Diffusion eigenstates of a porous medium with interface absorption

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The eigenvalues and general shapes of the low lying diffusion eigenstates are studied for the case of diffusion in a fluid-filled porous medium of arbitrary, though macroscopically homogeneous, microstructure with nonzero absorption at the pore walls. Those eigenstates are then used to discuss the tensor $\hat{D}_e$ of bulk effective *stationary* diffusion coefficients and other aspects of the diffusion at long times, such as the pulsed-gradient spin-echo amplitude and the return to the origin probability (RTOP). It is shown that, under quite general conditions the localized states are unimportant, and only the low-lying extended states make a significant contribution to the long time behavior of these quantities. The eigenvalues or decay rates of those states always have the form $\lambda_{\mathbf{q}}$ for small wave vectors $\mathbf{q}$, and $\lambda_{\mathbf{q}}$ is bounded from above by $\lambda_0+\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}$. A general connection is found between $\hat{D}_e$ and an electrical conductivity problem in the same medium. Using the bound on $\lambda_{\mathbf{q}}$, it is shown that the relative RTOP (i.e., the RTOP in a fluid-filled porous medium divided by the RTOP in the uniform fluid) exhibits a nonmonotonic dependence on time, reaching a maximum at some finite characteristic value. Similar considerations also lead to the possibility of nonmonotonic behavior of the bulk effective *time-dependent* diffusion coefficient. [S1063-651X(97)06404-0]

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The problem of time-dependent diffusion in a restricted pore space V_p has recently come under increased scrutiny. This is due, in part, to the increased exploitation of nuclear magnetic resonance (NMR) methods for measuring the diffusion of (nuclear spin) polarized molecules in a fluid-filled porous medium [1–3]. Such measurements are performed either in the presence of a *fixed* (i.e., time independent) gradient of the spin aligning magnetic field [4], or under application of a *pulsed field gradient* [5]. In the latter case, very detailed information can be obtained about the diffusion in such a restricted pore space, and it can be drastically affected by the microstructure [2,6,7].

The simplest situation is when the diffusing particles survive indefinitely—there is no absorption of particles, or decay of the spin polarization, either inside the pore space or at the pore-matrix interface. A finite decay probability for the diffusing particle poses no special problems if it has a uniform value throughout the pore space. However, if some kind of decay can occur only at the pore-matrix interface, the theoretical treatment can be quite considerably complicated. Such a decay phenomenon can be the result of a chemical reaction that occurs only at the interface, or a consequence of the presence of paramagnetic ions in the matrix or at the interface, leading to an enhanced decay of polarization when a spin polarized molecule reaches that interface [1].

Theoretical and numerical studies of restricted diffusion often focus on the diffusion eigenstates. In particular, for the case of a porous medium with a periodic microstructure, efficient techniques have been developed for computing those eigenstates [8,9]. In this way, interesting physical quantities could be calculated, such as the (time-dependent) bulk effective diffusion coefficient [8–10], spin polarization amplitudes that are measured in an NMR spin-echo measurement in the presence of either a static field gradient [11] or a pulsed field gradient [8–10], and the return to the origin probability (RTOP) for a diffusing particle [12,13].

In the case where there is no decay at the interface, a connection has long been known to exist between the stationary diffusion problem in such a medium, where diffusion can only take place in the pore space, and the electrical conduction problem, where only the pore space is conducting [14,8].

In this paper, we study some general properties of the low-lying diffusion eigenstates of the time-dependent diffusion problem in a porous medium. We consider the case of a general, though macroscopically homogeneous, microstructure, thus our results apply to disordered porous media as well as to periodic ones. We also allow for absorption at the interface. We identify a class of low-lying extended eigenstates that govern the bulk effective stationary diffusion in the porous medium, as well as the time-dependent diffusion at long times. The eigenvalues of those states are given by a dispersion expression $\lambda_{\mathbf{q}}$, where $\mathbf{q}$ is a wave vector that is small compared to the inverse size of the typical pores, and $\lambda_{\mathbf{q}}$ is shown to be bounded from above by a simple quadratic function of $\mathbf{q}$. We derive a very general connection between the tensor of bulk effective stationary diffusion coefficients $\hat{D}_e$ and the bulk effective conductivity tensor $\hat{\sigma}_e$ of a certain conductivity problem in a medium with the same microstructure. The upper bound on $\lambda_{\mathbf{q}}$ leads to predictions regarding the behavior of a particle diffusing in the fluid-filled pore space: the RTOP, when normalized by the RTOP in a uniform fluid, is a nonmonotonic function of time t, which increases with t at small t, then reaches a maximum value, and finally decreases towards an asymptotic constant value as $t\rightarrow\infty$. It is also shown that the bulk effective time-dependent diffusion coefficient can exhibit a nonmonotonic dependence on time under certain conditions. Finally, we discuss the possible influence of localized diffusion eigenstates on the macroscopic diffusion.

The rest of this paper is organized as follows: In Sec. I we discuss the properties of the low-lying diffusion eigenstates,

both extended and localized, and derive an upper bound for $\lambda_{\mathbf{q}}$. We also derive the connection between $\hat{D}_e$ and $\hat{\sigma}_e$. In Sec. II we discuss some physical implications for the diffusion propagator and its Fourier transform, for $\hat{D}_e$, and for the normalized RTOP. In the Appendix we provide proofs for some of the more technical points mentioned in this paper, and point out a curious, unexplained symmetry of $\lambda_{\mathbf{q}}$ and its associated eigenstates.

I. BASIC THEORY OF THE DIFFUSION EIGENSTATES

The time-dependent diffusion in a porous medium with interface absorption is described by the following equations for the density $n(\mathbf{r},t)$ of the diffusing particles:

$$\frac{\partial n}{\partial t}=D_0\nabla^2 n \quad \text{for } \mathbf{r}\in V_p, \tag{1.1}$$

$$0=D_0\mathbf{n}\cdot\boldsymbol{\nabla} n+\rho n \quad \text{for } \mathbf{r}\in \partial V_p, \tag{1.2}$$

where V_p is the pore space, ∂V_p is the pore-matrix interface, $\mathbf{n}$ is the outward pointing (from pore to matrix) normal vector at the interface, D_0 is the diffusion coefficient in the uniform fluid, and ρ is the interface absorption coefficient.

The diffusion eigenfunctions are solutions of the form $\psi_\lambda(\mathbf{r})e^{-\lambda t}$, where λ is the eigenvalue and $\psi_\lambda(\mathbf{r})$ satisfies the following equations:

$$\lambda\psi_\lambda+D_0\nabla^2\psi_\lambda=0, \quad \mathbf{r}\in V_p, \tag{1.3}$$

$$D_0\mathbf{n}\cdot\boldsymbol{\nabla}\psi_\lambda+\rho\psi_\lambda=0, \quad \mathbf{r}\in \partial V_p, \tag{1.4}$$

as well as some macroscopically uniform boundary conditions at the external surface of the system, which we denote by $\partial V_{\rm ex}$. As usual in such cases, the precise nature of those boundary conditions is unimportant, provided that the system size is much larger than the typical pore sizes.

