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Dispersion Resulting from Flow through Spatially Periodic Porous Media

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DISPERSION RESULTING FROM FLOW THROUGH SPATIALLY PERIODIC POROUS MEDIA

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CONTENTS

A rigorous theory of dispersion in both granular and sintered spatially-periodic porous media is presented, utilizing concepts originating from Brownian motion theory. A precise prescription is derived for calculating both the Darcy-scale interstitial velocity vector $\bar{\boldsymbol{v}}^*$ and dispersivity dyadic $\bar{\bar{\boldsymbol{D}}}^*$ of a tracer particle. These are expressed in terms of the local fluid velocity vector field $\boldsymbol{v}$ at each point within the interstices of a unit cell of the spatially periodic array and, for the dispersivity, the molecular diffusivity D of the tracer particle through the fluid.

Though the theory is complete, numerical results are not yet available owing to the complex structure of the local interstitial velocity field $\boldsymbol{v}$. However, as an illustrative exercise, the theory is shown to correctly reduce in an appropriate limiting case to the well-known Taylor–Aris results for dispersion in circular capillaries.

NOMENCLATURE

B	scalar component of vector $\boldsymbol{B}$ field
$\boldsymbol{B}$	vector field representing the solution of equation (5.6)
$\boldsymbol{B}_o$	non-convective vector $\boldsymbol{B}$ field
$\bar{\boldsymbol{B}}$	constant vector representing the mean value of the $\boldsymbol{B}$ field
c	local solute concentration
$\bar{c}$	mean or Darcy-scale solute concentration
C_{D}	drag coefficient
C_{L}	dimensionless longitudinal dispersion coefficient $= D_{\mathrm{L}}/\bar{v}l$
C_{T}	dimensionless transverse dispersion coefficient $= D_{\mathrm{T}}/\bar{v}l$
$\boldsymbol{C}$	'concentration' vector
d	sphere diameter
D	molecular diffusivity of tracer
D_{L}	longitudinal dispersivity component
D_{T}	transverse dispersivity component
$\mathrm{D}/\mathrm{D}t$	material derivative

$\bar{\boldsymbol{D}}^*$, $\bar{D}^*_{ij}$	dispersion dyadic or tensor
Exp	denotes terms of exponentially small order in time as $t \to \infty$
$\boldsymbol{f}(\boldsymbol{R})$	local tensor field
$\bar{\boldsymbol{f}}(\bar{\boldsymbol{R}})$	Darcy-scale tensor field
F	force on a sphere
$\boldsymbol{F}$	arbitrary local tensor field
$\bar{\boldsymbol{G}}$	constant Darcy-scale tensor representing a macroscopic gradient
$\breve{\boldsymbol{H}}$	arbitrary spatially periodic tensor field
$\boldsymbol{I}$	dyadic idemfactor
$\boldsymbol{j}$	solute flux vector for diffusive transport
$\boldsymbol{J}$	flux vector of probability density
l	characteristic linear length scale of a unit cell
$\boldsymbol{l}_j$	basic lattice vector ($j = 1, 2, 3$)
L_j	lattice point
$\overline{m}$	number of solute molecules in a unit cell
$\boldsymbol{M}_m$	mth total m-adic moment
n_j	integer taking on any positive or negative value, including zero ($j = 1, 2, 3$)
$\{\boldsymbol{n}\}$	refers to the 'coordinates' of the nth cell $= \{n_1, n_2, n_3\}$
N	number of solute molecules in the entire porous medium
o	origin of a local coordinate system within a unit cell
O	origin of a global coordinate system defined on the whole porous medium
$\{\boldsymbol{0}\}$	refers to centre of 'zero' unit cell
p	pressure field
P_j	point lying on the face s_j of a unit cell ($j = \pm 1, \pm 2, \pm 3$)
Pe	Péclet number $= \bar{v}l/D$
$P(\boldsymbol{R}, t \mid \boldsymbol{R}')$ or $P(\boldsymbol{R}_n, \boldsymbol{r}, t \mid \boldsymbol{R}'_n, \boldsymbol{r}')$	probability density for the instantaneous position of a Brownian tracer particle
q_j	volumetric flow rate of fluid or solute transport rate through face s_j of a unit cell
$\mathrm{d}q_\nu$	differential volumetric flow rate through a directed surface element possessing a unit normal vector $\boldsymbol{\nu}$
$\mathrm{d}\bar{q}_j$	Darcy-scale differential volumetric flow rate $= q_j$
(r, ϕ, z)	circular cylindrical coordinates
r_0	capillary tube radius
$\boldsymbol{r}$	local position vector within a unit cell
$\boldsymbol{r}'$	initial local position vector of tracer corpuscle
$\hat{\boldsymbol{r}}$	unit radial vector in circular cylindrical coordinates
$\mathrm{d}^3\boldsymbol{r}$	differential volume element within a unit cell
Re	Reynolds number
$\boldsymbol{R}$	global position vector in the porous medium
$\boldsymbol{R}'$	initial global position vector of tracer corpuscle
$\bar{\boldsymbol{R}}$	Darcy-scale position vector or centroid of a unit cell
$\boldsymbol{R}_n$	position vector of a lattice point
$\mathrm{d}^3\boldsymbol{R}$	differential global volume element
$\mathrm{d}\bar{\boldsymbol{R}}$	displacement vector between two adjacent lattice points
$\mathrm{d}^3\bar{\boldsymbol{R}}$	superficial volume of a unit cell

$\overline{\Delta \boldsymbol{R}}$	mean displacement vector of a Brownian corpuscle from its initial position
s_j	face of a unit cell ($j = \pm 1, \pm 2, \pm 3$)
s_{p}	wetted particle surface within a unit cell
$\boldsymbol{s}_j$	directed area of face s_j of a unit cell
$\mathrm{d}s$	scalar element of surface area
$\mathrm{d}\boldsymbol{s}$	directed vector element of surface area $= \boldsymbol{\upsilon}\,\mathrm{d}s$
$\mathrm{d}\bar{\boldsymbol{s}}_j$	Darcy-scale differential directed surface element $= \boldsymbol{s}_j$
$\mathrm{d}\boldsymbol{s}_\upsilon$	directed vector areal element possessing a unit normal $\boldsymbol{\upsilon}$
t	time
$\boldsymbol{u}$	tensor-valued field possessing a spatially-periodic gradient
U	stream velocity
$\bar{\boldsymbol{U}}^*$	mean velocity vector of tracer corpuscle
v	local Poiseuille velocity at a point in a capillary tube
$\boldsymbol{v}$	local interstitial fluid velocity vector
$\bar{\boldsymbol{v}}$	Darcy-scale seepage velocity vector
$\bar{\boldsymbol{v}}^*$	mean interstitial fluid velocity vector
$\bar{v}^*$	magnitude of vector $\bar{\boldsymbol{v}}^*$
$\bar{V}$	mean Poiseuille velocity
$V_{f\infty}$	fluid volume within the entire porous medium
y_k	eigenfunction
$\hat{\boldsymbol{z}}$	unit vector parallel to tube axis
$\boldsymbol{\alpha}$, α_{ij}	3×3 matrix with integer elements
δ	Dirac delta function
δ_{ij}	Kronecker delta
$\delta_{\boldsymbol{nn}'}$	Kronecker delta for the pair of cells $\{\boldsymbol{n}\}$ and $\{\boldsymbol{n}'\}$
ϵ	porosity of porous medium $= \tau_{\mathrm{f}}/\tau_0$
θ_i	angle between the basic lattice vectors $\boldsymbol{l}_j$ and $\boldsymbol{l}_k$, or the angle between the basic lattice vector $\boldsymbol{l}_i$ and the direction of mean flow
λ_k	eigenvalues
$\boldsymbol{\lambda}$	constant unit vector pointing in the direction of the mean flow
$\boldsymbol{\mu}_m$	mth local m-adic moment
ν	kinematic viscosity
ρ	fluid density
τ_0	superficial volume of a unit cell
τ_{f}	fluid domain within a unit cell
τ_{p}	particle domain within a unit cell
$\partial\tau_0$	external boundary of a unit cell, composed of its six faces
$\boldsymbol{\upsilon}$	unit normal vector to a surface
$\boldsymbol{\chi}$	arbitrary constant vector
∇	gradient operator
$\bar{\nabla}$	Darcy-scale gradient operator
$[\![\ ]\!]$	difference between the values of a function at equivalent points on opposite faces of a unit cell
$\oint$	integral over a closed surface bounding the fluid domain τ_{f}
$\dagger$	transposition operator

Marks over symbols

$-$ mean value or Darcy-scale function

$\smile$ denotes a spatially periodic function

$\wedge$ denotes a unit vector

1. Introduction

This contribution is devoted to the kinematics of flow and dispersion in porous media whose geometric structure is spatially periodic. Dispersion theory is concerned with the asymptotic time-dependent, spatial distribution of a passive tracer corpuscle introduced into a fluid flowing through the interstices of a porous medium under the influence of an externally applied pressure gradient. The primary aim of such theories is to predict the mean velocity with which the tracer moves,† and the dispersion about this mean, in terms of the fundamental physical parameters characterizing the transport system. These include the molecular diffusivity D of the tracer, the Darcy-scale seepage velocity vector $\bar{\boldsymbol{v}}$ of the flowing fluid, the kinematical and rheological properties of the fluid, and the geometry of the porous medium – especially its porosity ϵ and characteristic interstitial length scale l. Typically, the latter may be taken to be the mean particle size for unconsolidated or granular porous media, or the mean pore size for consolidated or capillary media.

