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Energy Dissipation in Porous Media for Equilibrium and Nonequilibrium Translational Motions

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Abstract

In the modelling of translational motion, the concepts of frequency-dependent (of the angular fluctuations of the velocity field) self-diffusion and the dispersion tensor are commonly used in its characterisation. Both of these parameters are related to velocity autocorrelation. An alternative means of modelling translational motion is via the equilibrium and nonequilibrium fluctuation-dissipation theorem in classical statistical mechanics. This alternative approach provides further insight into the molecular level processes occurring in the system. Here both of these theoretical fluctuation-dissipation approaches are employed to determine expressions for energy dissipation in simple equilibrium systems exhibiting asymptotic and preasymptotic diffusion and dispersion phenomena and also in a nonequilibrium preasymptotic system involving dispersion within and beyond the upper limit of heterogeneity of an isotropic porous medium. As an example the permeability of porous media due to diffusion and dispersion are studied and it is shown how a frequency-dependent permeability can be treated as a phasor.

Keywords

Energy dissipation, Diffusion, Dispersion, Permeability, Porous medium

1. Introduction

Diffusive phenomena, such as Brownian motion, involve the random movement of particles and are in essence many-body problems. At sufficiently long time scales the diffusive mechanism reduces to a one-body stochastic problem which can be formulated with diffusion theory. Diffusion theory characterises a pure liquid by a self-diffusion coefficient, D [1]. Many systems of interest are typically more complicated and involve other forms of translational motion. For example, a commonly encountered case is where molecules flowing through porous media are initially adjacent but become separated due to the combined effects of diffusion and flow, this process is termed dispersion. The dispersive process can be described by asymptotic dispersion tensors which express the correlations between the fluctuations in the velocity field of the fluid elements. Importantly, it is now possible to directly probe such phenomena using magnetic resonance based techniques [2-4].

One way of describing the fluctuations of a system is by formulating the dissipation of kinetic energy into that system. The dissipation function or energy absorption quantifies the fluctuation of the velocity field; for example, the Stokes-Einstein equation, which relates the diffusion coefficient of particles to the viscosity, is a consequence of the fluctuation dissipation theorem for Brownian motion and therefore describes the fluctuation of the velocity field in terms of the dissipation of kinetic energy (that is manifested as thermal energy) [5]. As it will be shown later, the energy dissipation functions for diffusion and dispersion in isotropic porous media are related to the corresponding diffusion and dispersion tensors, respectively, which characterise these translational phenomena. Here the dissipation of energy into continuous media of different uniformity scales using a general correlation function is studied. In particular, the energy dissipation behaviour of diffusive and dispersive phenomena in homogeneous and heterogeneous porous media using equilibrium and nonequilibrium approaches is investigated.

The energy dissipation function is related to the diffusion and dispersion tensors in the diffusing and dispersing phenomena respectively, and it has many applications in translational motions. The diffusion and dispersion tensors can be determined by using NMR spectroscopy (e.g., ref. [2]), thus according to this work the energy dissipation can be determined as a result of this methodology.

Fluid flow behaviour via a pressure gradient applied across a porous material can be characterised by a parameter called the permeability k. Knowledge of the permeability allows the quantification, via Darcy's law, of flow velocities through the material for fluids of varying viscosity (see Figure 1).

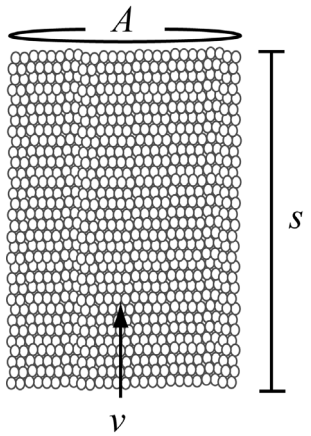

Figure 1: A fluid with velocity v flowing through a porous material (represented as spheres) with cross sectional area A and thickness s. Note that the flux q is related to A and v by $q = Av$.

The equation of motion of a homogenous fluid was first formulated experimentally by Henry Darcy and it was originally limited to one-dimensional flow. In three-dimensions Darcy's law for a flux vector **q** is given by [6]

$$\mathbf{q} = -K\nabla Q, \tag{1}$$

where Q is the energy loss or dissipation due to friction in the flow through the porous medium and $K = k\rho g/\mu_l$ is a coefficient called hydraulic conductivity, where μ_l is the viscosity and ρ is the fluid density. In this equation k is the permeability of the porous matrix. The permeability of a medium is a macroscopic property that measures the ability of the porous medium to transmit fluid through it [6].

These physical properties of porous media are very important in fluid dynamics as well as in understanding chemical and biological processes. For example permeabilities determine the intra- and extracellular lifetimes of species transporting across cell membranes (e.g., ref. [7]). Also blood flow in a placenta is a good example of dispersion in a biological porous medium and is related to circulation and oxygen delivery [8-13].

In Section 2 some pertinent concepts relating flux, diffusion and dispersion are briefly reviewed. The determination of the dissipation functions for free, asymptotic, and preasymptotic diffusion problems for equilibrium processes in porous media are presented in Section 3. Dispersion phenomena and the associated energy dissipation functions in homogeneous and heterogeneous media are studied in Section 4; Fickian dispersion of fluid elements in a homogenous porous medium, and preasymptotic dispersion in heterogeneous porous media as a nonequilibrium case are also considered. How the structure and geometry of a porous body can be related to the diffusion and dispersion tensors and consequently to energy absorption is considered in Section 5. Finally in Section 6 the permeability of the porous medium is obtained in terms of the diffusion and dispersion tensors. Also, it will be shown that frequency-dependent permeability, like in other physical cases (e.g. electromagnetism), can be a complex function with a phase delay.

2. Background

Porous media are classified as heterogeneous or homogenous according to their spectrum of uniformity. In heterogeneous media, which includes fractal media, the heterogeneities are within the measurement length scale whereas for homogeneous media the measurement length scale is beyond the spectrum of heterogeneity. Thus whether a system is classified as heterogeneous or homogeneous for a particular experiment is relative to the length scale to be probed. Dispersion in these systems has different characteristics. Cushman et al. [14] summarised the asymptotic and preasymptotic diffusion and dispersion theories in homogeneous and heterogeneous systems. The asymptotic diffusive and dispersive process refers to the Fickian and preasymptotic refers to the time and space-time convolution Fickian processes [15].

Diffusion and dispersion in a homogeneous medium is considered to be an equilibrium phenomenon, whereas turbulent flow in a heterogeneous medium is considered to be nonequilibrium. This is because the structure or local heterogeneity influences flow and transport. Nonideal or nonequilibrium transport can result from flow in a heterogeneous domain at the macroscopic scale (10^{-3} to 10^{-1} m) [16]. As will be discussed later, the equilibrium and nonequilibrium situations are characterised according to the probability of the corresponding dynamical variable in phase space (i.e., the position and momentum space), where a time-independent probability describes an equilibrium situation and a time-dependent probability describes a nonequilibrium physical process [14].