From these equations we easily get

$$\begin{aligned}\lambda\int_{V_p} dV\psi_\omega^*\psi_\lambda &= -D_0\int_{V_p} dV\psi_\omega^*\nabla^2\psi_\lambda \\ &= \rho\oint_{\partial V_p} dS\psi_\omega^*\psi_\lambda \\ &\quad +D_0\int_{V_p} dV(\boldsymbol{\nabla}\psi_\omega^*\cdot\boldsymbol{\nabla}\psi_\lambda),\end{aligned} \tag{1.5}$$

where there is no contribution in Eq. (1.5) from a surface integral over $\partial V_{\rm ex}$—this is ensured by the boundary conditions there. From this it follows that the eigenvalues are real and that eigenfunctions corresponding to different eigenvalues are orthogonal:

$$\int_{V_p} dV\psi_\omega^*\psi_\lambda=0 \quad \text{for } \omega\neq\lambda. \tag{1.6}$$

As usual, the eigenfunctions can be chosen to be mutually orthogonal even when the eigenvalues are degenerate, and they can be normalized so as to satisfy

$$\frac{1}{V_p}\int_{V_p} dV\psi_\omega^*\psi_\lambda=\delta_{\omega\lambda}. \tag{1.7}$$

From Eq. (1.5) it also follows that

$$\lambda\int_{V_p} dV|\psi_\lambda|^2=\rho\oint_{\partial V_p} dS|\psi_\lambda|^2+D_0\int_{V_p} dV|\boldsymbol{\nabla}\psi_\lambda|^2, \tag{1.8}$$

and therefore that $\lambda>0$, unless $\psi_\lambda\equiv$ const and $\rho=0$, in which case $\lambda=0$. If we treat the right-hand side (rhs) of this equation as a quadratic functional, namely,

$$F[\psi]\equiv\frac{\rho}{V_p}\oint_{\partial V_p} dS|\psi|^2+\frac{D_0}{V_p}\int_{V_p} dV|\boldsymbol{\nabla}\psi|^2, \tag{1.9}$$

then the requirement that $F[\psi]$ be stationary (i.e., that its first variation vanishes $\delta F[\psi]=0$), in the space of normalized functions $\psi(\mathbf{r})$ that have square integrable (partial) first derivatives in V_p, is equivalent to Eqs. (1.3), (1.4), and (1.7). The eigenfunctions will have continuous first and second partial derivatives throughout V_p.

The eigenvalues λ can also be calculated from

$$\lambda=F[\psi_\lambda]. \tag{1.10}$$

Moreover, because of the variational property of $F[\psi]$, when λ is calculated in this way, a small error $\boldsymbol{\epsilon}(\mathbf{r})$ in $\psi_\lambda(\mathbf{r})$ leads to only a *higher order* error in λ,

$$F[\psi_\lambda+\boldsymbol{\epsilon}]=\lambda+O(\boldsymbol{\epsilon}^2). \tag{1.11}$$

A. The lowest eigenstate

The lowest eigenvalue, denoted by λ_0, is just the minimum value of the functional $F[\psi]$. When $\rho=0$, that eigenvalue and its eigenfunction $\psi_0(\mathbf{r})$ are given by

$$\lambda_0=0, \quad \psi_0(\mathbf{r})\equiv 1 \quad \text{for } \rho=0, \tag{1.12}$$

but when $\rho\neq 0$, then $\lambda_0>0$ and $\psi_0(\mathbf{r})\neq$ const. We can show, however, that $\psi_0(\mathbf{r})>0$ throughout V_p.

In order to prove this, we first note that $F[\psi]=F[|\psi|]$ for any real $\psi(\mathbf{r})$. Also, since $\lambda>0$, any real eigenfunction $\psi_\lambda(\mathbf{r})$ cannot have a local minimum at any internal point where $\psi_\lambda(\mathbf{r})\geqslant 0$ (for a mathematical proof of this statement, see the Appendix). Thus, if $\psi_0(\mathbf{r})$, which minimizes $F[\psi]$, vanished at any internal point $\mathbf{r}_0\in V_p$, then $|\psi_0|$ is nonnegative, it also minimizes $F[\psi]$, and it has a minimum at $\mathbf{r}_0$, clearly a contradiction. We may conclude from this that $\psi_0(\mathbf{r})$ never vanishes inside V_p. Therefore, because $\psi_0(\mathbf{r})$ is a continuous function, it must have the *same sign everywhere*, and this can be chosen to be positive. Any other real eigenfunction must have alternating positive and negative values in order to be orthogonal to ψ_0.

The nonconstant nature of $\psi_0(\mathbf{r})$ is dictated by the condition (1.4), which must hold at the interface. Only far away from the interface will this function be nearly constant. In any case, if the porous medium is *macroscopically homogeneous*, then $\psi_0(\mathbf{r})$ will be *macroscopically uniform*, and will not exhibit any tendency to be localized in some macroscopic subvolume. The magnitude of ψ_0 will be $O(1)$ everywhere in the pore space, and its Fourier transform

$$\tilde{\psi}_0(\mathbf{k})\equiv\frac{1}{V_p}\int_{V_p} dV\psi_0(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{1.13}$$

will have the following property in the case of a disordered porous medium

$$\tilde{\psi}_0(\mathbf{0}) = O(1), \tag{1.14}$$

$$\tilde{\psi}_0(\mathbf{k}) = O\left(\left(\frac{a^3}{V_p}\right)\right)^{1/2} \quad \text{for } \mathbf{k} \neq \mathbf{0}, \tag{1.15}$$

where a is a typical pore size. The second result follows by considering the ensemble average of $|\tilde{\psi}_0(\mathbf{k})|^2$, treating the microstructure as random, and assuming that $\langle \psi_0(\mathbf{r})\psi_0(\mathbf{r}')\rangle$ quickly relaxes to a constant value of order $O(1)$ when $|\mathbf{r}-\mathbf{r}'| > a$. In the case of a medium with a periodic microstructure, $\psi_0(\mathbf{r})$ will also be periodic. In that case $\tilde{\psi}_0(\mathbf{k})$ is nonzero only when $\mathbf{k}$ is equal to one of the reciprocal lattice vectors $\mathbf{g}$, and then $\tilde{\psi}_0(\mathbf{g}) = O(1)$.

B. Low-lying extended eigenstates

We now show that a set of low-lying eigenstates exist, which have the form

$$\psi_\lambda \to \psi_{\mathbf{q}}(\mathbf{r}) = \psi_0(\mathbf{r}) e^{i\mathbf{q}\cdot\boldsymbol{\phi}(\mathbf{r})}[1 + \mathbf{q}\cdot\hat{f}(\mathbf{r})\cdot\mathbf{q}] + o(q^2), \tag{1.16}$$

$$\lambda \to \lambda_{\mathbf{q}} = \lambda_0 + \mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q} + o(q^2), \tag{1.17}$$

for small $\mathbf{q}$, where $f_{\alpha\beta}(\mathbf{r})$ is bounded and $\phi_\alpha(\mathbf{r})$ is unbounded. [Actually, we can show that the errors in these expressions are $O(q^3)$ and $O(q^4)$, respectively—see the Appendix.] To that end, we substitute Eq. (1.16) in Eqs. (1.3) and (1.4), and expand all quantities in powers of $\mathbf{q}$, except for the exponential factor $e^{i\mathbf{q}\cdot\boldsymbol{\phi}(\mathbf{r})}$: the special treatment of this factor is necessary because, in contrast with the functions $\psi_0(\mathbf{r})$ and $\hat{f}(\mathbf{r})$, $\boldsymbol{\phi}(\mathbf{r})$ will turn out to be unbounded. From the terms of order q^1, q^2 in the expansion, we find that $\boldsymbol{\phi}(\mathbf{r})$, $\hat{f}(\mathbf{r})$ must satisfy the following equations:

$$\boldsymbol{\nabla}\cdot(\psi_0^2\boldsymbol{\nabla}\phi_\alpha) = 0, \quad \mathbf{r} \in V_p, \tag{1.18}$$

$$(\mathbf{n}\cdot\boldsymbol{\nabla})\phi_\alpha = 0, \quad \mathbf{r} \in \partial V_p, \tag{1.19}$$

$$\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})] = \left([\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})]^2 + \frac{\lambda_0 - \lambda_{\mathbf{q}}}{D_0}\right)\psi_0^2, \quad \mathbf{r} \in V_p, \tag{1.20}$$

$$(\mathbf{n}\cdot\boldsymbol{\nabla})\hat{f} = 0, \quad \mathbf{r} \in \partial V_p. \tag{1.21}$$