Our approach to this subject will be modelled after the pioneering work of G. I. Taylor (1953, 1954*a*, *b*) on dispersion in cylindrical capillaries, by using the moment-analysis techniques introduced by Aris (1956), as subsequently extended and embedded in a much broader context by Horn (1971). Extensive reviews of the current state-of-the-art of dispersion theories are available (Bear 1969, 1972, Fried & Combarnous 1971, Whitaker 1966, 1967, 1969, 1971, 1973), including critical analyses of pertinent experimental data (de Ligny 1970, Edwards & Richardson 1968, Gunn 1969, Gunn & De Souza 1974, Gunn & England 1971, Gunn & Khalid 1975, Gunn & Pryce 1969, Urban & Gomezplata 1969, Vortmayer 1975, Votruba *et al.* 1972).

Since porous media are often modelled geometrically by so-called capillary models of the interstitial space, it might be expected that the Taylor–Aris theory would play an important quantitative role in rationalizing and correlating experimental observations of dispersion phenomena in porous media. Surprisingly, such is not the case. Rather, most theories (Aris & Amundson 1957, Bear 1969, 1972, Beran 1968, de Jong 1958, 1972, Saffman 1959*a*, *b*, 1960, Scheidegger 1963, Simpson 1969) of dispersion in such media tend to be of a much less rigorous nature, beginning as they generally do with *a priori*, *ad hoc*, random-walk or mixing-cell assumptions applied to a tracer particle, rather than with the fundamental convective-diffusion equation applied locally at each point within the interstitial fluid (Fried & Combarnous 1971, Gunn 1969, Rumer 1972, Whitaker 1966, 1967, 1969, 1971, 1973).

Apart from the complex interstitial geometrical characteristics of porous media, perhaps the major obstacle impeding application of the Taylor–Aris theory to such media lies in the fact that their mode of analysis is apparently restricted to fluid motions that are locally unidirectional; that is, where the local fluid velocity vector $\boldsymbol{v}$ is everywhere parallel to the mean fluid velocity vector $\bar{\boldsymbol{v}}$, as it is for the case of Poiseuille flow in a capillary tube. This condition does not obtain for flow through porous media, where the streamlines around the individual particles are

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† In ordinary circumstances the mean velocity of the tracer is identical to that of the fluid. However, situations exist (Brenner & Gaydos 1977) for which this is not true.

curvilinear rather than rectilinear, and therefore not generally locally parallel at each interstitial point to the Darcy-scale seepage velocity vector $\bar{\boldsymbol{v}}$.

A rigorous theory, on a par with that of Taylor–Aris, is herein presented for dispersion in *spatially-periodic* porous media. The conceptual basis for the subsequent analysis of such ordered arrays is implicit in Horn's (1971) general analysis of dispersion processes. Time and space constraints permit only a summary outline of the essential ideas. Detailed proofs, and generalizations to more complex dispersion phenomena in such media, including comparable *dynamical* studies, are available in a forthcoming monograph (Brenner 1981). Numerical results must await the detailed solutions of the boundary-value problems posed by the present theory, though some comments are offered at the conclusion of this paper on the anticipated structure of the results.

It is to be hoped that the results deduced here for the ordered model will find also application in practical situations involving disordered media. The latter are more frequently encountered in nature and industry than are ordered porous media.

Too often (Bear 1972, Beran 1968, Hashin 1970, Scheidegger 1963) so-called 'random' or 'statistical' mathematical models of such disordered media are regarded as being synonomous with the physical media themselves, merely because the latter appear to possess a complex geometric structure. This apparent confusion between complexity and randomness is unfortunate since to the best of my knowledge there exists no compelling empirical evidence that real porous media, or ensembles thereof, are random in structure. Indeed, most practitioners would be hard pressed to devise an unequivocal experimental test of randomness.

It is in this spirit of unbiased scientific inquiry that the concept of a perfectly ordered medium is advanced as representing one extreme mathematical model of a porous medium. Random models of perfectly disordered media lie at the opposite extreme. Which model, if either, best captures the essence of a given physical medium or ensemble can generally be rationally decided only by experimental observation and investigation, and not by any *a priori* appeal based upon the visual appearance of 'randomness' (complexity). Indeed, since examples of highly ordered porous media are found in nature, or are artificially created for specialized industrial or laboratory purposes, our model will clearly possess an *a priori* applicability to such systems. On the other hand, an equally casual inspection of a disordered medium could never logically lead one to the *a priori* conclusion that the medium was random. At best one may observe *a priori* that a porous medium is, or is not, spatially periodic. But this is not the same as saying that the system is random, nor even that a spatially periodic model will result in grossly erroneous predictions of transport properties in disordered systems. Thus, it may well be that our ordered model possesses practical utility even in circumstances where the porous medium to which the model is applied lacks any obvious geometrical order. Only experimental investigations can delineate bounds (or lack thereof) on the ability of the model to describe disordered systems.

2. GEOMETRICAL CHARACTERISTICS OF SPATIALLY PERIODIC POROUS MEDIA

Lattice geometry

Consider a three-dimensional granular (i.e. unconsolidated) porous medium, composed of a repetitive arrangement of rigid particles of any shape(s), extending indefinitely in every direction (figure 1). Such an array will be termed spatially periodic. The particles themselves need not possess any geometric symmetry elements. Though the particles in figure 1 are depicted, for simplicity, as not being in physical contact with each other, mechanical stability demands that the particles be in mutual contact, as in figure 2.

Attention will be focused on unconsolidated media, where the particulate solid phase is discontinuous. However, by means of an appropriate limiting process (Brenner 1981), typified by that suggested in figure 3 (with $\epsilon_i \to 0$), the results of the present analysis may also be applied to consolidated (capillary) media, where the solid phase is continuous, rather than discrete.

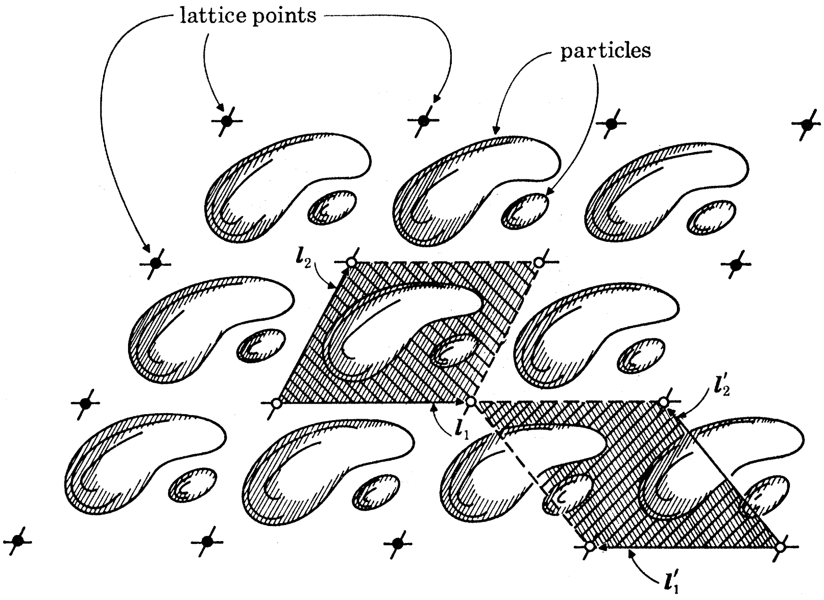

FIGURE 1. A two-dimensional spatially-periodic particle array. The spatially periodic character of the array is represented by the translational symmetry of the lattice points. The pair of planar basic vectors $(\boldsymbol{l}_1, \boldsymbol{l}_2)$ drawn between 'adjacent' lattice points forms a 'unit cell' in the shape of a parallelogram. Other choices, such as $(\boldsymbol{l}'_1, \boldsymbol{l}'_2)$, also qualify as a set of basic lattice vectors. These form a differently shaped unit cell, as shown. However, the magnitudes, $|\boldsymbol{l}_1 \times \boldsymbol{l}_2|$ and $|\boldsymbol{l}'_1 \times \boldsymbol{l}'_2|$, of the superficial unit cell areas are identical, as too are the respective particle and interstitial areas.

As is well known (Brillouin 1953, Hilton 1963, Sachs 1963), the principal geometric characteristic of a repetitive array is the existence of a group of translational symmetry operations, by means of which the repeating pattern may be brought into self coincidence. The translational symmetry of the array, expressing its invariance with respect to parallel displacements by definite amounts in definite directions, is represented geometrically by a three-dimensional lattice. This lattice consists of an infinite array of evenly spaced points (figure 1), such that the arrangement of particles appears the same, and in the same orientation, when viewed from each and every one of the lattice points.