In the presence of convection within a heterogeneous medium (i.e., the general nonequilibrium case), the dispersive flux is given by [14]

$$\mathbf{q} = \left\langle \mathbf{v}(t) \right\rangle G(\mathbf{x},t) - \int_0^t \int_{R^3} \mathbf{D}_1(\mathbf{y},t,\tau) G(\mathbf{x}-\mathbf{y},t-\tau)\, d\mathbf{y}\, d\tau \\ - \int_0^t \int_{R^3} \mathbf{D}_2(\mathbf{y},t,\tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y},t-\tau)\, d\mathbf{y}\, d\tau, \tag{2}$$

where ($\mathbf{x}$, t) and ($\mathbf{y}$, t) are space-time points, G is the self-part of the intermediate scattering function for a dynamical variable $\alpha_k(t)$ that may be set as

$$\alpha_k(t) = \exp\left[i\mathbf{k} \cdot \mathbf{x}(t) \right]. \tag{3}$$

$G(\mathbf{x}, t)$ is the Green's function of a trace particle and for given space-time point ($\mathbf{x}$, t) is given by

$$G(\mathbf{x},t) = \left\langle \delta\left[\mathbf{x} - \left(\mathbf{x}_j(t) - \mathbf{x}_j(0) \right) \right] \right\rangle, \tag{4}$$

where in this case the average is nonequilibrium. The nonequilibrium correlation function $\hat{G}(\mathbf{k}, t)$ is the corresponding wavevector Fourier transforms of the Green's function G. For the rest of the paper for simplicity we will recognize different Fourier transforms by their corresponding variables without the customary hat, for example $G(\mathbf{k}, t)$ is the Fourier transform of $G(\mathbf{x}, t)$ and $G(\mathbf{k}, \omega)$ is the frequency Fourier transform of the correlation function. In Eq.(2) $\mathbf{D}_1(\mathbf{y},t,\tau)$ and $\mathbf{D}_2(\mathbf{y},t,\tau)$ are the inverse Fourier transforms of the generalised wavevector- and frequency-dependent (i.e., angular frequency of fluctuations of the velocity field) dispersion tensors, respectively, and $\nabla_{\mathbf{x}-\mathbf{y}}$ is the gradient operator.

The dispersive flux with equilibrium fluctuations takes the simpler form [14]

$$\mathbf{q} = \left\langle \mathbf{v}(t) \right\rangle G(\mathbf{x},t) - \int_0^t \int_{R^3} \mathbf{D}(\mathbf{y},t,\tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y},t-\tau)\, d\mathbf{y}\, d\tau, \tag{5}$$

where the Green's function G differs from that in Eq. (4) by equilibrium averaging (i.e. $\langle ... \rangle_0$). $\mathbf{D}(\mathbf{y},t,\tau)$ is again a spatiotemporal dispersion tensor. Note that the dispersion tensor is a space and time dependent quantity and the flux is obtained by integration over space and time of this function multiplied by the gradient of the correlation function. The above is actually a preasymptotic dispersion problem under the local equilibrium assumption (LEA), which in the case of a renormalised transport (i.e., when an asymptotic limit exists) reduces to the classical Fickian dispersion given by [14]

$$\mathbf{q} = \left\langle \mathbf{v}(t) \right\rangle G(\mathbf{x},t) - \mathbf{D} \cdot \nabla_{\mathbf{x}} G(\mathbf{x},t), \tag{6}$$

which is applicable to homogeneous systems.

Analogous to dispersion in the heterogeneous medium (i.e., a nonequilibrium phenomenon), the diffusive flux for preasymptotic diffusion in the heterogeneous medium for an equilibrium correlation function G, was determined as [14]

$$\mathbf{q} = -\int_0^t \int_{R^3} \mathbf{D}(\mathbf{y},\tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x}-\mathbf{y},t-\tau)\, d\mathbf{y}\, d\tau, \tag{7}$$

where $\mathbf{D}(\mathbf{y},\tau)$ is a spatiotemporal diffusion tensor. Eq. (7) reduces to the Fickian asymptotic diffusion problem in the case of a homogeneous system, where the length scale is beyond the heterogeneity spectrum, that is [14]

$$\mathbf{q} = -\mathbf{D}\cdot\nabla_{\mathbf{x}} G(\mathbf{x},t). \tag{8}$$

The fluctuation-dissipation theorem, which is derived from linear response theory [17] provides a powerful formalism for relating the absorption (dissipation) of energy in a physical system and the fluctuation of the physical quantities in that system. In this approach the response of a system to an external force (i.e., a perturbation) is defined by a specific complex valued function termed a generalised susceptibility, $\chi(\omega)$. The imaginary part of this function describes the absorption or dissipation of energy into the system by an external perturbation [18, 19]. However, in the case of dispersion in a heterogeneous porous medium, where the heterogeneity cannot be ignored in the measurement scale, we encounter a nonequilibrium situation and the usual fluctuation-dissipation theorem no longer applies and a more comprehensive version of this theory (nonequilibrium fluctuation-dissipation theorem) is required. This is considered in the following section.

3. Dissipation in diffusive processes: equilibrium cases

In fluid mechanics two approaches are commonly used to describe flow. One can either concentrate on the velocity fluctuations of the fixed fluid elements (i.e., the Lagrangian perspective) or alternatively on the spatially-fixed velocity of the fluid in which the local fluid velocity is studied at each position (i.e., the Eulerian perspective). Thus, in the Lagrangian description the average parameters are based on the sum over the entire statistical ensemble of the particles, whereas in the Eulerian perspective the parameters are defined as an average over the spatial array [20]. Here we concentrate on the Lagrangian description which is most commonly used in the literature as it is a convenient basis for defining the dispersion tensor [6, 20]. The total velocity of the flow in either the Lagrangian or Eulerian perspective can be expressed as the superposition of a mean velocity, **V**, with a fluctuation in the velocity field, **u**(t),

$$\mathbf{v}(t) = \mathbf{V} + \mathbf{u}(t). \tag{9}$$

From classical equilibrium and also nonequilibrium statistical mechanics, the expected value of any dynamical variable $\alpha(t)$ in the case of an equilibrium system is given by [14]

$$\langle \alpha(t) \rangle_0 = \int_\Omega \alpha(t) P_0(\mathbf{x},\mathbf{p})\, d\mathbf{x}\, d\mathbf{p}, \tag{10}$$

where **x** and **p** are the components of the position coordinate and momentum in the phase space respectively and $P_0(\mathbf{x},\mathbf{p})$ is the probability per unit hypervolume Ω of the phase space. The nonequilibrium equivalent expectation value for this dynamical variable is

$$\langle \alpha(t) \rangle = \int_\Omega \alpha(t) P(\mathbf{x},\mathbf{p};t)\, d\mathbf{x}\, d\mathbf{p}. \tag{11}$$

The probability function is also a function of time. It is known that the expectation value of the quantity in equilibrium is constant in time therefore in the case of a velocity field the above statement will give

$$\frac{d}{dt}\langle \mathbf{v}(t) \rangle_0 = 0. \tag{12}$$

Hence the expectation value of velocity **v**(t) will be time-independent and from Eq. (9), since the expectation value of the fluctuation part is zero, the mean velocity **V** must be time-independent. In a nonequilibrium situation the expectation values vary in the course of time. For instance in a

non-Markovian process of dispersion in a heterogeneous medium the velocity field is time-dependent, that is

$$\frac{d}{dt}\langle \mathbf{v}(t)\rangle = \langle \dot{\mathbf{v}}(t)\rangle. \tag{13}$$