The equations for ϕ_α [Eqs. (1.18) and (1.19)] are the same as the equations for an electric potential in the pore space when the local conductivity is $\sigma_0\psi_0^2(\mathbf{r})$ (σ_0 is an arbitrary constant with the physical dimensions of electrical conductivity). In order to get a nontrivial solution for ϕ_α, we will impose the following boundary condition at the external surface (other choices can also be used—see discussion below and in the Appendix)

$$\phi_\alpha(\mathbf{r}) = r_\alpha, \quad \mathbf{r} \in \partial V_{\text{ex}}. \tag{1.22}$$

As a result of this condition, the volume averaged electric field produced by $\phi_\alpha(\mathbf{r})$ is the unit vector $\mathbf{e}_\alpha$:

$$\langle \boldsymbol{\nabla}\phi_\alpha \rangle = \mathbf{e}_\alpha. \tag{1.23}$$

Using the potential functions $\phi_\alpha(\mathbf{r})$, the bulk effective conductivity tensor of this porous medium $\hat{\sigma}_e$ can be calculated from [15]

$$\frac{\sigma_{\alpha\beta}^{(e)}}{\sigma_0} = \frac{1}{V}\int_{V_p} dV \psi_0^2(\boldsymbol{\nabla}\phi_\alpha\cdot\boldsymbol{\nabla}\phi_\beta), \tag{1.24}$$

where V is the *total volume*, i.e., pore space plus matrix space. Note that, although $\boldsymbol{\phi}(\mathbf{r})$ is unbounded, $\boldsymbol{\phi}(\mathbf{r}) - \mathbf{r}$ is bounded. In fact, in the case of a periodic microstructure, $\boldsymbol{\phi}(\mathbf{r}) - \mathbf{r}$ is also periodic.

The equations for $\hat{f}$ [(1.20), (1.21)] are equations for another electric potential in the same conducting pore space, with the same values of the local conductivity, but in the presence of a distribution of current sources [the rhs of Eq. (1.20)]. In order that $\hat{f}$ be bounded and independent of $\mathbf{q}$, those current sources must average out to 0, i.e., we must have

$$\lambda_{\mathbf{q}} = \lambda_0 + \mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q} + o(q^2), \tag{1.25}$$

where

$$\frac{D_{\alpha\beta}^{(e)}}{D_0} = \frac{1}{V_p}\int_{V_p} dV \psi_0^2 \boldsymbol{\nabla}\phi_\alpha\cdot\boldsymbol{\nabla}\phi_\beta = \frac{V}{V_p}\frac{\sigma_{\alpha\beta}^{(e)}}{\sigma_0}. \tag{1.26}$$

In order to fix $\hat{f}(\mathbf{r})$, we must also impose upon it some boundary conditions at the external system surface. Those are best chosen in accordance with the boundary conditions imposed upon the eigenfunctions, e.g., either vanishing or periodic at ∂V_{ex}. The result (1.26) means that $\hat{D}_e$ is simply related to the bulk effective conductivity tensor $\hat{\sigma}_e$ of the porous medium, where the matrix is perfectly insulating and the pore space has a local conductivity equal to $\sigma_0\psi_0^2(\mathbf{r})$. This result is a rigorous generalization of a similar result that has long been known to hold in the case of an *isotropic* porous medium when $\rho = 0$ [as noted in Eq. (1.12), in that case $\psi_0(\mathbf{r}) \equiv 1$] [14,8]. Here we have shown that Eq. (1.26) holds for a porous medium of *arbitrary microstructure* and arbitrary values of ρ. An important consequence of Eq. (1.26) is that the eigenvalues of $\hat{D}_e$ are all less than D_0 (see Appendix for a proof of this inequality),

$$\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q} \leqslant D_0 q^2. \tag{1.27}$$

The Fourier transform of $\psi_{\mathbf{q}}(\mathbf{r})$ for small $\mathbf{q}$ is given by

$$\tilde{\psi}_{\mathbf{q}}(\mathbf{k}) \cong \frac{1}{V_p}\int_{V_p} dV e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}}\psi_0(\mathbf{r})e^{i\mathbf{q}\cdot\boldsymbol{\phi}[(\mathbf{r})-\mathbf{r}]}[1 + \mathbf{q}\cdot\hat{f}(\mathbf{r})\cdot\mathbf{q}]$$

$$\cong \frac{1}{V_p}\int_{V_p} dV e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}}\psi_0(\mathbf{r}) = \tilde{\psi}_0(\mathbf{k}-\mathbf{q}), \tag{1.28}$$

where we used the fact that both $\hat{f}$ and $\boldsymbol{\phi} - \mathbf{r}$ are bounded to get the last line. Clearly, the difference $\tilde{\psi}_{\mathbf{q}}(\mathbf{k}) - \tilde{\psi}_0(\mathbf{k}-\mathbf{q})$ is $O(|\mathbf{q}|a)$. Also, from the previous subsection it follows that $\tilde{\psi}_{\mathbf{q}}(\mathbf{q}) = O(1)$, while $\tilde{\psi}_{\mathbf{q}}(\mathbf{k}) = O[(a^3/V_p)^{1/2}]$ for $\mathbf{q} \neq \mathbf{k}$.

We now recall that $\psi_{\mathbf{q}}(\mathbf{r})$ must also satisfy some boundary conditions at the external surface. It is easiest to use periodic boundary conditions in a cubic volume of size L^3. This means that $\psi_0(\mathbf{r})$ and $\hat{f}(\mathbf{r})$ must be L periodic in all directions and that the values of $\mathbf{q}$ are limited to the following discrete spectrum:

$$\mathbf{q}=\frac{2\pi}{L}(n_x,n_y,n_z), \quad n_x,n_y,n_z=\text{integers}. \tag{1.29}$$

Note that, if we assume a uniform boundary condition for $\phi_\alpha(\mathbf{r})$ that differs from Eq. (1.22) by a multiplicative constant, then that will change $\boldsymbol{\phi}$, $\hat{f}$ and the spectrum of allowed values of $\mathbf{q}$ in such a way that $\psi_{\mathbf{q}}$ remains unchanged.

The states $\psi_{\mathbf{q}}$ are approximately orthogonal for small $\mathbf{q}$, as can be seen by writing

$$\int_{V_p} dV\psi_{\mathbf{q}}^*\psi_{\mathbf{q}'}\cong\int_{V_p} dV\psi_0^2(\mathbf{r})e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}}, \tag{1.30}$$

where we exploited the fact that both $\mathbf{q}\cdot\hat{f}\cdot\mathbf{q}$ and $\mathbf{q}\cdot(\boldsymbol{\phi}-\mathbf{r})$ are everywhere small. Since $(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}$ only changes appreciably over a length scale that is much greater than the typical pore size a, therefore we can replace $\psi_0^2(\mathbf{r})$ approximately by its volume average over some intermediate scale, where the average already has an approximately uniform value, and the remaining integral of $e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}}$ over the *entire volume V* then vanishes.