The location $\boldsymbol{R}_n$ (figure 2) of each lattice point may be represented by one of the infinite set of position vectors,

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

with

$$n_j = 0, \pm 1, \pm 2, \pm 3, \ldots \quad (j = 1, 2, 3), \tag{2.2}$$

wherein $(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3)$ constitute a set of three non-coplanar vectors, termed basic lattice vectors. For a specified lattice, the set of basic lattice vectors is not unique. Rather, there exist infinitely many sets consistent with the specified translational symmetry of the lattice. The necessary and sufficient conditions that ($\boldsymbol{l}_1'$, $\boldsymbol{l}_2'$, $\boldsymbol{l}_3'$) (figure 1) constitute an alternative set of basic lattice vectors is that

$$\boldsymbol{l}_i' = \sum_{j=1}^{3} \alpha_{ij}\,\boldsymbol{l}_j \quad (i = 1, 2, 3), \tag{2.3}$$

wherein the nine scalar elements of the 3×3 $\boldsymbol{\alpha}$ matrix are any positive or negative integers, including zero, such that

$$\det \boldsymbol{\alpha} = \pm 1. \tag{2.4}$$

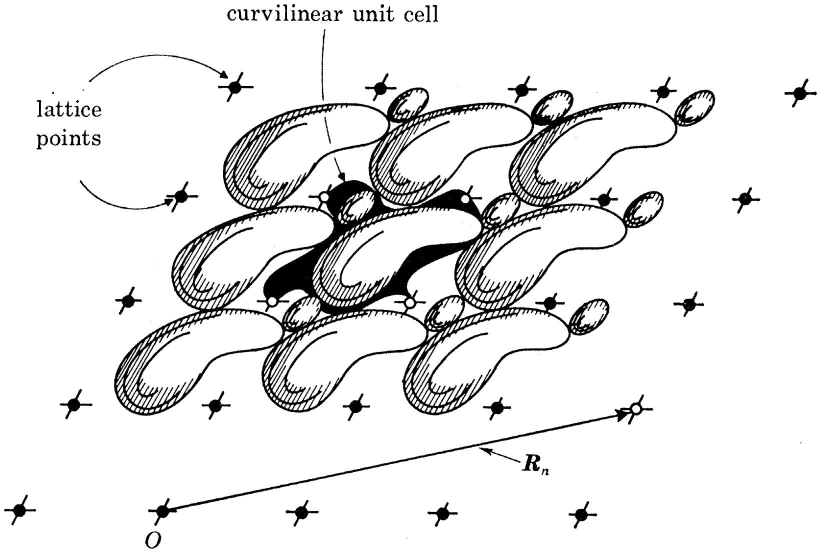

FIGURE 2. A two-dimensional spatially periodic array of particles in mutual physical contact. In general, it is not possible to construct a parallelogram-shaped unit cell whose boundaries do not pass through the interior(s) of the particle(s). A possible curvilinear unit cell is shown, possessing the property that its external boundaries do not pass through the particle interior(s). Given a fixed origin O at any one of the lattice points, the location of every other lattice point can be specified by means of the position vector $\boldsymbol{R}_n$.

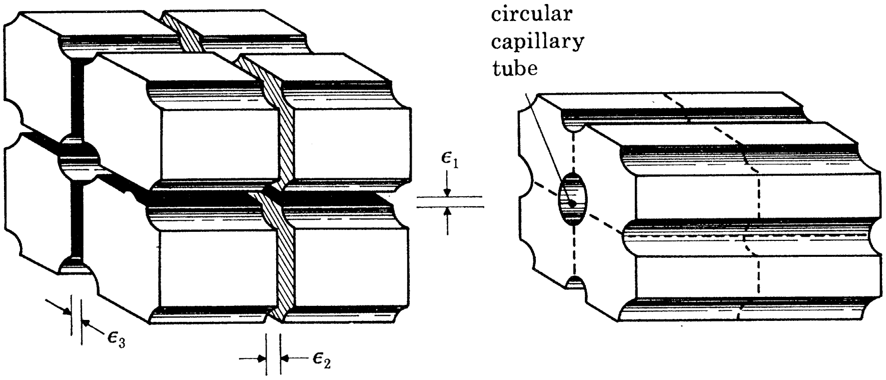

FIGURE 3. Formation of a spatially-periodic consolidated medium from a spatially periodic unconsolidated medium. By allowing the distances ϵ_1, ϵ_2 and ϵ_3 to tend to zero, the granular medium passes over to a system of parallel, circular cylindrical capillary tubes, arranged in a rectangular lattice. The solid phase is then continuous. Though the system of horizontal capillary tubes are disconnected from one another, they can be connected together by drilling circular vertical holes. In such circumstances, both the particulate and fluid phases (filling the interstices) will each be separately continuous.

Parallelepipedal unit cells

The parallelepiped whose edges are formed from a set $(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3)$ of basic lattice vectors constitutes a (primitive) unit cell of the lattice. The entire spatially periodic array may then be represented by such a set of identical parallelepipeds, regularly packed. Each cell in the array will contain one or more particles (figure 1). No restrictions exist as to the number, size, shape, orientation, or relative arrangement of particles within any one cell. However, the contents of each cell are an exact replica of these of every other cell.

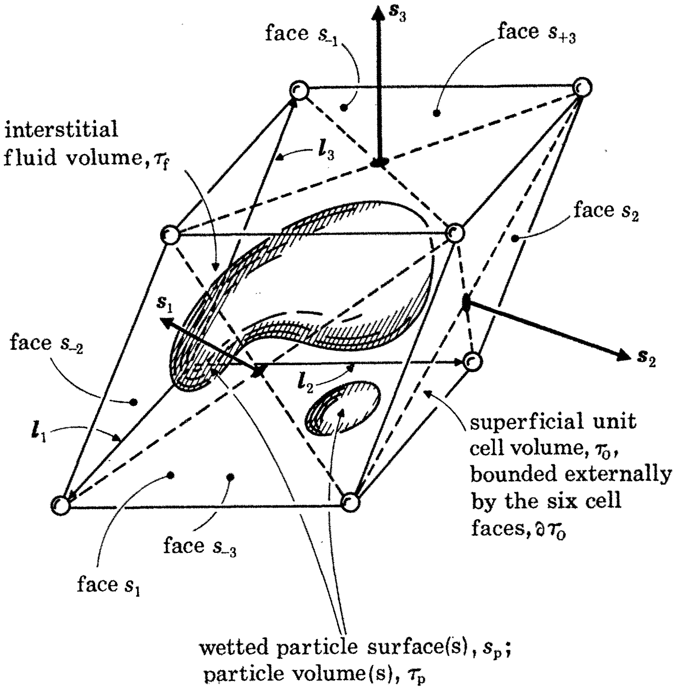

FIGURE 4. Unit cell of a spatially periodic array. The unit cell is a parallelepiped formed from the set of basic lattice vectors $(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3)$. The directed areal vectors $(\boldsymbol{s}_1, \boldsymbol{s}_2, \boldsymbol{s}_3)$ are normal to the respective faces, pointing out of the cell, and are equal in magnitude to the areas of the respective faces.

As in figure 4, the superficial region of space occupied by a unit cell will be denoted by τ_o. This same symbol will be utilized to represent the magnitude, $\tau_o = \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \times \boldsymbol{l}_3$, of the superficial unit cell volume. The external cell boundary $\partial\tau_o$ consists of the six cell faces, $s_{\pm j}$ $(j = 1, 2, 3)$. Thus, taken in pairs,

$$\partial\tau_o \equiv \sum_{j=1}^{3} s_{-j} \oplus s_{+j}. \tag{2.5}$$

The symbols τ_f and τ_p, respectively, will be used to denote the fluid and particle domains within a unit cell. Thus, $\tau_o \equiv \tau_f \oplus \tau_p$, or in terms of the magnitudes of the respective volumes, $\tau_o = \tau_f + \tau_p$. The porosity,

$$\epsilon = \tau_f / \tau_o, \tag{2.6}$$

of the unit cell is identical to that of porous medium as a whole. The (wetted) particle surface(s) within a unit cell are designated by the symbol s_p. This surface bounds the particle domain τ_p externally. Consequently, the fluid domain τ_f is bounded externally by $\partial\tau_o$ and internally by s_p.

For a specified decomposition of the porous medium into unit cells, the location of the nth cell in the array may be specified generically either by the position vector $\boldsymbol{R}_n$ or, equivalently, by the triplet of integers,

$$\{n_1, n_2, n_3\} \equiv \{\boldsymbol{n}\}, \quad \text{say.} \tag{2.7}$$

The affix $\{\boldsymbol{n}\}$ may be used as an argument to distinguish, where required, between comparable domains of different unit cells. Thus, for example, $\tau_f\{\boldsymbol{n}\}$ denotes the interstitial fluid domain within cell $\{\boldsymbol{n}\}$. Hence, if $V_{f\infty}$ represents the fluid domain for the entire porous medium,

$$V_{f\infty} \equiv \sum_{\boldsymbol{n}} \tau_f\{\boldsymbol{n}\}, \tag{2.8}$$

in which

$$\sum_{\boldsymbol{n}} \equiv \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty}. \tag{2.9}$$

As a consequence of the non-uniqueness of the basic lattice vectors, the spatial configuration of a unit cell is not unique for a specified lattice. Each of the infinitely many possible differently-shaped parallelepipedal unit cells, corresponding to the infinite multiplicity of choices for $(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3)$, is characterized by different edge lengths, $|\boldsymbol{l}_i|$ $(i = 1, 2, 3)$, and angles, $\theta_i = \arccos(\boldsymbol{l}_j \cdot \boldsymbol{l}_k / |\boldsymbol{l}_j|\,|\boldsymbol{l}_k|)$ $(i, j, k = \text{cycl.})$, between adjacent cell faces, as in figure 1. However, both the fluid and particle contents, τ_f and τ_p, are invariant to the choice made, as too is the superficial volume $\tau_o = \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \times \boldsymbol{l}_3 = \boldsymbol{l}'_1 \cdot \boldsymbol{l}'_2 \times \boldsymbol{l}'_3$ in consequence of equation (2.3) (Brenner 1981). The same is true of the porosity ϵ (Brenner 1981).