3.1. Free-diffusion

The autocorrelation function of velocity can be written in terms of the spectrum of the diffusion tensor, given by [3, 20-22]

$$\langle \mathbf{v}(t)\mathbf{v}(0)\rangle_{\mathbf{k}} = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathbf{D}(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega, \tag{14}$$

where $\mathbf{D}(\mathbf{k}, \omega)$ is the wavevector and frequency-dependent diffusion tensor and represents the spectrum of autocorrelation between the velocity components. Equation (14) is an extension to the Fourier transform of the velocity field of the Green-Kubo relations for the transport coefficient, A, described by [23, 24]

$$A = \int_0^{\infty} \langle \mathbf{J}_A(0)\cdot \mathbf{J}_A(t)\rangle\, dt\,, \tag{15}$$

where $\mathbf{J}_A(t)$ is the flux associated with A at time t. Further, in linear-response theory according to the definition of the spectral function of a fluctuating dynamical variable such as $\mathbf{v}(t)$ we have [19]

$$\langle \mathbf{v}(t)\mathbf{v}(0)\rangle_{\mathbf{k}} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathbf{S}(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega, \tag{16}$$

where $\mathbf{S}(\mathbf{k}, \omega)$ is the spectral function. By comparing Eqs. (14) and (16) we get

$$\mathbf{S}(\mathbf{k},\omega) = 2\mathbf{D}(\mathbf{k},\omega). \tag{17}$$

Therefore in the diffusion problem the diffusion tensor is identified as the spectral function for the fluctuation of the velocity field. The fluctuation-dissipation theorem for equilibrium processes reads [25, 26]

$$\boldsymbol{\chi}''(\mathbf{k},\omega) = \frac{\omega}{2K_B T}\mathbf{S}(\mathbf{k},\omega), \tag{18}$$

where K_B is the Boltzmann constant and T is the temperature. Therefore the energy dissipation function in a system due to self-diffusion is

$$\boldsymbol{\chi}''(\mathbf{k},\omega) = \frac{\omega}{K_B T}\mathbf{D}(\mathbf{k},\omega). \tag{19}$$

In a simple self-diffusion system the diffusion tensor is just a scalar multiplied by the identity matrix and thus Eq. (19) simplifies to

$$D(\omega)=\frac{\chi''(\omega)}{\omega}K_BT, \tag{20}$$

where $D(\omega)$ is the frequency-dependent diffusion coefficient. This is in accordance with the Einstein-Smoluchowski relation given by $D(\omega)=\mu_P(\omega)K_BT$, where μ_P is the mobility of a diffusing particle due to the dissipative random force [2, 5, 27] and is given by $\mu_P = 1/\zeta$, where ζ is the friction coefficient.

In free diffusion phenomena, by comparing Eq. (20) with the Einstein-Smoluchowski relation, we get $\chi''(\omega)=\omega\mu_P(\omega)$, where χ'' is the excess heat dissipation function into the system. In an equilibrium system the dissipation is associated with a transition between different equilibrium states (i.e. fluctuation of the velocity field) and in this case the total heat reduces to the excess heat as the housekeeping heat that is the dissipated heat necessary to maintain the violation in nonequilibrium steady states vanishes [28].

3.2. Asymptotic diffusion

From now on the correlation functions used in this work are the correlation functions defined in Section 2. Backgroundfor different equilibrium and non-equilibrium cases.

The asymptotic diffusion tensor applicable to a homogenous porous medium is given by a Fickian diffusive flux equation (i.e., Eq. (8)). This is a local Markovian result and its Fourier transform wavevector-dependent equation for the correlation function is used in the following diffusion equation

$$\frac{\partial G(\mathbf{k},t)}{\partial t}=i\mathbf{k}\cdot\left[\mathbf{D}\cdot i\mathbf{k}\,G(\mathbf{k},t)\right], \tag{21}$$

where **D** is the diffusion tensor given by [3, 20]

$$\mathbf{D}=\lim_{\tau\to\infty}\mathrm{sym}\int_0^\tau\left\langle\mathbf{u}(t)\mathbf{u}(0)\right\rangle dt, \tag{22}$$

where $\mathrm{sym}\,(\mathbf{A})=\frac{1}{2}\left(\mathbf{A}+\mathbf{A}^T\right)$. Note that here the correlation function is an equilibrium case. The spectral resolution $S(\mathbf{k}, \omega)$ of a general correlation function $G(\mathbf{k}, t)$ is defined as

$$G(\mathbf{k},t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathbf{S}(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega. \tag{23}$$

Again from the classical equilibrium fluctuation-dissipation theorem equation (18) applies and therefore a correlation function $G(\mathbf{k}, t)$ is related to the dissipation function $\chi''(\mathbf{k},\omega)$ by

$$G(\mathbf{k},t)=\frac{K_BT}{\pi}\int_{-\infty}^{\infty}\chi''(\mathbf{k},\omega)\exp(-i\omega t)\frac{d\omega}{\omega}. \tag{24}$$

Differentiating both sides of the above equation and applying Leibniz integral rule [29] gives

$$\frac{\partial G(\mathbf{k},t)}{\partial t}=\frac{-K_BT}{\pi}\int_{-\infty}^{\infty}i\,\chi''(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega. \tag{25}$$

The right-hand side is actually the Fourier transform of the imaginary part of the susceptibility and therefore it can be written as

$$\frac{\partial G(\mathbf{k},t)}{\partial t} = -i2K_B T\, \chi''(\mathbf{k},t), \tag{26}$$

since the Fourier transform of a constant function is the delta function

$$\hat{F}_t\left[f(t) = 1 \right](\omega) = \delta(\omega). \tag{27}$$

By substituting Eq. (26) into Eq. (21) and performing a Fourier transform (and making use of the convolution theorem for the product of two functions) with respect to frequency we obtain

$$-i2K_B T \int_{-\infty}^{\infty} \delta(\omega' - \omega)\, \chi''(\mathbf{k},\omega)\, d\omega = i\mathbf{k} \cdot \left[\mathbf{D} \cdot i\mathbf{k}\right] \int_{-\infty}^{\infty} \delta(\omega' - \omega) G(\mathbf{k},\omega)\, d\omega, \tag{28}$$

which for a dummy frequency parameter ω can be written as

$$\chi''(\mathbf{k},\omega) = \frac{1}{2iK_B T} \mathbf{k} \cdot \left[\mathbf{D} \cdot \mathbf{k}\right] G(\mathbf{k},\omega). \tag{29}$$

But $G(\mathbf{k}, \omega)$ in the above equation is the spectral resolution of the time autocorrelation $G(\mathbf{k}, t)$ (i.e. $S(\mathbf{k}, \omega)$). If compared to the ordinary fluctuation-dissipation theorem given by Eq. (18) it can be seen in this case that the dissipation function is related to the spectral resolution by a different wavevector-dependent function which is given in terms of a diffusion tensor independent of frequency. Eq. (29) is the dissipation function of a Markovian process for Fickian asymptotic diffusion in a homogeneous porous medium.

