}$$

Note because $\langle \cdot \rangle$ is a nonequilibrium average, $\langle \mathbf{v}'(t) \rangle$ is in general nonzero. Without loss of generality we can set $\langle \mathbf{v}'(0) \rangle = 0$. From (38), it follows that

$$\frac{\partial \hat{G}'}{\partial t} = -i\mathbf{k} \cdot \langle \mathbf{v}(t) \rangle\, e^{-i\mathbf{k} \cdot \langle \mathbf{x}(t) \rangle} \hat{G}(\mathbf{k}, t) + e^{-i\mathbf{k} \cdot \langle \mathbf{x}(t) \rangle} \frac{\partial \hat{G}}{\partial t} \tag{42}$$

Combining (42) with (40) gives

$$\begin{aligned} \frac{\partial \hat{G}}{\partial t} &= i\mathbf{k} \cdot \langle \mathbf{v}(t) \rangle\, \hat{G}(\mathbf{k}, t) - \left[\int_0^t \hat{\kappa}'(\mathbf{k}, \tau)\, \hat{G}'(\mathbf{k}, t-\tau)\, d\tau \right] \exp[i\mathbf{k} \cdot \langle \mathbf{x}(t) \rangle] \\ &= i\mathbf{k} \cdot \langle \mathbf{v}(t) \rangle\, \hat{G}(\mathbf{k}, t) - \int_0^t \hat{\kappa}'(\mathbf{k}, \tau) \\ &\quad \times \{ \exp[i\mathbf{k} \cdot \langle \mathbf{x}(t) \rangle_t] \exp[-i\mathbf{k} \cdot \langle \mathbf{x}(t-\tau) \rangle_{t-\tau}] \}\, \hat{G}(\mathbf{k}, t-\tau)\, d\tau \end{aligned} \tag{43}$$

or

$$\frac{\partial \hat{G}}{\partial t} = i\mathbf{k} \cdot \langle \mathbf{v}(t) \rangle\, \hat{G}(\mathbf{k}, t) - \int_0^t \hat{\kappa}'(\mathbf{k}, \tau)\, \Delta(\mathbf{k}, t, \tau)\, \hat{G}(\mathbf{k}, t-\tau)\, d\tau \tag{44}$$

where the exponential differential displacement $\Delta(\mathbf{k}, t, \tau)$ is given by

$$\Delta(\mathbf{k}, t, \tau) = \exp\{ i\mathbf{k}\tau \cdot [\langle \mathbf{x}(t) \rangle_t - \langle \mathbf{x}(t-\tau) \rangle_{t-\tau}]/\tau \} \tag{45}$$

which for small τ is

$$\Delta(\mathbf{k}, t, \tau) \approx \exp[i\mathbf{k}\tau \cdot \langle \mathbf{v}(t) \rangle] \tag{46}$$

6. ANALYSIS OF THE PERTURBED MEMORY FUNCTION

To return (44) to real space from wavevector space we must decompose $\hat{k}'$ into an invertible form. From (35) it follows that

$$\tilde{\tilde{k}}'(\mathbf{k}, s) = [1 - \tilde{\tilde{\Phi}}(\mathbf{k}, s)/s]^{-1}\, \tilde{\tilde{\Phi}}(\mathbf{k}, s) \tag{47}$$

Now

$$\begin{aligned}\hat{\Phi}(\mathbf{k}, t) &= -\frac{d^2\hat{G}'}{dt^2} = -\frac{d^2}{dt^2}\langle \exp[i\mathbf{k}\cdot\mathbf{x}'(t)] \exp[-i\mathbf{k}\cdot\mathbf{x}'(0)]\rangle \\ &= -i\mathbf{k}\cdot\langle \mathbf{a}'(t) \exp[i\mathbf{k}\cdot\mathbf{x}'(t)] \exp[-i\mathbf{k}\cdot\mathbf{x}'(0)]\rangle \\ &\quad - i\mathbf{k}\cdot\langle \mathbf{v}'(t) \exp[i\mathbf{k}\cdot\mathbf{x}'(t)] \exp[-i\mathbf{k}\cdot\mathbf{x}'(0)]\, \mathbf{v}'(t)\rangle \cdot i\mathbf{k}\end{aligned} \tag{48}$$

where $\mathbf{a}'(t)$ is the fluctuating component of the acceleration for the tagged particle.