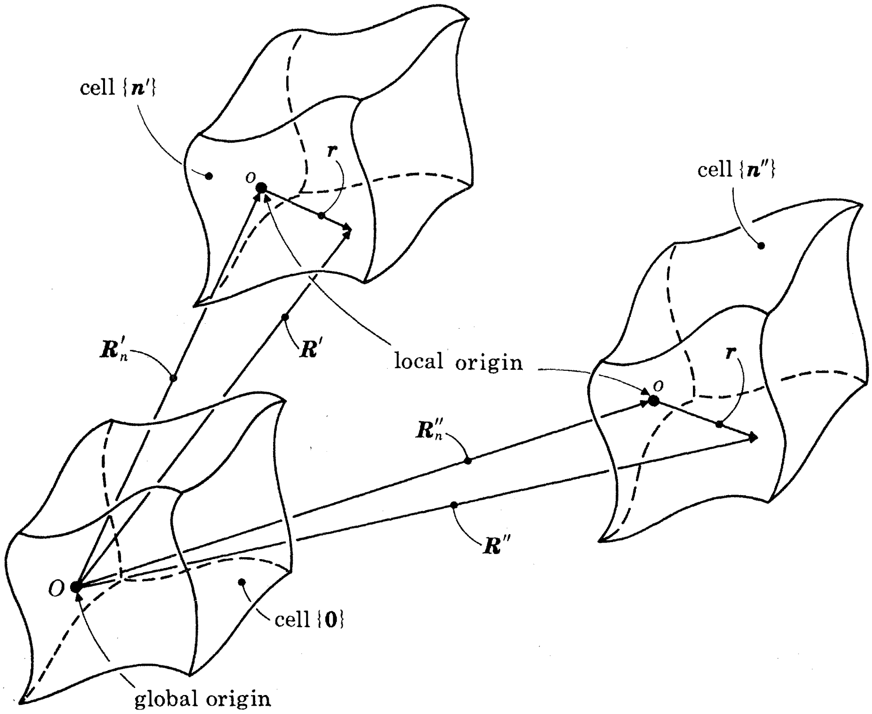

FIGURE 5. Global and local position vectors. O represents a fixed lattice point from which the global position vector $\boldsymbol{R}$ is drawn. This is also the origin from which the locations $\boldsymbol{R}_n$ of all other lattice points are measured. In the sketch, $\boldsymbol{R}' = \boldsymbol{R}'_n + \boldsymbol{r}$ and $\boldsymbol{R}'' = \boldsymbol{R}''_n + \boldsymbol{r}$, in which $\boldsymbol{R}'$ and $\boldsymbol{R}''$ are points lying within cells $\{\boldsymbol{n}'\}$ and $\{\boldsymbol{n}''\}$, respectively. The local position $\boldsymbol{r}$ is the same in both cells. For variety's sake, the lattice points have been shown as lying within the interiors of the unit cells, rather than at their vertices. This reflects the fact that the lattice points may all be displaced by the same (arbitrary) amount, and yet still qualify as lattice points, since the 'new' lattice possesses the same translational symmetry elements as does the 'original'.

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Elementary metrical properties

For a specified external cell shape $\partial\tau_o$, let $\boldsymbol{r}$ (figure 5) denote the *local* position vector of any interstitial point within the *n*th cell, relative to an arbitrary local origin 'o' within that cell. The (global) position vector $\boldsymbol{R}$ of that interstitial fluid point, relative to a globally-fixed origin O lying in any one of the cells (the 'zeroth' cell, $\{\boldsymbol{n}\} = \{\boldsymbol{0}\}$), may then be represented as

$$\boldsymbol{R} = \boldsymbol{R}_n + \boldsymbol{r}, \tag{2.10}$$

with $\boldsymbol{R} \in \tau_f\{\boldsymbol{n}\}$ and $\boldsymbol{r} \in \tau_f$.

For convenience, O and o may be regarded as 'equivalent' points with respect to their positions relative to the lattice.

The '*directed areas*' of the rectangular faces s_j ($j = \pm 1, \pm 2, \pm 3$) of a parallelepipedal unit cell can be represented by the set of areal vectors $(\boldsymbol{s}_1, \boldsymbol{s}_2, \boldsymbol{s}_3)$ (figure 4),

$$\boldsymbol{s}_1 = \boldsymbol{l}_2 \times \boldsymbol{l}_3, \quad \boldsymbol{s}_2 = \boldsymbol{l}_3 \times \boldsymbol{l}_1, \quad \boldsymbol{s}_3 = \boldsymbol{l}_1 \times \boldsymbol{l}_2, \tag{2.11}$$

along with $\boldsymbol{s}_{-j} = -\boldsymbol{s}_{+j}$. The magnitudes of these areal vectors correspond to the planar surface areas of the faces, whereas their directions lie parallel to the outward drawn normals to τ_o on $\partial\tau_o$.

Since $\tau_o = \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \times \boldsymbol{l}_3$, it readily follows that the vectors $\boldsymbol{l}_i$ are *reciprocal* to the $\boldsymbol{s}_j$, in the sense that

$$\boldsymbol{l}_i \cdot \boldsymbol{s}_j = \delta_{ij}\,\tau_o \quad (i; j = 1, 2, 3), \tag{2.12}$$

with δ_{ij} the Kronecker delta.

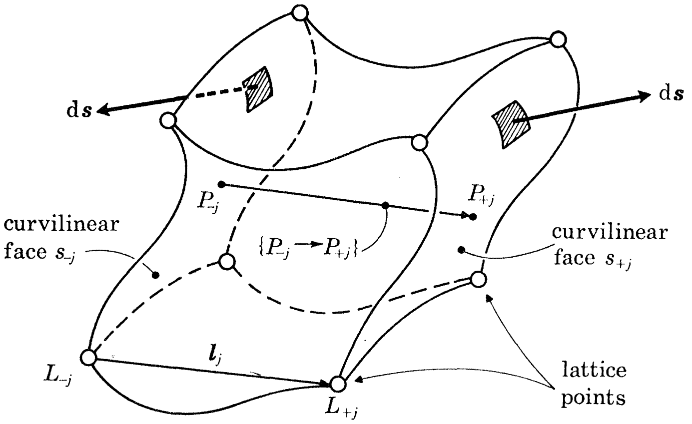

FIGURE 6. Curvilinear unit cell.

Curvilinear unit cells (figure 2)

It will prove convenient in subsequent calculations to use unit cells τ_o whose external boundaries $\partial\tau_o$ consist entirely of interstitial fluid points (except possibly for a set of points of zero measure, such as might arise from point contacts between particles in adjacent cells). This may be done by generally employing *curvilinear unit cells*, as in figure 6. Each such cell may be imagined to derive from the parallelepipedal unit cell with which it shares the same lattice points by congruously deforming each of the opposite pairs of parallelepipedal cell faces in such a manner that the external boundary $\partial\tau_o$ of the deformed cell does not pass through any particle interior.

Congruency is defined as follows: let L_{-j} and L_{+j} be a pair of adjacent lattice points, as in figure 6, such that $\{L_{-j} \rightarrow L_{+j}\} = \boldsymbol{l}_j$. Let P_{-j} and P_{+j} be equivalent points on the opposite cell faces,

s_{-j} and s_{+j}, respectively. By 'equivalent' is explicitly meant equality of the vectors $\{L_{-j} \rightarrow P_{-j}\} = \{L_{+j} \rightarrow P_{+j}\}$. Opposing pairs of cell faces are then congruent if, for each and every pair of equivalent points (P_{-j}, P_{+j}), the following vector equality holds:

$$\{P_{-j} \rightarrow P_{+j}\} = \boldsymbol{l}_j, \tag{2.13}$$

with $\boldsymbol{l}_j$ the appropriate basic lattice vector.

Such curvilinear unit cells do not possess a unique shape for two reasons: (i) the parallelepipedal unit cell from which it derives is not unique; (ii) even for a prescribed parallelepipedal cell shape (i.e. fixed values of $(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3)$), there exist an infinite variety of ways in which the external curvilinear cell boundaries $\partial\tau_o$ may be drawn so as to lie entirely in the fluid (see, for example, figure 9). Despite the variety of possible curvilinear cell shapes, all possess certain common features. In particular, the fluid and particle contents, τ_f and τ_p, of each such cell are identical to that of the parallelepipedal cell from which it derives by deformation, as is the superficial volume τ_o too (Brenner 1981). The same is true of the porosity ϵ.