3.3. Preasymptotic diffusion

Diffusion processes in a continuous medium with evolving heterogeneity such as structures with fractal character have a different form compared to asymptotic diffusion in a homogenous system as we encounter a non-Markovian process. The spatiotemporal-dependent flux associated with the equilibrium correlation function G is given by Eq. (7) and the wavevector-dependent Fourier transform of this correlation function is

$$\frac{\partial G(\mathbf{k},t)}{\partial t} = i\mathbf{k} \cdot \int_0^t \mathbf{D}(\mathbf{k},\tau) \cdot i\mathbf{k}\, G(\mathbf{k}, t-\tau)\, d\tau. \tag{30}$$

Since this is again an equilibrium process by applying the equilibrium classical fluctuation-dissipation theorem we again reach Eq. (26) and by combining this with Eq. (30) we obtain

$$\chi''(\mathbf{k},t) = \frac{-1}{2K_B T} \mathbf{k} \cdot \int_0^t \mathbf{D}(\mathbf{k},\tau) \cdot i\mathbf{k}\, G(\mathbf{k}, t-\tau)\, d\tau. \tag{31}$$

In this case the non-Markovian property of the diffusion in a length scale with heterogeneities contributes a time integral that provides a history of the process. The frequency-dependent Fourier transforms of the above results gives the dissipation function. For this purpose we introduce a Boxcar function (i.e. $H(\tau)$-$H(t$-$\tau)$, where $H(\tau)$ is the Heaviside step function) to the right-hand side of the above equation obtaining

$$\chi''(\mathbf{k},\omega)=\frac{-1}{2K_BT}\mathbf{k}\cdot\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty}\left(H(\tau)-H(\tau-t)\right)\mathbf{D}(\mathbf{k},\tau)\cdot i\mathbf{k}G(\mathbf{k},t-\tau)\,d\tau\right]e^{-i\omega t}dt, \tag{32}$$

which becomes

$$\chi''(\mathbf{k},\omega)=\frac{-1}{2K_BT}\mathbf{k}\cdot\left[G(\mathbf{k},\omega)\int_{-\infty}^{\infty}H(\omega-\omega')\mathbf{D}(\mathbf{k},\omega')\cdot i\mathbf{k}\,d\omega'\right.$$
$$\left.-\mathbf{D}(\mathbf{k},\omega)\cdot i\mathbf{k}\int_{-\infty}^{\infty}H(\omega-\omega')G(\omega')\,d\omega'\right]. \tag{33}$$

Since the Fourier transform of step function is $H(\omega)=\pi\delta(\omega)-\frac{i}{\omega}$, the dissipation function in this case, after some manipulation, is given by

$$\chi''(\mathbf{k},\omega)=\frac{1}{2K_BT}\mathbf{k}\cdot\int_{-\infty}^{\infty}\frac{\left[G(\mathbf{k},\omega)\mathbf{D}(\mathbf{k},\omega')-\mathbf{D}(\mathbf{k},\omega)G(\mathbf{k},\omega')\right]\cdot\mathbf{k}}{\omega-\omega'}\,d\omega' \tag{34}$$

In the case of the preasymptotic non-Markovian diffusion the dissipation function is again characterised by spectral density $G(\mathbf{k}, \omega)$ in terms of a more complicated combination with a diffusion tensor different than that of Eq. (18).

In this section asymptotic and preasymptotic diffusion phenomena for the equilibrium cases were studied in media with homogenous and heterogeneous spectra. The dispersion phenomena are discussed in the next section where the nonequilibrium case will be discussed for the case of a heterogeneous medium.

4. Dissipation in dispersive processes

In the previous section we derived expressions for the dissipation functions in equilibrium systems of asymptotic and preasymptotic diffusion in homogeneous and heterogeneous porous media, respectively, based on the classical fluctuation-dissipation theorem. It was shown how the dissipation functions of the diffusion equations are related to the diffusion tensor and also to the correlation functions of a corresponding physical quantity (e.g., fluctuation of velocity field) in the case of diffusion in a porous medium. Whilst the systems remain in equilibrium the usual fluctuation-dissipation theorem is sufficient to study the local Markovian and non-Markovian model of diffusion.

4.1. Fickian dispersion

In the asymptotic limit, where a local equilibrium assumption (LEA) is applied and the transport is said to be normalised, the preasymptotic dispersion reduces to a classical Fickian model given by Eq. (6) [6]. The Fickian model can be applied to a homogeneous porous medium. Again, an equilibrium approach to the problem through the classical equilibrium fluctuation-dissipation theorem is appropriate. The wavevector-dependent transport equation can be written as

$$\frac{\partial G(\mathbf{k},t)}{\partial t}=i\mathbf{k}\cdot\left[\left\langle\mathbf{v}(t)\right\rangle G(\mathbf{k},t)+\mathbf{D}\cdot i\mathbf{k}\,G(\mathbf{k},t)\right], \tag{35}$$

where **D** is now the asymptotic dispersion tensor. The left-hand side is related to the dissipation function of the dispersion equation given by Eq. (26)

$$\chi''(\mathbf{k},t)=\frac{-1}{2K_BT}\mathbf{k}\cdot\left[\left\langle\mathbf{v}(t)\right\rangle G(\mathbf{k},t)+\mathbf{D}\cdot i\mathbf{k}\,G(\mathbf{k},t)\right]. \tag{36}$$

The Fourier transform of both sides is

$$\chi''(\mathbf{k},\omega)=\frac{-1}{2K_BT}\mathbf{k}\cdot\left[\int_{-\infty}^{\infty}\left\langle\mathbf{v}(\omega'-\omega)\right\rangle G(\mathbf{k},\omega)\,d\omega+\mathbf{D}\cdot i\mathbf{k}\,G(\mathbf{k},\omega)\right]. \tag{37}$$

The above relation determines the dissipation function for a dispersive process in a homogenous porous medium. It is different to the ordinary fluctuation-dissipation theorem (i.e., Eq. (18)) as the spectral density is related to the dissipation function in a much more complicated combination with the dispersion tensor and the Fourier transform of the time dependent velocity. Note that for a system of asymptotic dispersion in a homogenous porous medium, when the velocity is time-independent the dissipation function is related to the spectral density by the complex wavevector-dependent function in terms of the dispersion tensor.

4.2. Preasymptotic dispersion: nonequilibrium case

Similar to turbulent fluid transport, the mixing mechanism based on dispersion in a heterogeneous porous medium is a nonequilibrium phenomenon [14]. It is necessary to use a general form of the classical nonequilibrium fluctuation-dissipation theorem given by [30, 31]

$$\omega\frac{\partial}{\partial E}\left\langle\alpha_i(\mathbf{k},\omega)\alpha_j(\mathbf{k},\omega)\right\rangle=\chi''(\mathbf{k},\omega), \tag{38}$$

where the α's are any fluctuating physical quantities. By definition the spectral function is the Fourier transform of the correlation function viz.

$$\left\langle\alpha_i(\mathbf{k},\omega)\alpha_j(\mathbf{k},\omega)\right\rangle=2\pi S(\mathbf{k},\omega). \tag{39}$$

Differentiating both sides of the above equation and combining with Eq. (38) gives

$$\omega\frac{\partial}{\partial E}\left\langle\alpha_i(\mathbf{k},\omega)\alpha_j(\mathbf{k},\omega)\right\rangle=2\pi\omega\frac{\partial}{\partial E}S(\mathbf{k},\omega)=\chi''(\mathbf{k},\omega). \tag{40}$$

Now from the definition of the spectral function the time-dependent autocorrelation function for a physical variable is

$$\left\langle\alpha(\mathbf{k},t)\alpha(\mathbf{k},0)\right\rangle=\int_{-\infty}^{\infty}S(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega. \tag{41}$$