Let

$$\hat{\mathbf{Y}}_1(\mathbf{k}, t) = -\langle \mathbf{a}'(t) \exp[i\mathbf{k}\cdot\mathbf{x}'(t)] \exp[-i\mathbf{k}\cdot\mathbf{x}'(0)]\rangle \tag{49}$$

and

$$\hat{\mathbf{Y}}_2(\mathbf{k}, t) = -\langle \mathbf{v}'(t) \exp[i\mathbf{k}\cdot\mathbf{x}'(t)] \exp[-i\mathbf{k}\cdot\mathbf{x}'(0)]\, \mathbf{v}'(t)\rangle \tag{50}$$

With these definitions we find

$$\tilde{\tilde{\Phi}}(\mathbf{k}, s) = i\mathbf{k}\cdot\tilde{\tilde{\mathbf{Y}}}_1(\mathbf{k}, s) + i\mathbf{k}\cdot\tilde{\tilde{\mathbf{Y}}}_2(\mathbf{k}, s)\cdot i\mathbf{k} \tag{51}$$

which when inserted into (47) gives

$$\tilde{\tilde{k}}'(\mathbf{k}, s) = i\mathbf{k}\cdot\tilde{\tilde{\mathbf{D}}}_1'(\mathbf{k}, s) + i\mathbf{k}\cdot\tilde{\tilde{\mathbf{D}}}_2'(\mathbf{k}, s)\cdot i\mathbf{k} \tag{52}$$

where

$$\tilde{\tilde{\mathbf{D}}}_1'(\mathbf{k}, s) = \tilde{\tilde{\mathbf{Y}}}_1(\mathbf{k}, s)[1 - \tilde{\tilde{\Phi}}(\mathbf{k}, s)/s]^{-1} \tag{53}$$

and

$$\tilde{\tilde{\mathbf{D}}}_2'(\mathbf{k}, s) = \tilde{\tilde{\mathbf{Y}}}_2(\mathbf{k}, s)[1 - \tilde{\tilde{\Phi}}(\mathbf{k}, s)/s]^{-1} \tag{54}$$

Set $\hat{\mathbf{D}}_1'(\mathbf{k}, t)$ and $\hat{\mathbf{D}}_2'(\mathbf{k}, t)$ to the inverse Laplace transforms of $\tilde{\tilde{\mathbf{D}}}_1(\mathbf{k}, s)$ and $\tilde{\tilde{\mathbf{D}}}_2(\mathbf{k}, s)$, respectively, and insert them into (44) to obtain

$$\begin{aligned}\frac{\partial\hat{G}}{\partial t} &= i\mathbf{k}\cdot\langle \mathbf{v}(t)\rangle\, \hat{G}(\mathbf{k}, t) - i\mathbf{k}\cdot\int_0^t \hat{\mathbf{D}}_1'(\mathbf{k}, \tau)\, \Delta(\mathbf{k}, t, \tau)\, \hat{G}(\mathbf{k}, t-\tau)\, d\tau \\ &\quad - i\mathbf{k}\cdot\int_0^t \hat{\mathbf{D}}_2'(\mathbf{k}, t)\, \Delta(\mathbf{k}, t, \tau)\cdot[i\mathbf{k}\hat{G}(\mathbf{k}, t-\tau)]\, d\tau\end{aligned} \tag{55}$$

Setting $\mathbf{D}_1(\mathbf{x}, t, \tau)$ and $\mathbf{D}_2(\mathbf{x}, t, \tau)$ equal to the inverse Fourier transforms of $\hat{\mathbf{D}}'_1 \Delta$ and $\hat{\mathbf{D}}'_2 \Delta$ and applying the inverse transform to (55) gives the final form of the balance law,

$$\frac{\partial G}{\partial t} = -\nabla_{\mathbf{x}} \cdot [\langle \mathbf{v}(t) \rangle G(\mathbf{x}, t)] + \nabla_{\mathbf{x}} \cdot \int_0^t \int_{R^3} \mathbf{D}_1(\mathbf{y}, t, \tau)\, G(\mathbf{x}-\mathbf{y}, t-\tau)\, d\mathbf{y}\, d\tau$$

$$+ \nabla_{\mathbf{x}} \cdot \int_0^t \int_{R^3} \mathbf{D}_2(\mathbf{y}, t, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y}, t-\tau)\, d\mathbf{y}\, d\tau \tag{56}$$