Define the directed (projected) area of a curvilinear face s_j via the relation

$$\boldsymbol{s}_j \equiv \int_{s_j} \mathrm{d}\boldsymbol{s}, \tag{2.14}$$

with $\mathrm{d}\boldsymbol{s}$ a differential element of directed area on the curvilinear face s_j (figure 6), parallel to the local outer normal to the volume τ_o. As shown in the next paragraph, the vector area $\boldsymbol{s}_i$ is identical in both magnitude and direction to the corresponding planar directed area $\boldsymbol{l}_j \times \boldsymbol{l}_k$ (i, j, k cycl.) defined in equation (2.11). Hence, when making reference to the directed area of a cell face, no distinction need be drawn between the curvilinear and planar faces sharing the same four lattice points.

[That the curvilinear and planar cell faces, $\hat{s}_j$ and $\bar{s}_j$, respectively, sharing the same four lattice points, possess the same directed areas may be demonstrated as follows: For any closed surface S,

$$\oint_S \mathrm{d}\boldsymbol{s} = 0.$$

In combination, the pair of open surfaces $\hat{s}_j$ and $\bar{s}_j$ constitute a closed surface. Choose $S \equiv \bar{s}_j \oplus \hat{s}_j$ to obtain

$$\int_{\bar{s}_j} \mathrm{d}\boldsymbol{s} = \int_{\hat{s}_j} \mathrm{d}\boldsymbol{s},$$

upon making an appropriate change in the direction of $\mathrm{d}\boldsymbol{s}$ on $\bar{s}_j$. By definition, on $\bar{s}_j$, $\mathrm{d}\boldsymbol{s} = \bar{\boldsymbol{v}}\mathrm{d}s$ where $\bar{\boldsymbol{v}}$ is a constant unit normal vector on the plane independent of position on the face. Thus,

$$\int_{\bar{s}_j} \mathrm{d}\boldsymbol{s} = \bar{\boldsymbol{v}} \int_{\bar{s}_j} \mathrm{d}s = \bar{\boldsymbol{v}}\bar{s}_j = \bar{\boldsymbol{s}}_j,$$

from which equation (2.14) now follows. Q.E.D.]

In view of the existence of the infinitely dense set of allowable basic lattice vectors, it follows from equation (2.11) that the set of directed curvilinear areas $\boldsymbol{s}_j$ is also infinitely dense. In particular, given any arbitrarily specified direction $\boldsymbol{v}$ in space (with $\boldsymbol{v}$ a unit vector parallel to the given direction), it is always possible (Brenner 1981) to find a unit cell one of whose faces possesses an orientation $\boldsymbol{v}_j = \boldsymbol{s}_j / |\boldsymbol{s}_j|$ which is arbitrarily close to the specified orientation $\boldsymbol{v}$.

3. KINEMATICS OF FLOW

Let $\boldsymbol{v} \equiv \boldsymbol{v}(\boldsymbol{R})$ denote the local fluid velocity vector at any point $\boldsymbol{R}$ in the interstices. Consider a situation involving the steady laminar flow of an incompressible fluid,

$$\nabla \cdot \boldsymbol{v} = 0, \tag{3.1}$$

through the interstices of a spatially-periodic porous medium composed of particles which are impervious to the passage of fluid through their surfaces:

$$\boldsymbol{\nu} \cdot \boldsymbol{v} = 0 \quad \text{on} \quad s_{\mathrm{p}}, \tag{3.2}$$

with $\boldsymbol{\nu}$ a unit normal vector on the particle surface(s). In particular, suppose that the mean flow velocity vector, defined as

$$\bar{\boldsymbol{v}} \equiv \frac{1}{\tau_0} \int_{\tau_{\mathrm{f}}\{\boldsymbol{n}\}} \boldsymbol{v}(\boldsymbol{R}) \, \mathrm{d}^3\boldsymbol{R}, \tag{3.3}$$

is constant throughout the entire porous medium; that is, it is independent of $\{\boldsymbol{n}\}$. As discussed in § 7, and in more detail elsewhere (Brenner 1981), the quantity $\bar{\boldsymbol{v}}$ thus defined represents the Darcy-scale seepage velocity vector. The value of the integral (3.3) which defines $\bar{\boldsymbol{v}}$ will be shown to be independent of the particular mode adopted for partitioning the space into unit cells; that is, it possesses the same value for all possible choices of parallelepipedal or curvilinear unit cells τ_0 consistent with the prescribed lattice.

The constancy of $\bar{\boldsymbol{v}}$ throughout the entire porous medium implies that the 'macroscopic' or Darcy-scale flow is rectilinear or unidirectional. This contrasts with the local or 'microscopic' flow $\boldsymbol{v}$, which is curvilinear. The constancy of the mean flow, coupled with the spatially periodic geometry of the porous medium, leads to the conclusion (Brenner 1981) that the local velocity field is itself spatially periodic, possessing the same periodicity $\boldsymbol{R}_n$ as the array. Explicitly,

$$\boldsymbol{v}(\boldsymbol{R}) = \boldsymbol{v}(\boldsymbol{R} + \boldsymbol{R}_n). \tag{3.4}$$

Equivalently, it may be concluded from equation (2.10) that

$$\boldsymbol{v} \equiv \boldsymbol{v}(\boldsymbol{r}). \tag{3.5}$$

In other words, the microscopic velocity field possesses the same value at equivalent points in every cell. This velocity is therefore of a local ($\boldsymbol{r}$), rather than global ($\boldsymbol{R}$), nature.

The analysis that follows does not require that the Reynolds number of the flow be small, nor even that the interstitial fluid be Newtonian as regards its rheological properties. Moreover, the direction of the prescribed mean rectilinear flow $\bar{\boldsymbol{v}}$ may possess any orientation relative to the 'crystallographic' axes of the lattice.

In the special case of a Newtonian fluid flowing at small (but not necessarily zero) Reynolds number, it can be shown (Brenner 1981) that the boundary-value problem posed by the Navier–Stokes and continuity equations, coupled with the condition (3.4) of spatial periodicity, and subject to the no-slip boundary condition $\boldsymbol{v} = 0$ on s_{p}, leads to a *unique* solution for any prescribed constant seepage velocity vector $\bar{\boldsymbol{v}}$ defined by equation (3.3). Thus, for a specified spatially periodic geometry, $\boldsymbol{v}(\boldsymbol{R})$ is uniquely determined at each point by $\bar{\boldsymbol{v}}$. (The corresponding local pressure field $p(\boldsymbol{R})$ is uniquely determined only to within an arbitrary additive constant, whose value is physically irrelevant for the incompressible fluids under consideration.)

4. Convective–diffusive phenomena

Probability density for the stochastic 'trajectory' of a tracer particle

Suppose that at time $t = 0$ a tracer corpuscle is instantaneously and passively introduced into the flowing fluid at some arbitrary interstitial position $\boldsymbol{R}'$. It is convenient to imagine that this tracer corpuscle consists of a single, neutrally buoyant, spherical Brownian particle (Brenner & Gaydos 1977) or 'solute molecule', having the effective dimensions of a point compared with the characteristic cell or pore size l. In general, such a particle will be convected, piggy-back fashion, by the interstitial fluid at a velocity $\boldsymbol{v}(\boldsymbol{R})$, where $\boldsymbol{R}$ denotes the instantaneous position occupied by the Brownian particle. Simultaneously, as a consequence of its Brownian movement, this tracer molecule will undergo translational diffusion relative to the surrounding fluid, the intensity of which is described by the molecular diffusivity D of the solute molecule through the solvent fluid.

The instantaneous position $\boldsymbol{R} \equiv \boldsymbol{R}(t|\boldsymbol{R}')$ of the Brownian particle is a stochastic variable. Let (Brenner & Gaydos 1977)

$$P \equiv P(\boldsymbol{R}, t|\boldsymbol{R}') \tag{4.1}$$

denote the probability density that the Brownian particle is situated at position $\boldsymbol{R}$ at time t, given that it was located at the point $\boldsymbol{R}'$ at time $t = 0$. The quantity $P\,\mathrm{d}^3\boldsymbol{R}$, with volume element $\mathrm{d}^3\boldsymbol{R}$, thus represents the probability of finding the tracer particle at time t lying somewhere within the infinitesimal volume $\mathrm{d}^3\boldsymbol{R}$ centred at $\boldsymbol{R}$.

Upon supposing that the particles comprising the porous medium are impermeable to the solute molecule, for $t > 0$ the Brownian particle must lie somewhere within the interstitial fluid volume $V_{\mathrm{f}\infty}$. Thus, P necessarily satisfies the normalization condition

$$\int_{V_{\mathrm{f}\infty}} P\,\mathrm{d}^3\boldsymbol{R} = 1, \tag{4.2}$$

for $t > 0$. In addition, $P = 0$ for $t < 0$. It will be assumed that

$$P \rightarrow 0 \quad \text{as} \quad |\boldsymbol{R} - \boldsymbol{R}'| \rightarrow \infty \tag{4.3}$$

at a sufficiently rapid rate with distance to insure convergence of the integral (4.2).