The time derivative of the above equation gives

$$\frac{\partial}{\partial t}\left\langle\alpha(\mathbf{k},t)\alpha(\mathbf{k},0)\right\rangle=-i\int_{-\infty}^{\infty}\omega\,S(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega. \tag{42}$$

By differentiating both sides of the above equation with respect to the energy we reach the following expression

$$\frac{\partial}{\partial E}\left[\frac{\partial}{\partial t}\left\langle\alpha(\mathbf{k},t)\alpha(\mathbf{k},0)\right\rangle\right]=-i\int_{-\infty}^{\infty}\omega\frac{\partial}{\partial E}S(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega. \tag{43}$$

Then inserting the expression for the susceptibility (Eq. (40)) we obtain

$$\frac{\partial}{\partial E}\frac{\partial G(\mathbf{k},t)}{\partial t}=\frac{-i}{2\pi}\int_{-\infty}^{\infty}\chi''(\mathbf{k},\omega)\exp(-i\omega t)\,d\omega. \tag{44}$$

The right-hand side of the above equation is again the Fourier transform of the time-dependent susceptibility, thus

$$\frac{\partial^2 G(\mathbf{k},t)}{\partial E\,\partial t}=-i\,\chi''(\mathbf{k},t). \tag{45}$$

Therefore in a heterogeneous porous medium the dissipation function is determined by the rate of change of the time-evolution of the correlation function with energy. The wavevector-dependent time-derivative of the correlation function has been given in [14] as

$$\begin{aligned}\frac{\partial G(\mathbf{k},t)}{\partial t}=&\,i\mathbf{k}\cdot\left\langle\mathbf{v}(t)\right\rangle G(\mathbf{k},t)-i\mathbf{k}\cdot\int_0^t\mathbf{D}_1'(\mathbf{k},\tau)\Delta(\mathbf{k},t,\tau)G(\mathbf{k},t-\tau)\,d\tau\\&-i\mathbf{k}\cdot\int_0^t\mathbf{D}_2'(\mathbf{k},\tau)\Delta(\mathbf{k},t,\tau)\cdot\left[i\mathbf{k}\,G(\mathbf{k},t-\tau)\right]d\tau,\end{aligned} \tag{46}$$

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

$$\Delta(\mathbf{k},t,\tau)\approx\exp\left[i\mathbf{K}\tau\cdot\left\langle\mathbf{v}(t)\right\rangle\right], \tag{47}$$

Combining Eqs. (45) with (46) we get

$$\begin{aligned}\chi''(\mathbf{k},t)=\frac{\partial}{\partial E}\Big\{&-\mathbf{k}\cdot\left\langle\mathbf{v}(t)\right\rangle G(\mathbf{k},t)+\mathbf{k}\cdot\int_0^t\mathbf{D}_1'(\mathbf{k},\tau)\Delta(\mathbf{k},t,\tau)G(\mathbf{k},t-\tau)\,d\tau\\&+\mathbf{k}\cdot\int_0^t\mathbf{D}_2'(\mathbf{k},\tau)\Delta(\mathbf{k},t,\tau)\cdot\left[i\mathbf{k}\,G(\mathbf{k},t-\tau)\right]d\tau\Big\}.\end{aligned} \tag{48}$$

The Fourier transform of the above equation becomes

$$\begin{aligned}\chi''(\mathbf{k},\omega)=\frac{\partial}{\partial E}\Big\{&-\mathbf{k}\cdot\int_{-\infty}^{\infty}\left\langle\mathbf{v}(\omega'-\omega)\right\rangle G(\mathbf{k},\omega)\,d\omega+\mathbf{k}\cdot\int_{-\infty}^{\infty}\left(\int_0^t\mathbf{D}_1'(\mathbf{k},\tau)\Delta(t,\tau)G(\mathbf{k},t-\tau)\,d\tau\right)e^{-i\omega t}dt\\&+\mathbf{k}\cdot\int_{-\infty}^{\infty}\left(\int_0^t\mathbf{D}_2'(\mathbf{k},\tau)\Delta(\mathbf{k},t,\tau)\cdot\left[i\mathbf{k}G(\mathbf{k},t-\tau)\right]d\tau\right)e^{-i\omega t}dt\end{aligned} \tag{49}$$

Again for determining the Fourier transform we use the Boxcar function, thus it becomes

$$\chi''(\mathbf{k},\omega)=\frac{\partial}{\partial E}\{-\mathbf{k}\cdot\int_{-\infty}^{\infty}\langle\mathbf{v}(\omega'-\omega)\rangle G(\mathbf{k},\omega)d\omega$$
$$+\mathbf{k}\cdot\int_{-\infty}^{\infty}\Big[H(\tau)\mathbf{D}_1'(\mathbf{k},\tau)\int_{-\infty}^{\infty}\Delta(\mathbf{k},t,\tau)G(\mathbf{k},t-\tau)e^{-i\omega t}dt$$
$$-\mathbf{D}_1'(\mathbf{k},\tau)\int_{-\infty}^{\infty}H(\tau-t)\Delta(\mathbf{k},t,\tau)G(\mathbf{k},t-\tau)e^{-i\omega t}dt\Big]d\tau$$
$$+\mathbf{k}\cdot\int_{-\infty}^{\infty}\Big[H(\tau)\mathbf{D}_2'(\mathbf{k},\tau)\int_{-\infty}^{\infty}\Delta(\mathbf{k},t,\tau)\cdot i\mathbf{k}G(\mathbf{k},t-\tau)e^{-i\omega t}dt$$
$$-\mathbf{D}_2'(\mathbf{k},\tau)\int_{-\infty}^{\infty}H(\tau-t)\Delta(\mathbf{k},t,\tau)\cdot i\mathbf{k}G(\mathbf{k},t-\tau)e^{-i\omega t}dt\Big]d\tau \tag{50}$$

Substituting the Fourier transform of the Heaviside step function and after some manipulation, the dissipation function takes the form

$$\chi''(\mathbf{k},\omega)=-\frac{\partial}{\partial E}\mathbf{k}\cdot\Big\{\int_{-\infty}^{\infty}\langle\mathbf{v}(\omega'-\omega)\rangle G(\mathbf{k},\omega)d\omega$$
$$+\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Big[G(\mathbf{k},\omega')H(\omega'-\omega'')\Delta(\mathbf{k},\omega-\omega',\omega'')\big(\mathbf{D}_1'(\mathbf{k},\omega'''-\omega'')+\mathbf{D}_2'(\mathbf{k},\omega'''-\omega'')\cdot i\mathbf{k}\big)$$
$$-G(\mathbf{k},\omega'')H(\omega-\omega')\Delta(\mathbf{k},\omega'-\omega'',\omega''')$$
$$\times\big(\mathbf{D}_1'(\mathbf{k},\omega-\omega'+\omega''-\omega''')+\mathbf{D}_2'(\mathbf{k},\omega-\omega'+\omega''-\omega''')\cdot i\mathbf{k}\big)\Big]d\omega'''d\omega''d\omega'\Big\}. \tag{51}$$

The above equation describes the dissipation of the energy in a nonequilibrium dispersive system (e.g., dispersion in a heterogeneous porous body). In this case the dissipation is a function averaged over the derivative of the energy distribution in the system in terms of the dispersion tensors.