In the case that the porous medium has a *periodic microstructure*, the Bloch-Floquet theorem applies. This means that *all* the eigenstates appear in bands and have the form

$$\psi_\lambda\to\psi_{n\mathbf{q}}(\mathbf{r})=u_{n\mathbf{q}}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}, \quad \lambda\to\lambda_{n\mathbf{q}}, \tag{1.31}$$

where $u_{n\mathbf{q}}(\mathbf{r})$ is a periodic function of $\mathbf{r}$, and $\mathbf{q}$ is a vector in the first Brillouin zone of reciprocal space. The lowest of these bands has the form (1.16) and (1.17) for small $\mathbf{q}$, where $\psi_0(\mathbf{r})$ and $\hat{f}(\mathbf{r})$ are periodic functions, as is also *the difference* $\boldsymbol{\phi}(\mathbf{r})-\mathbf{r}$.

C. Upper bound for $\lambda_{\mathbf{q}}$

In the case of a periodic porous medium, the Hilbert space of functions with square integrable first derivatives separates naturally into disjoint, mutually orthogonal subspaces of Bloch functions ψ, characterized by a given $\mathbf{q}$ vector

$$\psi(\mathbf{r})=u(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{1.32}$$

where $u(\mathbf{r})$ is periodic. This follows from the fact that two Bloch functions $u(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}$, $u'(\mathbf{r})e^{i\mathbf{q}'\cdot\mathbf{r}}$, which are characterized by different $\mathbf{q}$ vectors in the first Brillouin zone of reciprocal space, are always orthogonal:

$$\int_{V_p} dVu^*(\mathbf{r})u'(\mathbf{r})e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}} = \sum_{\mathbf{a}} e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{a}}\int_{V_p\cap V_a} dVu^*(\mathbf{r})u'(\mathbf{r})e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}}. \tag{1.33}$$

Here V_a is the volume of a single unit cell and the sum ranges over all the lattice vectors $\mathbf{a}$ of the periodic system in configuration space. Since the last integral is independent of $\mathbf{a}$, the sum vanishes unless $\mathbf{q}'=\mathbf{q}$. Since each of these subspaces is a closed Hilbert space, the variational properties of $F[\psi]$ that were described earlier hold separately in each of them. In particular, any of the eigenvalues $\lambda_{\mathbf{q}}$ that lie in the lowest band is given by the minimum of $F[\psi]$ over the $\mathbf{q}$ subspace of functions of the form (1.32).

An upper bound for $\lambda_{\mathbf{q}}$ can thus be obtained by using the trial function

$$\psi_{\mathbf{q}}(\mathbf{r})\equiv\psi_0(\mathbf{r})e^{i\mathbf{q}\cdot\boldsymbol{\phi}(\mathbf{r})} \tag{1.34}$$

in $F[\psi]$, resulting in

$$\lambda_{\mathbf{q}}<\lambda_0+\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}. \tag{1.35}$$

This means that the four-dimensional hyperparaboloid (i.e., the rhs of this equation), which describes the behavior of $\lambda_{\mathbf{q}}$ accurately for small $\mathbf{q}$, lies entirely above that band *for all* $\mathbf{q}$.

In the case of a nonperiodic medium, this variational argument cannot be invoked because the low-lying states that correspond to different $\mathbf{q}$ vectors do not lie in disjoint Hilbert spaces. Nevertheless, we can still show that $\lambda_{\mathbf{q}}$ lies below the hyperparaboloid (1.25) at small $\mathbf{q}$ by using the stationarity of $F[\psi]$ to calculate the next term in the expansion of $\lambda_{\mathbf{q}}$.

Noting that the error in Eq. (1.16) is $o(q^2)$, it is clear that by using the stationary expression (1.11) we will get a result for $\lambda_{\mathbf{q}}$ with an error that is only $o(q^4)$. In this way we get, after some tedious algebra (see Appendix for details),

$$\lambda_{\mathbf{q}}=\lambda_0+\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}-E^{(e)}_{\alpha\beta\gamma\omega}q_\alpha q_\beta q_\gamma q_\omega+o(q^4), \tag{1.36}$$

where $\hat{E}_e$ is a positive, rank-4 tensor, given by

$$\frac{E^{(e)}_{\alpha\beta\gamma\omega}}{D_0}\equiv\frac{1}{V_p}\int_{V_p} dV\psi_0^2(\boldsymbol{\nabla}f_{\alpha\beta}\cdot\boldsymbol{\nabla}f_{\gamma\omega})=O(a^2). \tag{1.37}$$

The meaning of Eq. (1.36) is that, even in a disordered porous medium, a bound of the form (1.35) holds *for sufficiently small* $\mathbf{q}$.

D. Localized eigenstates

In a nonperiodic medium, there may exist some low-lying eigenstates that are localized, even when there are no strictly isolated pores. Those are states with eigenfunctions $\psi_{\text{loc}}(\mathbf{r})$ that decay to exponentially small values outside a finite subvolume V_{loc}. The existence of such states is well known from extensive discussions of the time-independent Schrödinger equation in a random potential (see, e.g., Ref. [16]). The problem of diffusion eigenstates in a disordered composite medium is mathematically somewhat similar to that problem.

In contrast with the extended state $\psi_0(\mathbf{r})$, none of these localized states can produce a low-lying continuum of distinct states such as $\psi_{\mathbf{q}}(\mathbf{r})$ of Eq. (1.16): if we tried to use ψ_{loc} instead of ψ_0 in Eqs. (1.18)–(1.22), we would find that $\mathbf{q}\cdot\boldsymbol{\phi}(\mathbf{r})$ is approximately constant wherever $\psi_{\text{loc}}(\mathbf{r})$ differs appreciably from 0. Consequently, the $\mathbf{q}$-dependent state

would be given by $\psi_{\rm loc}(\mathbf{r})e^{i\mathbf{q}\cdot\phi(\mathbf{r})}$, and it would differ from $\psi_{\rm loc}(\mathbf{r})$ just by a constant phase factor.

The magnitudes of $\psi_{\rm loc}(\mathbf{r})$ and of its Fourier transform $\tilde{\psi}_{\rm loc}(\mathbf{k})$ depend on the size of the subvolume $V_{\rm loc}$:

$$\psi_{\rm loc}(\mathbf{r})=O\left(\left(\frac{V_p}{V_{\rm loc}}\right)\right)^{1/2}, \tag{1.38}$$

$$\tilde{\psi}_{\rm loc}(\mathbf{k})=O\left(\left(\frac{V_{\rm loc}}{V_p}\right)\right)^{1/2}. \tag{1.39}$$

In the following section we shall see that these states do not make a significant contribution to the diffusion in the pore space at long times.

II. PHYSICAL CONSEQUENCES FOR DIFFUSION IN A POROUS MEDIUM

A. The diffusion propagator

The diffusion propagator $G(\mathbf{r},\mathbf{r}',t)$ is a solution of Eqs. (1.1) and (1.2) which satisfies the initial condition

$$G(\mathbf{r},\mathbf{r}',0)=\delta^3(\mathbf{r}-\mathbf{r}'). \tag{2.1}$$

The importance of this function is due to the fact that, in principle, it contains *all the information* about diffusion in the medium. For example, the time-dependent spin polarization of diffusing molecules, which is measured in a pulsed-gradient spin-echo (PGSE) NMR experiment, is given by a spatial Fourier transform of this propagator [3,17]:

$$M(\mathbf{k},t)\equiv\frac{1}{V_p}\int_{V_p}dV\int_{V_p}dV'\,G(\mathbf{r},\mathbf{r}',t)e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}. \tag{2.2}$$

The wave vector $\mathbf{k}$ in such an experiment is actually determined by the magnetic field gradient ∇H and the length of time δ during which it is turned on (γ is the gyromagnetic ratio of the nuclear spin in question)

$$\mathbf{k}=\gamma\delta\nabla H, \tag{2.3}$$

while t is the time between successive gradient pulses.