7. LOCAL EQUILIBRIUM ASSUMPTION

When convective fluid velocities are low with respect to heterogeneity sharpness we may expect nonequilibrium displacement fluctuations to reduce to equilibrium behavior within some characteristic length of medium uniformity. This condition is

$$\int_0^{T_m} \| \langle \mathbf{v}(\tau) \rangle \| \, d\tau \ll X \tag{57}$$

where $\mathbf{v}(t)$ is the particle velocity, T_m is the relaxation time of the displacement fluctuation $\mathbf{x}'(t)$, and X is a measure of length of medium uniformity, such as a correlation length. In fractal domains, X is only defined below some fractal cutoff scale. In this case the displacement fluctuation $\mathbf{x}'(t)$ may be treated as an equilibrium process.

In this section we examine the ramification of this local equilibrium assumption (LEA). It is shown that the fundamental expression (48) reduces to a simple single quadratic form in Fourier space, and that the resulting transport equation is equivalent to that obtained through classical Mori–Zwanzig (equilibrium process projection operator) theory.

Equation (48), expressing the second derivative of the nonequilibrium fluctuation correlation function $\hat{G}(\mathbf{x}, t)$, reduces under equilibrium averaging as follows:

$$\begin{aligned}
&\langle i\mathbf{k} \cdot \mathbf{a}'(t)\, e^{i\mathbf{k}\cdot\mathbf{x}'(t)} e^{-i\mathbf{k}\cdot\mathbf{x}'(0)} + ik \cdot \mathbf{v}'(t)\, e^{i\mathbf{k}\cdot\mathbf{x}'(t)} e^{-i\mathbf{k}\cdot\mathbf{x}'(0)} \mathbf{v}'(t) \cdot i\mathbf{k} \rangle_0 \\
&= \langle i\mathbf{k} \cdot \{ iL[\mathbf{v}'(t)]\, e^{i\mathbf{k}\cdot\mathbf{x}'(t)} + \mathbf{v}'(t)\, iL[e^{i\mathbf{k}\cdot\mathbf{x}'(t)}] \}\, e^{-i\mathbf{k}\cdot\mathbf{x}'(0)} \rangle_0 \\
&= \langle iL[i\mathbf{k} \cdot \mathbf{v}'(t)\, e^{i\mathbf{k}\cdot\mathbf{x}'(t)}]\, e^{-i\mathbf{k}\cdot\mathbf{x}'(0)} \rangle_0 \\
&= -i\mathbf{k} \cdot \langle \mathbf{v}'(t)\, e^{i\mathbf{k}\cdot\mathbf{x}'(t)} iL e^{-i\mathbf{k}\cdot\mathbf{x}'(0)} \rangle_0 \\
&= i\mathbf{k} \cdot \langle \mathbf{v}'(t)\, e^{i\mathbf{k}\cdot\mathbf{x}'(t)} e^{-i\mathbf{k}\cdot\mathbf{x}'(0)} \mathbf{v}'(0) \rangle_0 \cdot i\mathbf{k} \\
&= i\mathbf{k} \cdot \mathbf{Q}(\mathbf{k}, t) \cdot i\mathbf{k}
\end{aligned} \tag{58}$$

where $\mathbf{Q}$ is the current density. This form in place of $\mathbf{Y}_1$ and $\mathbf{Y}_2$ of (51) renders the equilibrium analog to (52) as

$$\tilde{\tilde{K}}'(\mathbf{k}, s) = i\mathbf{k} \cdot \tilde{\hat{\mathbf{D}}}_e(\mathbf{k}, s) \cdot i\mathbf{k} \tag{59}$$

where now

$$\tilde{\hat{\mathbf{D}}}_e(\mathbf{k}, s) = \tilde{\hat{\mathbf{Q}}}(\mathbf{k}, s)[1 - \tilde{\hat{\Phi}}_e(\mathbf{k}, s)/\mathrm{s}]^{-1} \tag{60}$$