5. Structural effects in energy dissipation

The calculations in the previous sections for the dissipation function associated with diffusion and dispersion in both heterogeneous and homogenous porous media shows that energy absorption is related to the diffusion and dispersion tensors, respectively. We show in this section how the structure of the body affects this function.

The dispersion tensor in a general anisotropic porous medium is defined by [32, 33]

$$D_{jk}=D\left(\delta_{jk}+R\,B_{jk}^{I}\right)+A_{jik}^{I}\langle v_i\rangle+A_{jilk}^{II}\langle v_i\rangle\langle v_l\rangle+A_{jilk}^{III}\langle v_i\rangle\frac{\partial\overline{c}}{\partial x_k}. \tag{52}$$

Tensor $\boldsymbol{B}^{I}$ is a function of *t*, v_i, *D* and the geometry of the porous medium [33] and tensors $\mathbf{A}^{I}$, $\mathbf{A}^{II}$ and $\mathbf{A}^{III}$ are symmetric and functions of the structure of the porous medium and of the fluid transport properties such as viscosity [32] that were calculated by Whitaker [33] by expanding the dispersion vector ψ in a Taylor series about the point x_i. The first term on the right hand side is called the effective diffusion coefficient $\mathscr{D}_{\text{eff}}$, and it is the molecular diffusion coefficient multiplied by the factor ($\delta_{jk}+RB^{I}_{jk}$). The elements of $\mathbf{A^{I}}$, $\mathbf{A^{II}}$ and $\mathbf{A^{III}}$ are given by

$$A^{I}_{jik} = \left.\frac{\partial^2 \psi_j}{\partial v_i \partial \left(\frac{\partial c}{\partial x_k}\right)}\right|_{v_i=0,\frac{\partial c}{\partial x_k}=0},$$

$$A^{II}_{jilk} = \left.\frac{\partial^3 \psi_j}{\partial v_i \partial v_l \partial \left(\frac{\partial c}{\partial x_k}\right)}\right|_{v_i=0,v_l=0,\frac{\partial c}{\partial x_k}=0}, \tag{53}$$

$$A^{III}_{jilk} = \left.\frac{\partial^3 \psi_j}{\partial v_i \partial \left(\frac{\partial c}{\partial x_l}\right) \partial \left(\frac{\partial c}{\partial x_k}\right)}\right|_{v_i=0,\frac{\partial c}{\partial x_l},\frac{\partial c}{\partial x_k}=0}.$$

where c is the concentration. According to Nikolaevskii [34] the isotropic geometrical dispersive tensor must be of even rank in the case of an isotropic porous medium and thus we have $\mathbf{A}^I = 0$. When the velocity in the system becomes zero the dispersion tensor will be simply the diffusion tensor. For the case of high velocity the diffusion term is less important and therefore we will obtain an expression for the dispersion tensor independent of the diffusion term and given by only the second and third terms (NB the fourth term is negligible). The only remaining tensor component for the high velocity case in an isotropic porous medium is the third term in Eq. (52) that is

$$\mathbf{D} = \mathbf{A}^{II} \left\langle \mathbf{v}_i \right\rangle \left\langle \mathbf{v}_l \right\rangle. \tag{54}$$

For both diffusion and dispersion the corresponding tensors are described according to the structure or geometry of the porous medium, therefore the dissipation of energy and consequently the generated heat can be formulated in terms of the structural tensors of the medium.

6. Application for the permeability of the porous media

Permeability is closely related to excess energy dissipation on a small scale in a porous medium. It was mentioned earlier in this article that it is the energy due to the fluctuation in both equilibrium and nonequilibrium systems. In nonequilibrium situations there will be a contribution of the 'housekeeping' heat that is the one permanently dissipated while maintaining a nonequilibrium steady state at fixed external parameters α. The excess heat is associated with a transition between different steady states caused by changing α [28]. In this context the energy dissipation occurs due to fluid diffusion in the matrix of the porous medium (i.e., mixture of the medium and liquid) and also it happens due to the dissipation of mechanical energy of a flow field in this medium. In this section we study the permeability and separate the problem for the cases of diffusion and dispersion. We show how permeability can be expressed in terms of the diffusion and dispersion tensors.

6.1. Permeability and energy dissipation due to fluid diffusion

The energy balance law for a saturated porous medium reservoir gives an energy balance equation for a mixture of matrix and fluid that contains a term formulating the energy dissipation rate due to fluid diffusion through the porous matrix. This equation is given by [35]

$$Q = \frac{\phi^2 \mu_l}{k} |v_l - v_s|^2, \tag{55}$$

where ϕ is the porosity of the medium, μ_l is the viscosity, v_l and v_s are the liquid and matrix velocities, respectively, and k is the permeability of the medium. According to Kubo [23] for a stochastic equation of motion of a Brownian system given in terms of a generalised Langevin equation [36, 37]

$$m\dot{u}(t) = -m\int_{-\infty}^{t} \gamma(t-t')u(t')dt' + f(t), \tag{56}$$

where $\gamma(t)$ is a time-dependent memory function that represents the retarding effect of the frictional force, whose Fourier transform is related to the mobility by

$$\mu_p(\omega) = \frac{1}{m}\frac{1}{i\omega + \gamma(\omega)}. \tag{57}$$

Since $u(t)$ is stationary the force $f(t)$ must be stationary, then Eq. (56) results in the relation

$$u(\omega) = \frac{1}{m}\frac{1}{i\omega + \gamma(\omega)} f(\omega). \tag{58}$$

And since $\mu_p = 1/\zeta$ ($\zeta = b\pi r \mu_l$, where r is particle's effective hydrodynamic radius and b is a dimensionless parameter characterising the boundary condition [2]) therefore

$$f(\omega) = u(\omega)\zeta(\omega). \tag{59}$$

The stochastic perturbation $f(t)$ can be reduced by means of a Fourier expansion to a set of monochromatic components. Therefore the dissipation energy in the linear response theory for a monochromatic force f (i.e., a force at a single frequency) is given by [19]

$$Q = \frac{1}{2}\omega \chi''(\omega) f^2. \tag{60}$$

For a solid matrix of the porous medium $v_s = 0$, therefore for a monochromatic force combining equations (55), (59) and (60) gives us an expression for the permeability due to diffusion through the medium, that is

$$k(\omega) = \frac{\mu_l}{\zeta^2}\frac{2\phi^2}{\omega \chi''(\omega)}. \tag{61}$$

Substituting the corresponding χ'' functions from Eq. (29) for the case of asymptotic diffusion in a homogenous porous medium and also Eq. (34) for the case of preasymptotic diffusion in a

heterogeneous porous medium gives the permeability of the respective medium as a function of the diffusion tensors. As it can be seen the permeability is now a function of frequency.