Conservation and continuity of probability density requires that P satisfy the 'continuity' equation (Brenner & Gaydos 1977),

$$\partial P/\partial t + \nabla\cdot\boldsymbol{J} = \delta(\boldsymbol{R} - \boldsymbol{R}')\,\delta(t), \tag{4.4}$$

at each interstitial point $\boldsymbol{R} \in V_{\mathrm{f}\infty}$. Here, $\boldsymbol{J}$ is the flux vector density of probability (relative to an observer fixed in the porous medium), $\nabla \equiv \partial/\partial\boldsymbol{R}$ is the gradient operator, and δ is the Dirac delta function. The instantaneous 'source' term appearing on the right-hand side expresses the fact that the tracer particle was introduced into the fluid at position $\boldsymbol{R} = \boldsymbol{R}'$ at $t = 0$. That the coefficient of this source term is unity is demanded by the normalization condition (4.2) (Brenner & Gaydos 1977).

The flux $\boldsymbol{J}$ consists of a convective contribution arising from the piggy-back transport, and diffusive contribution given by Fick's law. Thus,

$$\boldsymbol{J} = \boldsymbol{v}P - D\,\nabla P. \tag{4.5}$$

Impenetrability of the bed granules to solute transport through their surfaces requires that

$$\boldsymbol{\nu}\cdot\boldsymbol{J} = 0 \quad \text{on} \quad s_{\mathrm{p}}. \tag{4.6}$$

Equivalently, in view of equations (3.2) and (4.5),

$$v \cdot \nabla P = 0 \quad \text{on} \quad s_p. \tag{4.7}$$

Equations (4.4) and (4.5) combine to yield the convective–diffusion equation,

$$\partial P/\partial t = -\nabla \cdot (\boldsymbol{v} P) + D\,\nabla^2 P + \delta(\boldsymbol{R}-\boldsymbol{R}')\,\delta(t). \tag{4.8}$$

For a given $\boldsymbol{v}$, this equation governs the temporal evolution of the probability density P. Subject to boundary conditions (4.3) and (4.7) this equation can be shown (Brenner & Gaydos 1977) to possess a unique solution P.

In view of equation (2.10), P may be regarded as being of the functionally dependent form

$$P \equiv P(\boldsymbol{R}_n, \boldsymbol{r}, t \,|\, \boldsymbol{R}'_n, \boldsymbol{r}'), \tag{4.9}$$

rather than equation (4.1). Apropos of this, equation (2.8) may be employed to express the normalization condition (4.2) in the alternative form

$$\sum_n \int_{\tau_f} P\,\mathrm{d}^3\boldsymbol{r} = 1, \tag{4.10}$$

with $\mathrm{d}^3\boldsymbol{r}$ a volume element within a unit cell. Similarly, since $|\boldsymbol{r}-\boldsymbol{r}'| = O(l)$, condition (4.3) may be written alternatively as

$$P \to 0 \quad \text{as} \quad |\boldsymbol{R}_n - \boldsymbol{R}'_n| \to \infty. \tag{4.11}$$

Upon adopting this cellular, rather than global, viewpoint, equation (4.8) becomes, *for a fixed cell* $\{\boldsymbol{n}\}$,

$$\partial P/\partial t = -\nabla \cdot [\boldsymbol{v}(\boldsymbol{r})\,P] + D\,\nabla^2 P + \delta_{\boldsymbol{nn}'}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t), \tag{4.12}$$

in which $\nabla \equiv \partial/\partial \boldsymbol{r}$ is a local gradient operator, and

$$\delta_{\boldsymbol{nn}'} = \delta_{n_1 n'_1}\,\delta_{n_2 n'_2}\,\delta_{n_3 n'_3},$$

with δ_{ij} the Kronecker delta. Thus, the tracer is regarded as having been initially located (at $t = 0$) at the local point $\boldsymbol{r}'$ within cell $\{\boldsymbol{n}'\}$.

As follows from the differential equation and boundary conditions satisfied by P, the latter is necessarily functionally dependent only upon the difference $\boldsymbol{R}_n - \boldsymbol{R}'_n$, rather upon $\boldsymbol{R}_n$ and $\boldsymbol{R}'_n$ separately. Hence, equation (4.9) may be replaced by

$$P \equiv P(\boldsymbol{R}_n - \boldsymbol{R}'_n, \boldsymbol{r}, t \,|\, \boldsymbol{r}'). \tag{4.13}$$

For specified values of the initial location $\{\boldsymbol{n}'\}$ and $\boldsymbol{r}'$ of the tracer, the differential equation (4.12) is to be solved for P as a function of the local coordinate $\boldsymbol{r}$ for each and every different cell $\{\boldsymbol{n}\}$. The infinite sequence of such local differential equations for each $\{\boldsymbol{n}\}$ is to be regarded as joined together by appropriate continuity requirements imposed upon P and $\boldsymbol{J}$ (or, equivalently, ∇P) across the faces of adjacent cells. These are derived in the following paragraph.

As in figure 7, let $\{\boldsymbol{n}^*\}$ and $\{\boldsymbol{n}\}$ be two adjacent cells, whose common boundary corresponds to the curvilinear face s_j. Let $\boldsymbol{R}$ denote the global position vector of any point P_j lying upon s_j. This point may be parameterized by either of the pair of coordinates $(\boldsymbol{R}^*_n, \boldsymbol{r}^*)$ or $(\boldsymbol{R}_n, \boldsymbol{r})$; that is, as in equation (2.10),

$$\boldsymbol{R} \equiv \boldsymbol{R}^*_n + \boldsymbol{r}^* = \boldsymbol{R}_n + \boldsymbol{r}, \tag{4.14}$$

with (figure 7)

$$\boldsymbol{R}_n - \boldsymbol{R}^*_n = \boldsymbol{l}_j. \tag{4.15}$$

Continuity of P across s_j requires that

$$P(\boldsymbol{R}^*_n, \boldsymbol{r}^*) = P(\boldsymbol{R}_n, \boldsymbol{r}) \tag{4.16}$$

upon suppressing the fixed arguments, $\boldsymbol{R}'_n$, $\boldsymbol{r}'$, and t, common to both sides. This relation may be written alternatively as

$$P(\boldsymbol{R}^*_n, \boldsymbol{r}+\boldsymbol{l}_j) = P(\boldsymbol{R}_n, \boldsymbol{r}). \tag{4.17}$$

Similarly, one may consider the continuity of the flux $\boldsymbol{J}$ across the common boundary. In view of equations (4.5), (4.16), and the continuity of $\boldsymbol{v}$ across the cell boundary, which is guaranteed by its spatial periodicity, it proves sufficient to require that

$$\nabla P(\boldsymbol{R}^*_n, \boldsymbol{r}+\boldsymbol{l}_j) = \nabla P(\boldsymbol{R}_n, \boldsymbol{r}), \tag{4.18}$$

with $\nabla \equiv \partial/\partial \boldsymbol{r}$. This is the analogue of equation (4.17).

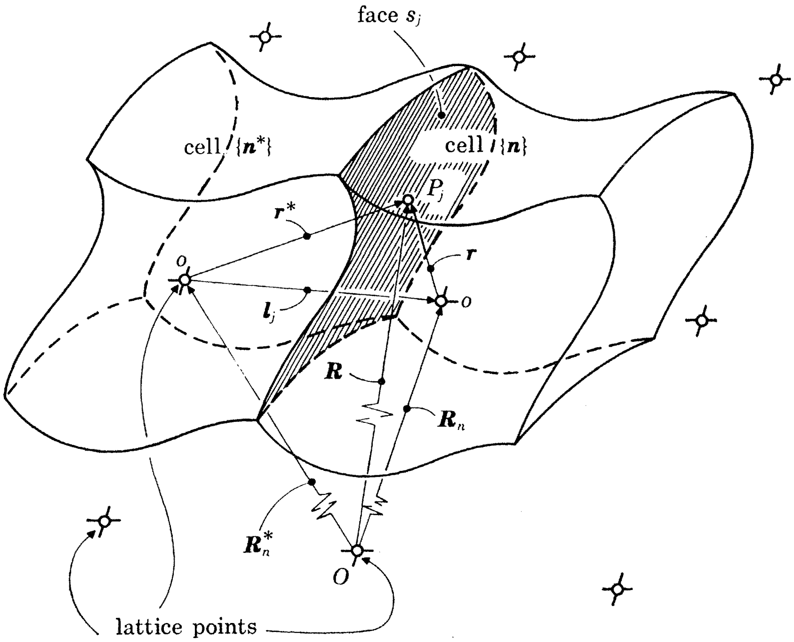

FIGURE 7. Two adjacent unit cells sharing a common face, s_j. The global 'coordinates' of the two cells are respectively, $\{\boldsymbol{n}\} = \{n_i, n_j, n_k\}$ and $\{\boldsymbol{n}^*\} = \{n_i, n_j - 1, n_k\}$ with i, j, k a cyclic permutation of the integers 1, 2, 3.

Local moments

Define the mth local moment of the distribution P within a unit cell as the sum,

$$\boldsymbol{\mu}_m(\boldsymbol{r}, t|\boldsymbol{r}') = \sum_{\boldsymbol{n}} (\boldsymbol{R}_n - \boldsymbol{R}'_n)^m P(\boldsymbol{R}_n - \boldsymbol{R}'_n, \boldsymbol{r}, t|\boldsymbol{r}') \quad (m = 0, 1, 2, \ldots). \tag{4.19}$$

Generically, for any vector $\boldsymbol{V}$, $\boldsymbol{V}^m$ is the m-adic,

$$\boldsymbol{V}^m = \boldsymbol{V}\boldsymbol{V}\ldots\boldsymbol{V}\boldsymbol{V} \quad (m\text{-times}), \tag{4.20}$$

consisting of m successive vectors without any operational symbol between them. Thus, the fields μ_0, $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$, ..., are, respectively, scalar, vector, dyadic, ..., fields.