In a uniform fluid, both G and M have simple Gaussian shapes

$$G(\mathbf{r},\mathbf{r}',t)=\left(\frac{1}{4\pi D_0 t}\right)^{3/2}e^{-(\mathbf{r}-\mathbf{r}')^2/4D_0t}, \tag{2.4}$$

$$M(\mathbf{k},t)=e^{-D_0k^2t}. \tag{2.5}$$

In a fluid-filled porous medium, these functions have a much more complicated shape, but they always have simple expansions in terms of the diffusion eigenstates

$$G(\mathbf{r},\mathbf{r}',t)=\frac{1}{V_p}\sum_{\lambda}\,e^{-\lambda t}\psi_\lambda(\mathbf{r})\psi_\lambda^*(\mathbf{r}'), \tag{2.6}$$

$$M(\mathbf{k},t)=\sum_{\lambda}\,e^{-\lambda t}|\tilde{\psi}_\lambda(\mathbf{k})|^2, \tag{2.7}$$

where $\tilde{\psi}_\lambda(\mathbf{k})$ is the Fourier transform of $\psi_\lambda(\mathbf{r})$, restricted to the pore space V_p

$$\tilde{\psi}_\lambda(\mathbf{k})\equiv\frac{1}{V_p}\int_{V_p}dV\psi_\lambda(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{2.8}$$

The results of the previous section regarding low-lying eigenstates will now be used to determine the shape of $M(\mathbf{k},t)$ at long times t.

Assuming that there are $N_{\rm loc}$ localized states with eigenvalue $\lambda_{\rm loc}$, the contribution of those states to $M(\mathbf{k},t)$ is of order

$$\frac{N_{\rm loc}V_{\rm loc}}{V_p}e^{-\lambda_{\rm loc}t}. \tag{2.9}$$

A similar estimation of the contribution of the extended states leads to [see (1.14) and (1.15)]

$$e^{-\lambda_0 t}\sum_{|\mathbf{q}|\ll 1/a}e^{-(\lambda_\mathbf{q}-\lambda_0)t}|\tilde{\psi}_0(\mathbf{k}-\mathbf{q})|^2$$
$$=e^{-\lambda_0 t}\left[|\tilde{\psi}_0(\mathbf{0})|^2e^{-(\lambda_\mathbf{k}-\lambda_0)t}+O\left(\frac{a^3}{\sqrt{t^3\det\hat{D}_e}}\right)\right]. \tag{2.10}$$

We conclude that, if $N_{\rm loc}V_{\rm loc}/V_p\ll 1$ then $M(\mathbf{0},t)$ is determined mostly by the low-lying extended states. Furthermore, if either $N_{\rm loc}V_{\rm loc}/V_p\ll a^3/\sqrt{t^3\det\hat{D}_e}$ or $t\gg 1/(\lambda_{\rm loc}-\lambda_0)$, then this continues to hold also for $M(\mathbf{k},t)$. We also conclude that the normalized PGSE amplitude $M(\mathbf{k},t)/M(\mathbf{0},t)$ is given by

$$\frac{M(\mathbf{k},t)}{M(\mathbf{0},t)}\cong e^{-(\lambda_\mathbf{k}-\lambda_0)t}>e^{-(\mathbf{k}\cdot\hat{D}_e\cdot\mathbf{k})t} \tag{2.11}$$

for $a|\mathbf{k}|\ll 1$ and $(\det\hat{D}_e)^{1/3}t\gg a^2$. This means that the decrease of $M(\mathbf{k},t)$ with increasing $|\mathbf{k}|$ is less pronounced than one would expect just from the value of $\hat{D}_e$—this is in agreement with numerical calculations [8–10]. As $\mathbf{k}\to 0$, the decay rate $\lambda_\mathbf{k}-\lambda_0$ in Eq. (2.11) tends to its upper bound $\mathbf{k}\cdot\hat{D}_e\cdot\mathbf{k}$.

A comparison of this result with Eq. (2.5) permits us to identify $\hat{D}_e$ as the tensor of bulk effective stationary diffusion coefficients. The relation between $\hat{D}_e$ and $\hat{\sigma}_e$, which was derived earlier [see Eq. (1.26)], provides an alternative route for calculating $\hat{D}_e$—one that differs from the straightforward evaluation of the low-lying eigenstates which was used in Ref. [9].

In periodic systems with cubic symmetry, as well as in random porous media, it was found in calculations that, for small $\mathbf{k}$ and arbitrary times, the ratio $M(\mathbf{k},t)/M(\mathbf{0},t)$ is well described by a Gaussian shape with a *time-dependent* effective diffusion coefficient $D(t)$ [17,18,8–10]

$$\frac{M(\mathbf{k},t)}{M(\mathbf{0},t)}\cong e^{-D(t)k^2t}, \tag{2.12}$$

where $D(0)=D_0$ and $D(\infty)=D_e<D_0$. (Note that, when the system has either cubic or isotropic rotational symmetry, $\hat{D}_e=D_e\hat{I}$ is a scalar tensor.) In all of those calculations, $D(t)$ was always found to decrease monotonically with time

towards D_e. However, the above discussion indicates that, under certain circumstances, $D(t)$ might undershoot this value, attaining a lower minimum value at some intermediate time [see Eq. (2.11) and the discussion surrounding it]. This prediction is still waiting to be tested either by an experiment or by a numerical computation of $D(t)$.

B. The return-to-the-origin probability

The fact that the low-lying eigenvalue band $\lambda_{\mathbf{q}}$ lies below its asymptotic quadratic form $\lambda_0+\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}$ has important consequences for the time-dependent relative return-to-the-origin probability (RTOP) of a surviving random walker in the pore space [12]

$$P_s(t|\rho)=\frac{(4\pi D_0 t)^{3/2}}{V_p}\frac{\sum_{\lambda} e^{-\lambda t}}{\sum_{\lambda}|\tilde{\psi}_{\lambda}(\mathbf{0})|^2 e^{-\lambda t}}. \tag{2.13}$$

This quantity is equal to the probability that a particle, which diffuses through the fluid-filled pore space with interface absorption, if it survives after a time t, has returned to its initial position, divided by the probability for a similar event in the uniform fluid, where there are no interfaces and hence no decay of the diffusing particle other than bulk decay in the fluid. Using the fact that for a uniform fluid the eigenfunctions are all plane waves,

$$\psi_{\lambda}(\mathbf{r})\to e^{i\mathbf{k}\cdot\mathbf{r}},\quad \lambda\to D_0 k^2, \tag{2.14}$$

it is easy to verify that Eq. (2.13) leads to $P_s(t|\rho)\equiv 1$ in that case. For other systems, short time asymptotics show that $P_s(t|\rho)$ starts out at 1 when $t=0$, and then increases as $\sqrt{t}$ for short times [12] ($\langle 1/R_1+1/R_2\rangle$ is the sum of reciprocal local radii of curvature of the interface, averaged over the interface)

$$P_s(t|\rho)=1+\frac{\sqrt{\pi}}{2}\frac{S}{V_p}(D_0 t)^{1/2}-\left[\frac{1}{3}\left\langle\frac{1}{R_1}+\frac{1}{R_2}\right\rangle+\frac{\rho}{D_0}\right]\times\frac{S}{V_p}(D_0 t)+O((D_0 t)^{3/2}). \tag{2.15}$$