6.2. Permeability and energy dissipation due to fluid dispersion

In this section we investigate how the energy dissipation for a dispersive system in a homogeneous medium can describe the permeability of the medium and how the dispersion tensor may affect this quantity. For this purpose our initial assumptions are that the flow is incompressible, isothermal and stationary. The local rate of dissipation energy per unit mass of fluid due to viscosity is given by [38]

$$Q = \frac{2\mu_l}{\rho} e_{ij} e_{ij}, \tag{62}$$

where μ_l is again the viscosity, ρ is the fluid density and e_{ij} is a symmetrical strain tensor [39]. The scalar absolute permeability in this case is given by

$$k = \frac{\mu_l q^2 s}{A} \frac{1}{\int_0^s \int_{A(s)} 2\mu_l e_{ij} e_{ij} dA ds}, \tag{63}$$

where q is the volumetric flow through the cross-section, s is the curvilinear coordinate along the average flow direction and A is the cross-section at point s. The above equation can be manipulated to obtain

$$k = \frac{\mu_l q^2 s}{A} \frac{1}{V \rho \langle Q \rangle}, \tag{64}$$

where V is the total volume of the medium and $\langle Q \rangle$ is the volume average of the dissipated energy function that is defined as

$$\langle Q \rangle = \frac{1}{V} \int_V Q dV.$$

For a homogeneous porous medium the volume averaged function is constant $\langle Q \rangle = Q$, also the flux q is defined as $q = Au$ and therefore combining Eqs. (59), (60) and (64) for a monochromatic force gives

$$k(\omega) = \frac{\mu_l}{\zeta^2} \frac{2A(s)s}{\rho V \omega \chi''(\omega)}. \tag{65}$$

The above equation can also be written in terms of the porosity of the medium as $\phi = V_v / V$, where V_v is the volume of the void space. This equation then can be written as

$$k(\omega) = \frac{\mu_l}{\zeta^2} \frac{2\phi A(s)s}{M \omega \chi''(\omega)}, \tag{66}$$

where M is the mass of fluid in the medium. As it can be seen this equation has a similar form to Eq. (61) for the case of pure diffusion. For a very low Reynolds number fluid like water the friction constant ζ according to Stokes's law is given by $\zeta = 6\pi r\mu_l$, where r is the radius of the spherical objects (i.e., grains in the medium). Therefore the above equation can be simplified to

$$k(\omega) = \frac{1}{(6\pi r)^2 \mu_l} \frac{2\phi A(s) s}{M\omega\chi''(\omega)}. \tag{67}$$

We have determined the dissipation function χ'' in the above equation for asymptotic dispersion in a homogeneous porous medium in terms of the dispersion tensor given by Eq. (37); therefore according to Eq. (67) the frequency-dependent permeability of the medium can be obtained from this tensor.

6.3. Absorption for a dispersive process in a homogenous porous medium

Eqs. (61) and (66) reveal that the permeability of a medium for either a diffusive or dispersive process is inversely related to the excess energy absorption in those systems. In this section we examine a homogenous porous medium, where the correlation function is approximated by a Markovian process. For this purpose we consider a specific correlation function of the velocity substituted for the general correlation function used earlier in this article. The velocity correlation function which is now a specialisation of the more general non-Markovian case is given by an exponential function [14]

$$C_v(t) = \exp\left(\frac{-\mu_l t}{m}\right) C_v(0), \tag{68}$$

where μ_l is again the friction constant and m is the mass of the particle. The spectrum of energy absorption (i.e., Eq. (37)) is the Fourier transform of Eq. (36), where the velocity correlation function is now identified by the above equation. The average velocity in this formula is a time-independent variable and therefore this Fourier transform is obtained as

$$\chi''(\mathbf{k},\omega) = -\frac{1}{\sqrt{2\pi}} \frac{C_v(0)}{2K_B T} \left[\frac{\mu_l m - im^2\omega}{\mu_l^2 + (\omega m)^2}\right] \mathbf{k}\cdot\left[\langle \mathbf{v}\rangle + i\mathbf{D}\cdot\mathbf{k}\right]. \tag{69}$$

Note that in the above we only consider positive values for t by introducing a Heaviside step function into the Fourier transform integral for the correlation function as this function has a definite Fourier transform for positive values of t only. The components of the velocity vector can be determined from NMR measurements of translational motion [2, 40, 41]; therefore we are concerned with the diagonal elements of the dispersion tensor [3]. Thus the above equation for the component of the velocity field in the z-direction (the direction of flow) is reduced to the following

$$\chi''_{zz}(k_z,\omega) = -\frac{k_z}{\sqrt{2\pi}} \frac{C_v(0)}{2K_B T} \left[\frac{\mu_l m - im^2\omega}{\mu_l^2 + (\omega m)^2}\right] \left[\langle v_z\rangle + iD_{zz}k_z\right]. \tag{70}$$

The above equation can be simplified to

$$\chi''_{zz}\left(k_z,\omega\right)=-\frac{k_z}{\sqrt{2\pi}\left(\mu_l^{\,2}+\left(\omega m\right)^2\right)}\frac{C_v\left(0\right)}{2K_BT}\left\{\left[\mu_l m\left\langle v_z\right\rangle+m^2D_{zz}k_z\omega\right]+i\left[\mu_l mD_{zz}k_z-m^2\left\langle v_z\right\rangle\omega\right]\right\}. \tag{71}$$

By substituting the above function in the expression for the permeability given by Eq. (67) we obtain

$$k\left(\omega\right)=\frac{4\sqrt{2\pi}K_BT\phi A\left(s\right)s\left(\mu_l^2+m^2\omega^2\right)\left[\left(-\mu_l m\left\langle v_z\right\rangle-m^2D_{zz}k_z\omega\right)+i\left(\mu_l mD_{zz}k_z-m^2\left\langle v_z\right\rangle\omega\right)\right]}{C_v\left(0\right)\left(6\pi r\right)^2k_z\mu_l M\omega\left[\left(\mu_l m\left\langle v_z\right\rangle^2+m^2D_{zz}k_z\omega\right)^2+\left(\mu_l mD_{zz}k_z-m^2\left\langle v_z\right\rangle\omega\right)^2\right]} \tag{72}$$

Using the following trigonometric identities

$$\sin\left(x+y\right)=\sin\left(x\right)\cos\left(y\right)+\sin\left(y\right)\cos\left(x\right),$$

and

$$\cos\left(x+y\right)=\cos\left(x\right)\cos\left(y\right)-\sin\left(x\right)\sin\left(y\right),$$

for the real and imaginary parts of the above equation and solving for x and y and also writing the wave-number k_z as $k_z=2\pi/\lambda=\omega/v_z$, (here v_z is the most probable velocity), we can rewrite this equation as

$$\begin{aligned}k\left(\omega\right)=\frac{4\sqrt{2\pi}K_BT\phi A\left(s\right)s\,v_z}{C_v\left(0\right)\left(6\pi r\right)^2\mu_l M}\Bigg[&\cos\left(\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)+\cos^{-1}\left(\frac{\mu_l mD_{zz}\omega}{v_z\sin\left(\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)\right)}\right)\right)\\&+i\sin\left(\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)+\cos^{-1}\left(\frac{\mu_l mD_{zz}\omega}{v_z\sin\left(\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)\right)}\right)\right)\Bigg],\end{aligned} \tag{73}$$

or

$$k\left(\omega\right)=\frac{4\sqrt{2\pi}K_BT\phi A\left(s\right)s\,v_z}{C_v\left(0\right)\left(6\pi r\right)^2\mu_l M}\exp\left\{i\left[\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)+\cos^{-1}\left(\frac{\mu_l mD_{zz}\omega}{v_z\sin\left(\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)\right)}\right)\right]\right\}. \tag{74}$$