The summation operator (2.9), which is global in character, commutes with all $\boldsymbol{r}$-space operations in equation (4.12), since the latter are local in character. Hence, the moments $\boldsymbol{\mu}_m$ satisfy the differential equations

$$\partial\boldsymbol{\mu}_m/\partial t = -\nabla\cdot(\boldsymbol{v}\boldsymbol{\mu}_m) + D\,\nabla^2\boldsymbol{\mu}_m + \delta_{m0}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t) \quad (m = 0, 1, 2, \ldots), \tag{4.21}$$

with $\nabla \equiv \partial/\partial \boldsymbol{r}$. For similar reasons, from equation (4.7), these fields satisfy the boundary conditions

$$\boldsymbol{\nu}\cdot\nabla \boldsymbol{\mu}_m = 0 \quad \text{on} \quad s_p. \tag{4.22}$$

In addition to the latter, the local moments also satisfy certain boundary conditions on the cell faces $\partial\tau_o$. These may be deduced from the global continuity conditions (4.17) and (4.18) as follows: the affix $\boldsymbol{n}$ appearing in the summation operator (2.9) is a dummy index; hence,

$$\sum_{\boldsymbol{n}*} \equiv \sum_{\boldsymbol{n}}, \tag{4.23}$$

since the sum extends over all the infinitely many cells in the array. Application of this operator to the equality (4.17) thus yields

$$\sum_{\boldsymbol{n}*} P(\boldsymbol{R}_n^*, \boldsymbol{r}+\boldsymbol{l}_j) = \sum_{\boldsymbol{n}} P(\boldsymbol{R}_n, \boldsymbol{r}).$$

From equation (4.19) this is equivalent to

$$\mu_0(\boldsymbol{r}+\boldsymbol{l}_j) - \mu_0(\boldsymbol{r}) = 0, \tag{4.24}$$

upon suppressing the fixed arguments t and $\boldsymbol{r}'$ on both sides. Similarly, multiply both sides of equation (4.17) by $\boldsymbol{R}_n^* \equiv \boldsymbol{R}_n - \boldsymbol{l}_j$ and sum over all cells to obtain

$$\sum_{\boldsymbol{n}*} \boldsymbol{R}_n^* P(\boldsymbol{R}_n^*, \boldsymbol{r}+\boldsymbol{l}_j) = \sum_{\boldsymbol{n}} \boldsymbol{R}_n P(\boldsymbol{R}_n, \boldsymbol{r}) - \boldsymbol{l}_j \sum_{\boldsymbol{n}} P(\boldsymbol{R}_n, \boldsymbol{r}).$$

This is equivalent to the relation $\boldsymbol{\mu}_1(\boldsymbol{r}+\boldsymbol{l}_j) = \boldsymbol{\mu}_1(\boldsymbol{r}) - \boldsymbol{l}_j \mu_0(\boldsymbol{r})$.

In alternative form,

$$\boldsymbol{\mu}_1(\boldsymbol{r}+\boldsymbol{l}_j) - \boldsymbol{\mu}_1(\boldsymbol{r}) = (\boldsymbol{r}+\boldsymbol{l}_j)\,\mu_0(\boldsymbol{r}+\boldsymbol{l}_j) - \boldsymbol{r}\mu_0(\boldsymbol{r}), \tag{4.25}$$

obtained by adding and subtracting the term $\boldsymbol{r}\mu_0$ to and from the preceding equation, and using equation (4.24). In a similar manner, multiply equation (4.17) by $(\boldsymbol{R}_n^*)^2 \equiv (\boldsymbol{R}_n - \boldsymbol{l}_j)^2$, and sum to obtain

$$\boldsymbol{\mu}_2(\boldsymbol{r}+\boldsymbol{l}_j) = \boldsymbol{\mu}_2(\boldsymbol{r}) - [\boldsymbol{l}_j\, \boldsymbol{\mu}_1(\boldsymbol{r}) + \boldsymbol{\mu}_1(\boldsymbol{r})\, \boldsymbol{l}_j] + \mu_0(\boldsymbol{r})\, \boldsymbol{l}_j\, \boldsymbol{l}_j.$$

With the use of equations (4.24) and (4.25) this may eventually be written as

$$\boldsymbol{\mu}_2(\boldsymbol{r}+\boldsymbol{l}_j) - \boldsymbol{\mu}_2(\boldsymbol{r}) = \frac{\boldsymbol{\mu}_1(\boldsymbol{r}+\boldsymbol{l}_j)\, \boldsymbol{\mu}_1(\boldsymbol{r}+\boldsymbol{l}_j)}{\mu_0(\boldsymbol{r}+\boldsymbol{l}_j)} - \frac{\boldsymbol{\mu}_1(\boldsymbol{r})\, \boldsymbol{\mu}_1(\boldsymbol{r})}{\mu_0(\boldsymbol{r})}. \tag{4.26}$$

As in figure 8, let P_{-j} and P_{+j} be equivalent points (in the sense of equation (2.13)) lying on opposite faces s_{-j} and s_{+j} of cell $\{\boldsymbol{n}\}$. Within cell $\{\boldsymbol{n}\}$ the local coordinates of P_{-j} and P_{+j} are, respectively, $\boldsymbol{r}$ and $\boldsymbol{r}+\boldsymbol{l}_j$. Let $\boldsymbol{F}$ be any tensor-valued field, which is either global or local with respect to its functional dependence upon position; that is, either $\boldsymbol{F} \equiv \boldsymbol{F}(\boldsymbol{R})$ or $\boldsymbol{F}(\boldsymbol{r})$. Define the 'jump' $[\![\boldsymbol{F}]\!]$ in the value of this function across an opposite pair of cell faces as

$$[\![\boldsymbol{F}]\!] = \boldsymbol{F}(P_{+j}) - \boldsymbol{F}(P_{-j}) \quad (j = 1, 2, 3). \tag{4.27}$$

Equivalently,

$$[\![\boldsymbol{F}]\!] = \left.\begin{array}{l} \boldsymbol{F}(\boldsymbol{R}_n, \boldsymbol{r}+\boldsymbol{l}_j) - \boldsymbol{F}(\boldsymbol{R}_n, \boldsymbol{r}), \\ \text{or} \quad \boldsymbol{F}(\boldsymbol{r}+\boldsymbol{l}_j) - \boldsymbol{F}(\boldsymbol{r}), \end{array}\right\} \tag{4.28}$$

according as $\boldsymbol{F}$ is global or local.

Equations (4.24), (4.25) and (4.26) may therefore be expressed as the comparable local jump conditions,

$$[\![\mu_0]\!] = 0, \tag{4.29a}$$

$$[\![\boldsymbol{\mu}_1]\!] = -[\![\boldsymbol{r}\mu_0]\!], \tag{4.29b}$$

$$[\![\boldsymbol{\mu}_2]\!] = [\![\boldsymbol{\mu}_1\, \boldsymbol{\mu}_1/\mu_0]\!], \tag{4.29c}$$

which apply at each point $\boldsymbol{r}$ on opposite pairs of faces. Similarly, beginning with equation (4.18), one may deduce comparable jump boundary conditions imposed upon $\nabla\boldsymbol{\mu}_m$ across the cell faces (cf. equations (4.30)–(4.32)). These jump boundary conditions play a role in the present theory analogous to that of integration by parts in the Taylor–Aris theory (see the discussion of this point in § 11).

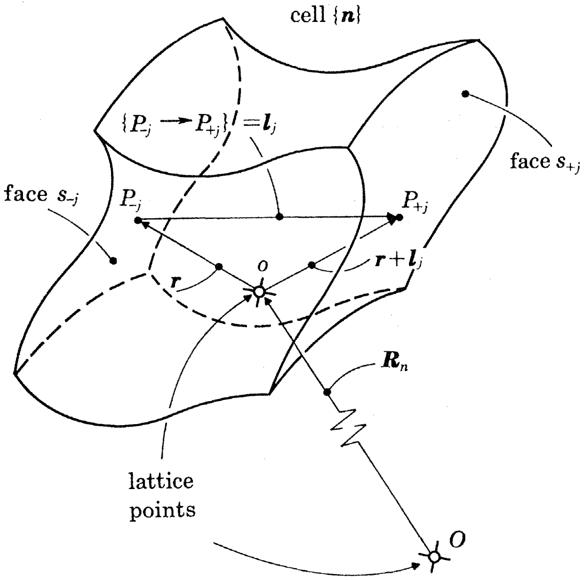

Figure 8. Equivalent points on opposite faces of a unit cell, expressed in terms of the local position vector.