is the equilibrium fluctuation dispersion tensor in Fourier–Laplace space. In (60), Φ_e is the equilibrium analogy to Φ of (48):

$$\hat{\Phi}_e(\mathbf{k}, t) = -\frac{d^2}{dt^2} G_e'(\mathbf{k}, t) = -\frac{d^2}{dt^2} \langle e^{i\mathbf{k} \cdot \mathbf{x}'(t)} e^{-i\mathbf{k} \cdot \mathbf{x}'(0)} \rangle_0 \tag{61}$$

Following the course previously taken in development of the general non-equilibrium transport equation (56), we find in the LEA case that [analogous to (55)]

$$\frac{\partial \hat{G}}{\partial t} = i\mathbf{k} \cdot \langle \mathbf{v}(t) \rangle \hat{G}(\mathbf{k}, t) - i\mathbf{k} \cdot \int_0^t \hat{\mathbf{D}}_e(\mathbf{k}, \tau)\, \Delta(\mathbf{k}, t, \tau) \cdot i\mathbf{k}\hat{G}(\mathbf{k}, t - \tau)\, d\tau \tag{62}$$

and the final transport equation with equilibrium fluctuations becomes

$$\begin{aligned} \frac{\partial G}{\partial t} = &-\nabla_{\mathbf{x}} \cdot [\langle \mathbf{v}(t) \rangle G(\mathbf{k}, t)] \\ &+ \nabla_{\mathbf{x}} \cdot \int_0^t \int_{R^3} \mathbf{D}_e(\mathbf{y}, t, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x} - \mathbf{y}, t - \tau)\, d\mathbf{y}\, d\tau \end{aligned} \tag{63}$$

where $\mathbf{D}_e(\mathbf{x}, t, \tau)$ is the inverse Fourier transform of $\hat{\mathbf{D}}_e(\mathbf{k}, \tau)\, \Delta(\mathbf{k}, t, \tau)$, and $\hat{\mathbf{D}}_e(\mathbf{k}, \tau)$ is in turn the inverse Laplace transform of $\tilde{\hat{\mathbf{D}}}_e(\mathbf{k}, s)$.

It remains to show equivalence between (63) and the equilibrium fluctuation transport equation obtained via classical projection operator techniques. It is convenient to first demonstrate equivalence between the two respective fluctuation memory functions, starting from the wavevector-dependent generalization of the projection operator form in (13)[14]

$$\hat{K}'(\mathbf{k}, s) = \langle \dot{\alpha}^*(\mathbf{k}, 0) \exp(itQ_\alpha L)\, \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \tag{64a}$$

and working toward the equilibrium form of the memory function developed here in (47),

$$\tilde{\hat{K}}'(\mathbf{k}, s) = [1 - s^{-1}\tilde{\hat{\Phi}}(\mathbf{k}, s)]^{-1}\, \tilde{\hat{\Phi}}(\mathbf{k}, s) \tag{64b}$$

The term $\alpha(\mathbf{k}, t)$ is the Fourier transform of an equilibrium phase variable {as in (13), in our case $\alpha(\mathbf{k}, t) = \exp[i\mathbf{k} \cdot \mathbf{x}'(t)]$}, and Q_α is defined in (14). Note the important difference between this specification and that of (21)—here $\mathbf{x}'(t)$ is the particle displacement fluctuation resulting from both diffusive and hydrodynamic dispersive forces, whereas (21) represents complete particle displacement resulting solely from diffusion.