The discussion in the previous subsection showed that the sum in the denominator of Eq. (2.13), which is just $M(\mathbf{0},t)$, is dominated by the extended states. The sum in the numerator has a contribution from the low-lying localized states, which can be estimated by

$$N_{\mathrm{loc}}e^{-\lambda_{\mathrm{loc}}t}, \tag{2.16}$$

as well as a contribution from the low-lying extended states, which is given by

$$\sum_{|\mathbf{q}|\ll 1/a} e^{-\lambda_{\mathbf{q}}t} > e^{-\lambda_0 t}V\int\frac{d^3q}{(2\pi)^3}e^{-(\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q})t} = \frac{Ve^{-\lambda_0 t}}{(4\pi t)^{3/2}\sqrt{\det\hat{D}_e}}. \tag{2.17}$$

It is easy to show that the terms that were discarded in order to derive this inequality are $O(a^2/(D_0 t))$ compared to the rhs (see Appendix). Furthermore, if either

$$N_{\mathrm{loc}}\sqrt{t^3\det\hat{D}_e}\ll V \tag{2.18}$$

or

$$t\gg\frac{1}{\lambda_{\mathrm{loc}}-\lambda_0}, \tag{2.19}$$

then the localized states make a negligible contribution. In that case we get

$$P_s(t|\rho)>\frac{1}{\phi}\left(\frac{D_0^3}{\det\hat{D}_e}\right)^{1/2}\frac{1}{|\tilde{\psi}_0(\mathbf{0})|^2}\geq\frac{1}{\phi}\left(\frac{D_0^3}{\det\hat{D}_e}\right)^{1/2}>1, \tag{2.20}$$

where $\phi\equiv V_p/V$ is the total volume fraction of pore space, and where we used the Cauchy-Schwartz inequality to get [equality holds only if $\psi_0(\mathbf{r})\equiv 1$, i.e., when $\rho=0$]

$$|\tilde{\psi}_0(\mathbf{0})|^2=\left|\frac{1}{V_p}\int_{V_p}dV\psi_0(\mathbf{r})\right|^2\leq\frac{1}{V_p}\int_{V_p}dV\psi_0^2(\mathbf{r})=1. \tag{2.21}$$

As $t\to\infty$, $P_s(t|\rho)$ tends to its long time lower bound of Eq. (2.20):

$$\lim_{t\to\infty}P_s(t|\rho)=\frac{1}{\phi}\left(\frac{D_0^3}{\det\hat{D}_e}\right)^{1/2}\frac{1}{|\tilde{\psi}_0(\mathbf{0})|^2}. \tag{2.22}$$

This result follows from Eq. (2.13) by noting that, as t approaches ∞, only the lowest-lying eigenstates contribute to the sums in both numerator and denominator, which can then be evaluated using Eqs. (1.25) and (1.28). The relative error is governed by the largest $\mathbf{q}$ that contributes significantly to those sums, and arises mostly from the use of Eq. (1.28) in the denominator. This leads to a relative error of order $O(a^3/(t^3\det\hat{D}_e)^{1/2})$, which tends to 0 as $t\to\infty$.

From Eq. (2.20), which holds for long times, and Eq. (2.15), which holds for short times, we conclude that $P_s(t|\rho)$ is a *nonmonotonic* function of t. At short times it increases and overshoots its long time asymptote, reaching a maximum value at some intermediate time, which must clearly lie between a^2/D_0 and $a^2/(\det\hat{D}_e)^{1/3}$, and then decreases towards $P_s(\infty|\rho)$. This behavior has been found recently both in experiments and in numerical calculations of $P_s(t|\rho)$ [13]. In that reference it was already shown that this kind of behavior must indeed occur in composites with a periodic microstructure of cubic symmetry and $\rho=0$. Here we have shown that this behavior can be expected to occur for *any type of porous medium*, whatever the microstructure and whatever the magnitude of ρ.

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APPENDIX

We first prove that any real diffusion eigenstate can have a local minimum (maximum) only at a point where its value is strictly negative (positive). To this end, let us first note that, for any function $\psi(\mathbf{r})$ that is twice differentiable inside a sphere of radius a surrounding the point $\mathbf{r}_0$, and for any twice differentiable function $f(\rho)$ that is nonzero only in a proper subsegment of $[0,a]$, we can use Green's theorem and integration by parts over ρ to show that

$$\int_{|\mathbf{r}-\mathbf{r}_0|<a} dV f(|\mathbf{r}-\mathbf{r}_0|)\nabla^2\psi(\mathbf{r}) = \int_0^a d\rho f(\rho)\frac{d}{d\rho}\rho^2\frac{d}{d\rho}\oint_{|\mathbf{r}-\mathbf{r}_0|=\rho} d\Omega\,\psi(\mathbf{r}). \tag{A1}$$

It follows that

$$\oint_{|\mathbf{r}-\mathbf{r}_0|=\rho} d\Omega\nabla^2\psi(\mathbf{r}) = \frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{d}{d\rho}\oint_{|\mathbf{r}-\mathbf{r}_0|=\rho} d\Omega\,\psi(\mathbf{r}). \tag{A2}$$

Denoting by $g_\lambda(\rho)$ the similar angular average of any solution of Eq. (1.3),

$$g_\lambda(\rho)\equiv \oint_{|\mathbf{r}-\mathbf{r}_0|=\rho}\frac{d\Omega}{4\pi}\psi_\lambda(\mathbf{r}), \tag{A3}$$

it follows that g_λ satisfies the $l=0$ spherical Bessel equation

$$D_0\frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{dg_\lambda}{d\rho}+\lambda g_\lambda=0. \tag{A4}$$

Since $g_\lambda(\rho)$ must be regular at $\rho=0$, therefore it must be equal, up to a constant factor, to the spherical Bessel function

$$j_0(x)=\left.\frac{\sin x}{x}\right|_{x=(\lambda/D_0)^{1/2}\rho}. \tag{A5}$$

Since $j_0(0)=1$, and $j_0(x)$ is a strictly positive and strictly decreasing function for $0<x<\pi/2$, it clearly follows that $\psi_\lambda(\mathbf{r})$ can have a minimum (maximum) at $\mathbf{r}_0$ only if $\psi_\lambda(\mathbf{r}_0)$ is strictly negative (positive).

We now derive the result (1.36) for $\lambda_\mathbf{q}$ by substituting the expression (1.16) for $\psi_\mathbf{q}$ in $F[\psi_\mathbf{q}]$ of Eq. (1.9), noting that $\psi_\mathbf{q}$ is not normalized, i.e. [the fact that the error here can be made as small as $o(q^4)$ and not merely $o(q^2)$ as one might have concluded from Eq. (1.16), is due to the possibility of adding an arbitrary constant to $\mathbf{q}\cdot\hat{f}\cdot\mathbf{q}$–see the discussion below],

$$\frac{1}{V_p}\int_{V_p} dV|\psi_\mathbf{q}|^2=\frac{1}{V_p}\int_{V_p} dV\psi_0^2(1+\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+o(q^4). \tag{A6}$$