Without loss of generality $C_v(0)=1$, [14] then Eq. (74) gives a phasor with phase delay determined by

$$\delta = \tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right) + \cos^{-1}\left(\frac{\mu_l m D_{zz}\omega}{v_z \sin\left(\tan^{-1}\left(\frac{-D_{zz}\omega}{v_z^2}\right)\right)}\right). \tag{75}$$

Before we proceed further, it is worth comparing the permeability phenomena in the porous medium with phenomena in other areas of physics such as electromagnetism. For example in analogy with electrostatics, where the magnetic flux vector **B** is determined by the gradient of a scalar potential,

$$\mathbf{B} = -\nabla \phi_m,$$

where ϕ_m is called as the magnetic scalar potential; in fluid transport in a porous media also there is a similar equation characterising the flux vector **q** that is given by

$$\mathbf{q} = -\nabla \Phi, \tag{76}$$

where Φ is called velocity potential [42]. The permeability of a medium to the magnetic field is actually the ratio of the magnetic field **B** to the modification of this field in the medium **H**. This quantity is a phasor since the fields are frequency dependent and it reflects the fact that the response of the medium to the field is not instantaneous. Thus the response is represented by a phase difference and the magnetic permeability is often treated as a complex function as it reflects the phase delay of the response. In analogy with the permeability of porous medium the response to the applied velocity field determines a phase delay given by Eq. (75) and therefore it is a phasor represented as a complex function. In electromagnetism the real part of the magnetic phasor determines how much dissipated energy is stored in the medium and the imaginary part represents the loss of the energy in the system. Similarly in the porous medium the storage and loss of the dissipated energy is related to the real and imaginary part of the permeability (i.e. Eq. (73)). The ratio of the lost to the stored energy is called the loss tangent and is given by [43]

$$\tan\delta = \frac{k''}{k'}. \tag{77}$$

flow velocities up to $v_z = 6.7 \times 10^{-3}$ m s^{-1} in a porous medium consisting of coarse/medium sand (average diameter ~ 1 mm) have been measured with MRI [44]. In the following we use this value for the velocity of the flow. Also the longitudinal component of the dispersion tensor for a porous medium consisting of an array of spheres was obtained as $D_{zz} = 2.3 \times 10^{-5}$ m s^{-2} [45]. The above values for the velocity and diameter of the sands has been used to determine the Peclet's number using the equation

$$\mathrm{Pe} = v_z a / D, \tag{78}$$

where a is the sphere diameter and D is the diffusion coefficient of water [45, 46].

The energy stored and lost in a homogenous porous medium consisting of spherical grains of radius one millimetre in terms of the frequency of the fluctuation of the velocity for water flowing in this medium at 25 °C is shown in Figure 2 and Figure 3.

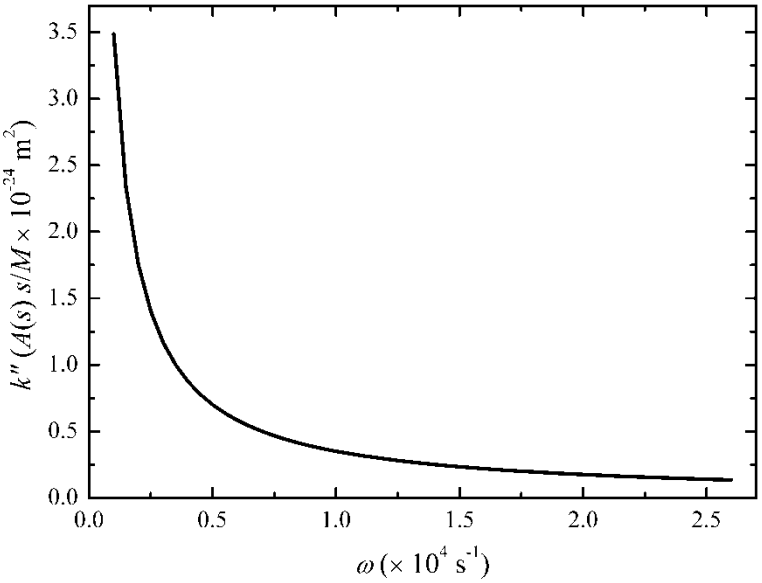

Figure 2: Imaginary part of the permeability characterising the energy lost for dispersion of water molecules with viscosity 8.9 × 10^{-4} Pa s through a homogenous porous medium versus the frequency of the fluctuations of the velocity field at 25 °C by using the imaginary part of Eq. (73). The grain size is 1 mm and the medium is packed with a porosity of 0.5.

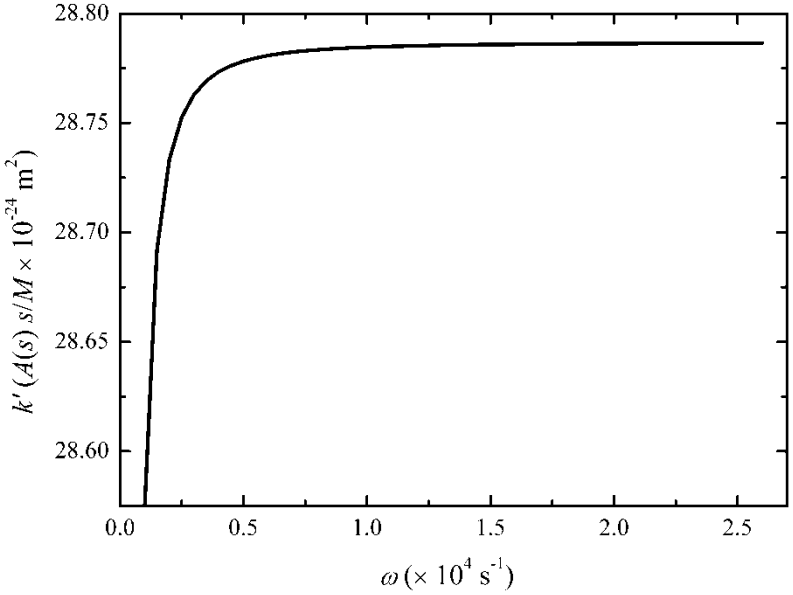

Figure 3: Real part of the permeability characterising the energy stored for dispersion of water molecules with viscosity 8.9 × 10^{-4} Pa s through a homogenous porous medium versus the frequency of the fluctuations of the velocity field at 25 °C by using the real part of Eq. (73). The grain size is 1 mm and the medium is packed with a porosity of 0.5.

7. Concluding remarks

Translational dynamics is characterised by diffusion and dispersion resulting from fluctuations in the velocity fields of the particles in the fluid. In a simple diffusing system, the

system is in an equilibrium state whence the more complicated motion of flow in a porous medium with evolving heterogeneity on the measurement length scale is considered as a nonequilibrium system. This work has shown how the energy dissipation function and the diffusion and dispersion tensors may be connected via the fluctuation-dissipation theorem in equilibrium and nonequilibrium systems, respectively. In both cases the dissipation tensors were determined as a function of diffusion and dispersion tensors and also the corresponding spectral resolution of correlation functions. It was shown that in nonequilibrium preasymptotic dispersion the energy dissipation function is actually obtained by statistical averaging of the frequency-dependent dispersion tensor and correlation function over the derivative of the energy distribution in the system.

The permeability of the porous medium for the cases of diffusion and dispersion are studied and it was found that the frequency-dependent permeability can be written as a complex function; hence a phasor models flow which then determines a phase delay for water flowing in a homogenous porous medium.

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