The Laplace transform of (64a),

$$\tilde{K}'(\mathbf{k}, s) = \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \tag{65}$$

admits the operator identity $A^{-1} = B^{-1} + A^{-1}[B - A] B^{-1}$, where $[s - iQ_\alpha L]$ is A and $[s - iL]$ is B, to yield

$$\begin{aligned} \tilde{K}'(\mathbf{k}, s) = {} & \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iL)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \\ & - \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} iP_\alpha L(s - iL)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \end{aligned} \tag{66}$$

The action of the projection operator in the second term is

$$P_\alpha L(s - iL)^{-1} \dot{\alpha}(\mathbf{k}, 0) = i\alpha(\mathbf{k}, 0) \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iL)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \tag{67}$$

which renders (66) as

$$\begin{aligned} \tilde{K}'(\mathbf{k}, s) = {} & \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iL)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \\ & + \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} \alpha(\mathbf{k}, 0) \rangle_0 \\ & \times \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iL)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \end{aligned} \tag{68}$$

Now we revise the first factor of the second term, $\langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} \alpha(\mathbf{k}, 0) \rangle_0$. Applying again the same operator identity as before, now with $A = [s - iQ_\alpha L]$ and $B = s$, we find that this term distributes to

$$\begin{aligned} & \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} \alpha(\mathbf{k}, 0) \rangle_0 \\ & \quad = s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)\, \alpha(\mathbf{k}, 0) \rangle_0 + \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} Q_\alpha iL\alpha(\mathbf{k}, 0) \rangle_0 \\ & \quad = s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)\, \alpha(\mathbf{k}, 0) \rangle_0 + s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} iL\alpha(\mathbf{k}, 0) \rangle_0 \\ & \qquad + s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} P_\alpha iL\alpha(\mathbf{k}, 0) \rangle_0 \\ & \quad = s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)\, \alpha(\mathbf{k}, 0) \rangle_0 + s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \\ & \qquad + s^{-1} \langle \dot{\alpha}^*(\mathbf{k}, 0)(s - iQ_\alpha L)^{-1} \alpha(\mathbf{k}, 0) \rangle_0 \langle \alpha^*(\mathbf{k}, 0)\, \dot{\alpha}(\mathbf{k}, 0) \rangle_0 \end{aligned} \tag{69}$$

where the last line is reached using $\dot{\alpha}(\mathbf{k}, 0) = iL\alpha(\mathbf{k}, 0)$ and the fact that

$$P_\alpha iL\alpha(\mathbf{k}, 0) = \alpha(\mathbf{k}, 0) \langle \alpha^*(\mathbf{k}, 0)\, \dot{\alpha}(\mathbf{k}, 0) \rangle_0$$

Now

$$\langle \alpha^*(\mathbf{k},0)\,\dot{\alpha}(\mathbf{k},0)\rangle_0 = \langle \dot{\alpha}^*(\mathbf{k},0)\,\alpha(\mathbf{k},0)\rangle_0 = 0$$

so (69) becomes simply

$$\begin{aligned}&\langle \dot{\alpha}^*(\mathbf{k},0)(s-iQ_\alpha L)^{-1}\,\alpha(\mathbf{k},0)\rangle_0\\&\quad = s^{-1}\langle \dot{\alpha}^*(\mathbf{k},0)(s-iQ_\alpha L)^{-1}\,\dot{\alpha}(\mathbf{k},0)\rangle_0 = s^{-1}\tilde{K}'(\mathbf{k},s)\end{aligned} \tag{70}$$

This allows us to rewrite expression (68) for the fluctuation memory function in the implicit form

$$\begin{aligned}\tilde{K}'(\mathbf{k},s) &= \langle \dot{\alpha}^*(\mathbf{k},0)(s-iL)^{-1}\,\dot{\alpha}(\mathbf{k},0)\rangle_0\\&\quad + s^{-1}\tilde{K}'(\mathbf{k},s)\langle \dot{\alpha}^*(\mathbf{k},0)(s-iL)^{-1}\,\dot{\alpha}(\mathbf{k},0)\rangle_0\end{aligned} \tag{71}$$

which upon rearrangement becomes

$$\begin{aligned}&\tilde{K}'(\mathbf{k},s)[1-s^{-1}\langle \dot{\alpha}^*(\mathbf{k},0)(s-iL)^{-1}\,\dot{\alpha}(\mathbf{k},0)\rangle_0]\\&\quad = \langle \dot{\alpha}^*(\mathbf{k},0)(s-iL)^{-1}\,\dot{\alpha}(\mathbf{k},0)\rangle_0\end{aligned} \tag{72}$$