In this way we get

$$\lambda_\mathbf{q}\frac{1}{V_p}\int_{V_p} dV|\psi_\mathbf{q}|^2=F[\psi_\mathbf{q}]=\frac{D_0}{V_p}\int_{V_p} dV\{(\nabla\psi_0)^2(1+\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+\psi_0^2[\nabla(\mathbf{q}\cdot\boldsymbol{\phi})]^2(1+2\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\psi_0^2[\nabla(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]^2$$
$$+2\psi_0\nabla\psi_0\cdot\nabla(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})(1+\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\}+\frac{\rho}{V_p}\oint_{\partial V_p} dS\psi_0^2(1+\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+o(q^4)$$
$$=\frac{D_0}{V_p}\int_{V_p} dV(\nabla\psi_0)^2+\frac{\rho}{V_p}\oint_{\partial V_p} dS\psi_0^2 \tag{A7}$$

$$+\frac{D_0}{V_p}\int_{V_p} dV\{2(\nabla\psi_0)^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\psi_0^2[\nabla(\mathbf{q}\cdot\boldsymbol{\phi})]^2+2\psi_0\nabla\psi_0\cdot\nabla(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\}$$
$$+\frac{\rho}{V_p}\oint_{\partial V_p} dS\,2\psi_0^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q}) \tag{A8}$$

$$+\frac{D_0}{V_p}\int_{V_p} dV\{(\nabla\psi_0)^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+2\psi_0^2[\nabla(\mathbf{q}\cdot\boldsymbol{\phi})]^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\psi_0^2[\nabla(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]^2$$
$$+2\psi_0\nabla\psi_0\cdot\nabla(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\}+\frac{\rho}{V_p}\oint_{\partial V_p} dS\psi_0^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2 \tag{A9}$$

$$+o(q^4), \tag{A10}$$

where Eqs. (A7)–(A10) represent terms of order q^0, q^2, q^4, and $o(q^4)$, respectively. The expression in (A7) is clearly equal to λ_0. The expressions in Eq. (A8) can be transformed by using Green's theorem, (1.3), (1.4), (1.18)–(1.21), (1.26), and the fact that $\hat{f}$ is either periodic or vanishes at $\partial V_{\rm ex}$, to yield

$$\frac{D_0}{V_p}\int_{V_p} dV\{-2\psi_0(\nabla^2\psi_0)(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})]^2\}=\frac{\lambda_0}{V_p}\int_{V_p} dV\psi_0^2 2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}. \tag{A11}$$

Similar transformations, applied to the expressions in Eq. (A9), lead to

$$\begin{aligned}
&\frac{D_0}{V_p}\int_{V_p} dV\{-\psi_0\nabla^2\psi_0(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+2\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})]^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]^2\}\\
&\quad=\frac{\lambda_0}{V_p}\int_{V_p} dV\psi_0^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+\frac{\lambda_{\mathbf{q}}-\lambda_0}{V_p}\int_{V_p} dV\psi_0^2 2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+\frac{1}{V_p}\int_{V_p} dV\{2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]+\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]^2\}\\
&\quad=\frac{\lambda_0}{V_p}\int_{V_p} dV\psi_0^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+\frac{\lambda_{\mathbf{q}}-\lambda_0}{V_p}\int_{V_p} dV\psi_0^2 2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})-\frac{1}{V_p}\int_{V_p} dV\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]^2\\
&\quad=\frac{\lambda_0}{V_p}\int_{V_p} dV\psi_0^2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})^2+\frac{\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}}{V_p}\int_{V_p} dV\psi_0^2 2(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})-E^{(e)}_{\alpha\beta\gamma\omega}q_\alpha q_\beta q_\gamma q_\omega+o(q^4),
\end{aligned} \tag{A12}$$

where $\hat{E}_e$ is given by Eq. (1.37). Using Eq. (A6) we finally get the result of Eq. (1.36).

We now show that the errors in Eqs. (1.16) and (1.17) are actually smaller than the estimates quoted for them in those equations.

To that end, we try the following expansions in powers of $q\equiv|\mathbf{q}|$ for the eigenfunction $\psi_{\mathbf{q}}(\mathbf{r})$ and eigenvalue $\lambda_{\mathbf{q}}$:

$$\psi_{\mathbf{q}}(\mathbf{r})=\psi_0(\mathbf{r})\exp[i\mathbf{q}\cdot\boldsymbol{\phi}(\mathbf{r})+iq_\alpha q_\beta q_\gamma\omega_{\alpha\beta\gamma}(\mathbf{r})]\cdot[1+\mathbf{q}\cdot\hat{f}\cdot\mathbf{q}+q_\alpha q_\beta q_\gamma q_\omega g_{\alpha\beta\gamma\omega}(\mathbf{r})], \tag{A13}$$

$$\lambda_{\mathbf{q}}=\lambda_0+\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}+\lambda_3+\lambda_4, \tag{A14}$$

where $\lambda_3=O(q^3)$ and $\lambda_4=O(q^4)$ are real, and the functions $\hat{f}(\mathbf{r})$, $\hat{g}(\mathbf{r})$ must be bounded, while $\mathrm{Im}[\boldsymbol{\phi}(\mathbf{r})]$, $\mathrm{Im}[\hat{\omega}(\mathbf{r})]$ must be bounded from below, because $\psi_{\mathbf{q}}(\mathbf{r})$ is bounded. The functions $\boldsymbol{\phi}(\mathbf{r})$, $\hat{\omega}(\mathbf{r})$ are kept in the exponent, which is *not expanded* in powers of $\mathbf{q}$. In the case of $\boldsymbol{\phi}$ this is necessary, because that function is unbounded. We shall see below that $\hat{f}$, $\hat{\omega}$, $\hat{g}$ are all bounded, but we nevertheless keep $\hat{\omega}$ in the exponent too, without expanding, for reasons of convenience.

Substituting these expansions in Eqs. (1.3), (1.4), and satisfying those equations order by order in q, we get the following equations that must be satisfied in V_p or on ∂V_p, respectively:

$$q^0{:}\,D_0\nabla^2\psi_0+\lambda_0\psi_0=0,\quad D_0\frac{\partial\psi_0}{\partial n}+\rho\psi_0=0, \tag{A15}$$

$$q^1{:}\,\boldsymbol{\nabla}\cdot[\psi_0^2\nabla(\mathbf{q}\cdot\boldsymbol{\phi})]=0,\quad \frac{\partial\boldsymbol{\phi}}{\partial n}=0, \tag{A16}$$

$$q^2{:}\,\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]=\psi_0^2\{[\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})]^2-\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}\},\quad \frac{\partial\hat{f}}{\partial n}=0, \tag{A17}$$

$$q^3{:}\,\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(q_\alpha q_\beta q_\gamma\omega_{\alpha\beta\gamma})]+2\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})\cdot\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})=i\lambda_3\psi_0^2,\quad \frac{\partial\hat{\omega}}{\partial n}=0, \tag{A18}$$

$$q^4{:}\,\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(q_\alpha q_\beta q_\gamma q_\omega g_{\alpha\beta\gamma\omega})]=\psi_0^2\{([\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})]^2-\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q})(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})+2\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})\cdot\boldsymbol{\nabla}(q_\alpha q_\beta q_\gamma\omega_{\alpha\beta\gamma})-\lambda_4\},\quad \frac{\partial\hat{g}}{\partial n}=0. \tag{A19}$$

The first pair of equations (A15) identifies ψ_0, λ_0 as the ground-state quantities, while Eqs. (A16), (A17) are essentially the same as Eqs. (1.18)–(1.21). These equations must be supplemented by boundary conditions at the external surface $\partial V_{\rm ex}$ for the various functions. In a large system, the boundary condition for $\psi_{\mathbf{q}}$ or ψ_0 can be any macroscopically uniform boundary condition—we usually choose periodic boundary conditions. A boundary condition for $\boldsymbol{\phi}$ that is consistent with this, as well as with Eq. (1.23), is

$$\boldsymbol{\phi}(\mathbf{r})-\mathbf{r}=(\text{periodic for } \mathbf{r}\in\partial V_{\rm ex}). \tag{A20}$$

This determines $\boldsymbol{\phi}(\mathbf{r})$ as a real vector function up to an unimportant additive constant.