Noting that

$$\langle \dot{\alpha}^*(\mathbf{k},0)(s-iL)^{-1}\,\dot{\alpha}(\mathbf{k},0)\rangle_0 = \tilde{\Phi}_e(\mathbf{k},s) \tag{73}$$

where Φ_e is defined in (61), we have from (72) the form of the desired result, (64b),

$$\tilde{K}'(\mathbf{k},s) = [1-s^{-1}\tilde{\Phi}(\mathbf{k},s)]^{-1}\,\tilde{\Phi}(\mathbf{k},s) \tag{74}$$

Equivalence between the memory functions in Eqs. (64a) and (64b) means that the transport equation arising from specification of the memory function in (44) is the same regardless of the memory function form used (under the LEA). Therefore, the LEA-based transport equation (63) derived here is equivalent to the analogous form previously derived through the projection operator technique.[14]

8. RESUME OF CONSTITUTIVE THEORY

In this section we summarize the hierarchy of constitutive theories for diffusion and dispersion of a conservative tracer in a nondeforming porous medium. This listing encapsulates the results of this and previous efforts into a catalogue highlighting the general effects of heterogeneities of various spectra related to the scales of measurement.[1] Such effects translate (to concordant degrees) into wavevector and frequency dependences of the flux coefficients. While the general notions of wavevector- and frequency-dependent diffusive transport are established,[11,12] the deployment of these concepts in hydrogeology especially is recent[16] and so we begin here.

8.1. Diffusive Flux

For *preasymptotic diffusion*,[16]

$$\mathbf{q} = -\int_0^t \int_{R^3} \mathbf{D}(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y}, t-\tau)\, d\mathbf{y}\, d\tau \tag{75}$$

For *asymptotic diffusion*,[10]

$$\mathbf{q} = -\mathbf{D} \cdot \nabla_{\mathbf{x}} G(\mathbf{x}, t) \tag{76}$$

Preasymptotic diffusion as depicted in Eq. (75) portrays diffusive spreading on a measurement scale within a continuous spectrum of heterogeneities, that is, spreading as observed in a medium with continuously evolving heterogeneities, such as a fractal medium. In many natural cases, the measurement scale may grow beyond the upper end of the heterogeneity spectrum (e.g., above the upper fractal cutoff), in which case the model collapses to its Fickian precursor equation (76). The Fickian model is also applicable to homogenized systems and is a local, Markovian result.

8.2. Dispersive Flux

Analogous descriptors for dispersive fluxes arise in the presence of convection within the heterogeneous medium. These forms discriminate further under conditions of the LEA and/or temporal stationarity.

For *preasymptotic dispersion*, the general nonequilibrium case,

$$\mathbf{q} = \langle \mathbf{v}(t) \rangle G(\mathbf{x}, t) - \int_0^t \int_{R^3} \mathbf{D}_1(\mathbf{y}, t, \tau)\, G(\mathbf{x}-\mathbf{y}, t-\tau)\, d\mathbf{y}\, d\tau$$
$$- \int_0^t \int_{R^3} \mathbf{D}_2(\mathbf{y}, t, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y}, t-\tau)\, d\mathbf{y}\, d\tau \tag{77}$$

For *preasymptotic LEA dispersion*,[14] with particle fluctuation $\mathbf{x}'(t)$ under equilibrium conditions,[15]

$$\mathbf{q} = \langle \mathbf{v}(t) \rangle G(\mathbf{x}, t) - \int_0^t \int_{R^3} \mathbf{D}(\mathbf{y}, t, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y}, t-\tau)\, d\mathbf{y}\, d\tau \tag{78}$$

For *stationary preasymptotic LEA dispersion*,[17]

$$\mathbf{q} = \langle \mathbf{v}(t) \rangle \, G(\mathbf{x}, t) - \int_0^t \int_{R^3} \mathbf{D}(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y}, t-\tau) \, d\mathbf{y} \, d\tau \tag{79}$$

For *quasi-Fickian dispersion*,[18,19]

$$\mathbf{q} = \langle \mathbf{v}(t) \rangle \, G(\mathbf{x}, t) - \mathbf{D}(\mathbf{x}, t) \cdot \nabla_{\mathbf{x}} G(\mathbf{x}, t) \tag{80}$$

For *Fickian dispersion*,[20]

$$\mathbf{q} = \langle \mathbf{v}(t) \rangle \, G(\mathbf{x}, t) - \mathbf{D} \cdot \nabla_{\mathbf{x}} G(\mathbf{x}, t) \tag{81}$$

The general nonequilibrium result for dispersion [analogous to (75)] is (77); this form is linear, nonlocal, and non-Markovian and applies to systems exhibiting continuously evolving scales of heterogeneity. This form is distinguished from previous equilibrium expositions of nonlocal dependences of hydrodynamic dispersion[14] through the additional term involving the particle location probability (as opposed to its gradient alone). This result has been found recently also from continuum arguments.[6] When the convective velocity is small relative to the scales of heterogeneity, the assumption of local equilibrium of the particle displacement from the average is befitting, and (78) applies. Further, when time stationarity is invoked also [requiring the differential displacement (45) to be time-invariant], (79) is obtained. If the support of the dispersion tensor is highly localized in space and time, and if the assumptions leading to (79) hold, the model reduces to the quasi-Fickian form (80). Finally, if the transport is renormalized, i.e., if an asymptotic limit exists, then the classical Fickian model is obtained.

9. EXAMPLES: SMALL-WAVE-VECTOR REPRESENTATION OF THE DISPERSION TENSORS

In this section we look at explicit representations of $\mathbf{D}_1$ and $\mathbf{D}_2$ under certain simplifying assumptions and specifications of the nonequilibrium average velocity. All simplifications derive from directing our focus on the small-$|\mathbf{k}|$ limit. We present first the simple velocity field $\langle \mathbf{v}(t) \rangle = \mathbf{v}$, a constant, with $\hat{K}$ time stationary, i.e.,

$$\begin{aligned} \hat{K}(\mathbf{k}, t, \tau) &= k'(\mathbf{k}, \tau) \, \Delta(\mathbf{k}, t, \tau) \\ &\approx k'(\mathbf{k}, \tau) \, \Delta(\mathbf{k}, \tau) \end{aligned} \tag{82}$$

Under these conditions, from (44) we find

$$\tilde{\tilde{G}}(\mathbf{k}, s) = [s - i\mathbf{k}\cdot\mathbf{v} + \tilde{\tilde{K}}]^{-1} \tag{83}$$

A Taylor series expansion in **k** of

$$\hat{G} = \langle e^{i\mathbf{k}\cdot[\mathbf{x}(t) - \mathbf{x}(0)]]} \rangle \tag{84}$$

to order k^2 gives

$$\hat{G}(\mathbf{k}, t) \approx 1 + i\mathbf{k}\cdot\mathbf{v}t + \tfrac{1}{2}i\mathbf{k}\cdot\xi\cdot i\mathbf{k} \tag{85}$$

where

$$\xi = \langle [\mathbf{x}(t) - \mathbf{x}(0)][\mathbf{x}(t) - \mathbf{x}(0)] \rangle \tag{86}$$

is the mean square displacement of the sample particle. The Laplace transform of (84) is

$$\tilde{\tilde{G}}(\mathbf{k}, s) \approx s^{-1} + i\mathbf{k}\cdot\mathbf{v}s^{-2} - \tfrac{1}{2}\mathbf{k}\cdot\tilde{\xi}\cdot\mathbf{k} \tag{87}$$

From (87) and (83) to order k^2 we have

$$\begin{aligned}\tilde{\tilde{K}} &\approx \frac{1 - [s - i\mathbf{k}\cdot\mathbf{v}][s^{-1} + i\mathbf{k}\cdot\mathbf{v}s^{-2} - \frac{1}{2}\mathbf{k}\cdot\tilde{\xi}\cdot\mathbf{k}]}{s^{-1} + i\mathbf{k}\cdot\mathbf{v}s^{-2} - \frac{1}{2}\mathbf{k}\cdot\tilde{\xi}\cdot\mathbf{k}} \\ &\approx -\mathbf{k}\cdot[\mathbf{v}\mathbf{v}s^{-1} - \tfrac{1}{2}\tilde{\xi}s^2]\cdot\mathbf{k}\end{aligned} \tag{88}$$