In order to ensure that $\hat{f}(\mathbf{r})$ is bounded, we must require that the rhs of the first equation of (A17) vanish when averaged over the pore space—this leads to the result (1.26) for $\hat{D}_e$. It is also convenient and consistent to impose periodic boundary conditions on $\hat{f}(\mathbf{r})$:

$$\hat{f}(\mathbf{r})=(\text{periodic for } \mathbf{r}\in\partial V_{\rm ex}). \tag{A21}$$

These conditions determine $\hat{f}(\mathbf{r})$ as a real tensor function up to an arbitrary additive constant tensor. They also lead to the result that the second term on the left-hand side of the first equation of (A18) vanishes when averaged: using Green's theorem we get

$$\begin{aligned}\int_{V_p} dV\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})\cdot\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})&\\ =-\int_{V_p} dV(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi})]&\\ +\left[\oint_{\partial V_p}+\oint_{\partial V_{\rm ex}}\right]dS\psi_0^2\frac{\partial(\mathbf{q}\cdot\boldsymbol{\phi})}{\partial n}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q}).&\end{aligned} \tag{A22}$$

Here the integrands of the first and second integrals on the rhs vanish according to Eq. (A16), while the integrand of the third integral vanishes due to Eqs. (A20) and (A21). In order that $\mathrm{Im}\hat{\omega}$ be bounded from below, we must have $\lambda_3=0$. If we also impose upon $\hat{\omega}$ the periodic boundary condition

$$\hat{\omega}(\mathbf{r})=(\text{periodic for } \mathbf{r}\in\partial V_{\rm ex}), \tag{A23}$$

then $\hat{\omega}$ will be a bounded real function, determined up to an unimportant additive constant. As another consequence of this boundary condition, the second term in the curly brackets on the rhs of the first equation of (A19) can be shown to vanish when averaged, in the same way that we obtained Eq. (A22):

$$\begin{aligned}\int_{V_p} dV\psi_0^2\boldsymbol{\nabla}\boldsymbol{\phi}\cdot\boldsymbol{\nabla}\hat{\omega}=-\int_{V_p} dV\hat{\omega}\boldsymbol{\nabla}\cdot(\psi_0^2\boldsymbol{\nabla}\boldsymbol{\phi})&\\ +\left[\oint_{\partial V_p}+\oint_{\partial V_{\rm ex}}\right]dS\psi_0^2\frac{\partial\boldsymbol{\phi}}{\partial n}\hat{\omega}=0.&\end{aligned} \tag{A24}$$

Using Eq. (A17), the first term in those same curly brackets can be rewritten as $(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]$. This means that if we added some constant f_0 to $\mathbf{q}\cdot\hat{f}\cdot\mathbf{q}$, then that would lead to the replacement of $q_\alpha q_\beta q_\gamma q_\omega g_{\alpha\beta\gamma\omega}$ by $q_\alpha q_\beta q_\gamma q_\omega g_{\alpha\beta\gamma\omega}+f_0(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})$. Thus, we can determine f_0 by demanding that

$$\int_{V_p} dV\psi_0^2\hat{g}=0. \tag{A25}$$

If we use this option, then the normalization of $\tilde{\psi}_{\mathbf{q}}$ will satisfy Eq. (A6).

Turning again to (A19), we can ensure that $\hat{g}$ is bounded by choosing λ_4 so as to make the rhs of the first equation vanish when averaged. Using the last result together with (A17), we get

$$\begin{aligned}\lambda_4&=\frac{1}{V_p}\int_{V_p} dV(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})\boldsymbol{\nabla}\cdot[\psi_0^2\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]\\ &=-\frac{1}{V_p}\int_{V_p} dV\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\hat{f}\cdot\mathbf{q})]^2\\ &=-E^{(e)}_{\alpha\beta\gamma\omega}q_\alpha q_\beta q_\gamma q_\omega.\end{aligned} \tag{A26}$$

From the above results, it is clear that the errors in Eqs. (1.16) and (1.17) are in fact $O(q^3)$, $O(q^4)$, respectively, and that in (1.36) the error is $o(q^4)$, as stated there.

It is curious that $\lambda_{\mathbf{q}}$ is an even function of $\mathbf{q}$, at least up to $O(q^4)$. This symmetry is also reflected in the eigenfunction (A13), where $\mathrm{Re}\psi_{\mathbf{q}}$ is even and $\mathrm{Im}\psi_{\mathbf{q}}$ is odd in $\mathbf{q}$ up to $O(q^4)$. The reason for this behavior is unclear. In particular, inversion symmetry was not assumed to hold and therefore $\psi_{\mathbf{q}}(\mathbf{r})$ does not, in general, exhibit any symmetry under space inversion $\mathbf{r}\to-\mathbf{r}$.

In order to prove the inequality (1.27), we note that $\boldsymbol{\phi}(\mathbf{r})$ can also be found by minimizing the functional

$$G_{\mathbf{q}}[\boldsymbol{\phi}']\equiv\frac{1}{V_p}\int_{V_p} dV\psi_0^2[\boldsymbol{\nabla}(\mathbf{q}\cdot\boldsymbol{\phi}')]^2 \tag{A27}$$

over all vector functions $\boldsymbol{\phi}'(\mathbf{r})$ that have square integrable first derivatives and satisfy either Eq. (A20) or Eq. (1.22) as a boundary condition. The minimum value of $G_{\mathbf{q}}[\boldsymbol{\phi}']$ is then given by $G_{\mathbf{q}}[\boldsymbol{\phi}]=\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}$. Using $\boldsymbol{\phi}'(\mathbf{r})\equiv\mathbf{r}$ as trial function, we get

$$\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q}\leq D_0G_{\mathbf{q}}[\mathbf{r}]=\frac{D_0q^2}{V_p}\int_{V_p} dV\psi_0^2=D_0q^2. \tag{A28}$$

In order to estimate the terms that were discarded on the rhs of Eq. (2.17), we reconsider the sum in that inequality, using (1.36) and (1.37):

$$\sum_{|\mathbf{q}|\ll 1/a} e^{-\lambda_{\mathbf{q}} t} \cong e^{-\lambda_0 t} V \int \frac{d^3q}{(2\pi)^3} e^{-(\mathbf{q}\cdot\hat{D}_e\cdot\mathbf{q})t}(1+E^{(e)}_{\alpha\beta\gamma\omega} q_\alpha q_\beta q_\gamma q_\omega t)$$

$$= \frac{V e^{-\lambda_0 t}}{(4\pi t)^{3/2}\sqrt{\det \hat{D}_e}} \left\{ 1 + \frac{1}{t} E^{(e)}_{\alpha\beta\gamma\omega} [(\hat{D}_e^{-1})_{\alpha\beta}(\hat{D}_e^{-1})_{\gamma\omega} + (\hat{D}_e^{-1})_{\alpha\gamma}(\hat{D}_e^{-1})_{\beta\omega} + (\hat{D}_e^{-1})_{\alpha\omega}(\hat{D}_e^{-1})_{\beta\gamma}] \right\}$$

$$= \frac{V e^{-\lambda_0 t}}{(4\pi t)^{3/2}\sqrt{\det \hat{D}_e}} \left\{ 1 + O\left(\frac{a^2}{D_0 t} \right) \right\}. \tag{A29}$$

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