But

$$\tilde{\tilde{K}} = i\mathbf{k}\cdot\tilde{\tilde{\mathbf{D}}}_1 - \mathbf{k}\cdot\tilde{\tilde{\mathbf{D}}}_2\cdot\mathbf{k} \tag{89}$$

implies

$$\tilde{\tilde{\mathbf{D}}}_1 = 0 \tag{90}$$

and

$$\tilde{\tilde{\mathbf{D}}}_2 = \mathbf{v}\mathbf{v}s^{-1} - \tfrac{1}{2}\tilde{\xi}s^2 \tag{91}$$

In the asymptotic results of (90) and (91) all terms are measurable experimentally. Should the mean square displacement ξ scale as a power law in principal directions (e.g., as in fractional Brownian motion), then

$$\xi(t) = \begin{pmatrix} a_x t^{d_x} & 0 & 0 \\ 0 & a_y t^{d_y} & 0 \\ 0 & 0 & a_z t^{d_z} \end{pmatrix} \tag{92}$$

and

$$\tilde{\xi}(s) = \begin{pmatrix} a_x \Gamma[d_x+1]\, s^{-d_x-1} & 0 & 0 \\ 0 & a_y \Gamma[d_y+1]\, s^{-d_y-1} & 0 \\ 0 & 0 & a_z \Gamma(d_z+1)\, s^{-d_z-1} \end{pmatrix} \tag{93}$$

In this special case we have

$$\tilde{\mathbf{D}}_2 = s^{-1} \begin{pmatrix} a_x \Gamma(d_x+1)\, s^{-d_x} + V_x^2 & V_x V_y & V_x V_z \\ V_x V_y & a_y \Gamma(d_y+1)\, s^{-d_y} + V_y^2 & V_y V_z \\ V_x V_z & V_x V_y & a_z \Gamma(d_z+1)\, s^{-d_z} + V_z^2 \end{pmatrix} \tag{94}$$

The constant-velocity case illustrates the phenomenological nature of the model, in that the small-$|\mathbf{k}|$ behavior of the system is captured in the mean square displacement. This is the case for small-$|\mathbf{k}|$ approximations under different assumed ensemble velocity fields in general. For instance, under conditions of uniform spatiotemporal recharge to unidirectional flow in a conceptual one-dimensional aquifer, the corresponding large-scale convective velocity (Eulerian) is linear in the space coordinate.[21] If one endorses this depiction and the resulting exponential Lagrangian velocity $\langle v(t) \rangle = \exp(at)$ as the nonequilibrium ensemble average velocity of the system, then an $O(\mathbf{k}^2)$ analysis yields, similarly to the foregoing,

$$D_1 = 0 \tag{95}$$

$$D_2 = \tfrac{1}{2}[1 - s^2 \xi(s)] \tag{96}$$

where again the D_1 term is zero and the model is controlled through the mean square displacement function.

A tangential yet important implication appears through such examinations of (77). The small-$|\mathbf{k}|$ expansion of the exponential in the differential displacement term of (45) illustrates, for instance, that this term will become stationary only under time linearity of the displacement, or rather, constant ensemble velocity. The ramification is that time stationarity as required for the utility of the simplified models (79) (stationary pre-asymptotic LEA dispersion), (80) (quasi-Fickian dispersion), and (81) (Fickian dispersion) is not available without the assumption of constant ensemble average velocity.

10. DISCUSSION

The evolution of a tracer in a velocity field exhibiting excitements on a continuum of scales leads to a spatially and temporally nonlocal generalization of Fick's first law. The law has been derived herein via a nonequilibrium generalized hydrodynamics based upon a newly derived generalized Liouville equation. The most general result was derived in the classical limit without approximation. This result is consistent with that of Neuman,[6] which was derived from a continuum perspective. Under appropriate limiting conditions, the theory was shown consistent with earlier work by the authors. A hierarchy of constitutive theories based on the complexity of the heterogeneities (excitations) was summarized and various limiting conditions for the dispersion coefficients were analyzed. In the case of constant expected velocity with stationary fluctuations and with power law scaling of the mean square displacement, a very simple expression for the dispersion tensor in the small-$|\mathbf{k}|$ limit was derived in terms of measurable quantities.

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