In summary, the sets of equations governing the lower-order fields $\boldsymbol{\mu}_m$ for $m = 0, 1$, and 2 are as follows:

$$\partial\mu_0/\partial t = -\nabla\cdot(\boldsymbol{v}\mu_0) + D\,\nabla^2\mu_0 + \delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t), \tag{4.30a}$$

$$\boldsymbol{\upsilon}\cdot\nabla\mu_0 = 0 \quad \text{on} \quad s_{\mathrm{p}}, \tag{4.30b}$$

$$[\![\mu_0]\!] = 0, \quad [\![\nabla\mu_0]\!] = 0; \tag{4.30c, d}$$

and

$$\partial\boldsymbol{\mu}_1/\partial t = -\nabla\cdot(\boldsymbol{v}\boldsymbol{\mu}_1) + D\,\nabla^2\boldsymbol{\mu}_1, \tag{4.31a}$$

$$\boldsymbol{\upsilon}\cdot\nabla\boldsymbol{\mu}_1 = 0 \quad \text{on} \quad s_{\mathrm{p}}, \tag{4.31b}$$

$$[\![\boldsymbol{\mu}_1]\!] = -[\![\boldsymbol{r}\mu_0]\!], \quad [\![\nabla\boldsymbol{\mu}_1]\!] = -[\![\nabla(\boldsymbol{r}\mu_0)]\!]; \tag{4.31c, d}$$

and

$$\partial\boldsymbol{\mu}_2/\partial t = -\nabla\cdot(\boldsymbol{v}\boldsymbol{\mu}_2) + D\,\nabla^2\boldsymbol{\mu}_2, \tag{4.32a}$$

$$\boldsymbol{\upsilon}\cdot\nabla\boldsymbol{\mu}_2 = 0 \quad \text{on} \quad s_{\mathrm{p}}, \tag{4.32b}$$

$$[\![\boldsymbol{\mu}_2]\!] = [\![\boldsymbol{\mu}_1\,\boldsymbol{\mu}_1/\mu_0]\!], \quad [\![\nabla\boldsymbol{\mu}_2]\!] = [\![\nabla(\boldsymbol{\mu}_1\,\boldsymbol{\mu}_1/\mu_0)]\!]. \tag{4.32c, d}$$

The above systems of differential equations and boundary conditions defining each of the $\boldsymbol{\mu}_m(\boldsymbol{r}, t|\boldsymbol{r}')$ $(m = 0, 1, 2, \ldots)$ within a unit cell $(\boldsymbol{r}\in\tau_{\mathrm{f}})$ can, in principle, be solved recursively, beginning with μ_0. Each such system can be shown (Brenner & Gaydos 1977) to possess a unique solution for $\boldsymbol{\mu}_m$, which is independent of the particular shape selected for the unit cell (Brenner 1981).

Note that the normalization condition

$$\int_{\tau_{\mathrm{f}}} \mu_0\,\mathrm{d}^3\boldsymbol{r} = 1, \tag{4.33}$$

which follows as a consequence of equations (4.10) and (4.19), is automatically satisfied (Brenner & Gaydos 1977) as a consequence of the appearance of the unit source term in equation (4.30a).

Total moments

In addition to the local moments $\boldsymbol{\mu}_m$, define the total moments,

$$\boldsymbol{M}_m(t|\boldsymbol{r}') = \int_{\tau_f} \boldsymbol{\mu}_m(\boldsymbol{r}, t|\boldsymbol{r}')\,\mathrm{d}^3\boldsymbol{r} \quad (m = 0, 1, 2, \ldots), \tag{4.34}$$

of the probability distribution. In particular, from equation (4.33) it follows immediately that

$$M_0 = 1 \tag{4.35}$$

for all $t > 0$, independently of the value of $\boldsymbol{r}'$.

Differentiate equation (4.34) with respect to t for a fixed value of $\boldsymbol{r}'$ and employ equation (4.21) in conjunction with the divergence theorem to successively obtain

$$\begin{aligned}\frac{\mathrm{d}\boldsymbol{M}_m}{\mathrm{d}t} &= \int_{\tau_f} \frac{\partial \boldsymbol{\mu}_m}{\partial t}\,\mathrm{d}^3\boldsymbol{r} \\ &= -\int_{\tau_f} \nabla\cdot(\boldsymbol{v}\boldsymbol{\mu}_m - D\,\nabla\,\boldsymbol{\mu}_m)\,\mathrm{d}^3\boldsymbol{r} + \delta_{m0}\,\delta(t) \\ &= -\oint_{\partial\tau_o + s_p} \mathrm{d}\boldsymbol{s}\cdot(\boldsymbol{v}\boldsymbol{\mu}_m - D\,\nabla\,\boldsymbol{\mu}_m) + \delta_{m0}\,\delta(t) \\ &= -\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot(\boldsymbol{v}\boldsymbol{\mu}_m - D\,\nabla\,\boldsymbol{\mu}_m) + \delta_{m0}\,\delta(t)\end{aligned} \tag{4.36}$$

with $\mathrm{d}\boldsymbol{s} = \boldsymbol{\nu}\,\mathrm{d}s$ a directed element of surface area parallel to the outer normal to τ_f. The last of equations (4.36) follows from the penultimate member of the sequence by using equations (3.2) and (4.22).

The following lemmas hold for any function $\boldsymbol{F}$, with $[\![\boldsymbol{F}]\!]$ defined as in equation (4.27):

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{F} = \sum_{j=1}^{3}\int_{s_{+j}} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}[\![\boldsymbol{F}]\!], \tag{4.37}$$

and

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{F} = \sum_{j=1}^{3}\int_{s_{+j}} \mathrm{d}\boldsymbol{s}\cdot[\![\boldsymbol{F}]\!]. \tag{4.38}$$

These are readily proved by observing that at equivalent points P_{-j} and P_{+j} on opposite faces of a unit cell,

$$\boldsymbol{v}(P_{-j}) = \boldsymbol{v}(P_{+j}), \tag{4.39}$$

as follows from equation (2.13) in conjunction with the spatial periodicity (3.5) of $\boldsymbol{v}$. In addition, because opposite cell faces are congruent,

$$\mathrm{d}\boldsymbol{s}(P_{-j}) = -\mathrm{d}\boldsymbol{s}(P_{+j}). \tag{4.40}$$

Furthermore, from equation (2.5),

$$\int_{\partial\tau_o}(\ldots) = \sum_{j=1}^{3}\left[\int_{s_{+j}}(\ldots) + \int_{s_{-j}}(\ldots)\right] \tag{4.41}$$

for any integrand. These identities suffice to prove the pair of lemmas.

With the use of these lemmas, equation (4.36) may be expressed as

$$\frac{\mathrm{d}\boldsymbol{M}_m}{\mathrm{d}t} = -\sum_{j=1}^{3}\int_{s_{+j}} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}[\![\boldsymbol{\mu}_m]\!] + D\sum_{j=1}^{3}\int_{s_{+j}} \mathrm{d}\boldsymbol{s}\cdot[\![\nabla\boldsymbol{\mu}_m]\!] + \delta_{m0}\,\delta(t). \tag{4.42}$$

Since the boundary conditions on the cell faces permit $[\![\boldsymbol{\mu}_m]\!]$ and $[\![\nabla\boldsymbol{\mu}_m]\!]$ to be expressed entirely in terms of the lower-order moments $\boldsymbol{\mu}_{m-1}, \boldsymbol{\mu}_{m-2}, \ldots, \boldsymbol{\mu}_1, \mu_0$, the integration scheme implicit in equation (4.42) permits $\boldsymbol{M}_m$ to be calculated solely from knowledge of these lower-order local moments. In particular, from equations (4.32*c*, *d*), $\boldsymbol{M}_2$ can be calculated from knowledge of $\boldsymbol{\mu}_1$ and μ_0 alone. Explicit knowledge of $\boldsymbol{\mu}_2$ is not required, despite the definition (4.34) (for $m = 2$).

As an immediate application of equation (4.42) for the case $m = 0$ we find from equation (4.30*c*, *d*) that $\mathrm{d}M_0/\mathrm{d}t = \delta(t)$. Integration of this yields $M_0 = 1$ for $t > 0$, in accord with equation (4.35). (An additive function of $\boldsymbol{r}'$, which might otherwise have appeared upon integration, vanishes in consequence of the implicit condition that $M_0 = 0$ for $t < 0$.)

5. ASYMPTOTIC LONG-TIME MOMENTS

Zero-order moments

As $t \to \infty$, the asymptotic solution of the system of equations (4.30) is, as shown in appendix C,

$$\mu_0 \simeq 1/\tau_{\mathrm{f}} + \mathrm{Exp}, \tag{5.1}$$

where 'Exp' denotes terms in $\boldsymbol{r}$, $\boldsymbol{r}'$, and t that vanish exponentially rapidly with t. The leading term, $1/\tau_{\mathrm{f}}$, of this solution represents the *steady-state* solution. By 'long time' is meant, more precisely,

$$\mathrm{D}t/l^2 \gg 1, \tag{5.2}$$

when expressed in non-dimensional form. Here, l is a characteristic linear unit cell dimension.

The zero-order total moment M_0 is, of course, already given exactly by equation (4.35).

First-order moments

Introduction of equation (5.1) into equations (4.31*c*, *d*) furnishes the boundary conditions

$$[\![\boldsymbol{\mu}_1]\!] \simeq -[\![\boldsymbol{r}]\!]/\tau_{\mathrm{f}} + \mathrm{Exp}, \tag{5.3a}$$

and

$$[\![\nabla\boldsymbol{\mu}_1]\!] \simeq \mathrm{Exp}, \tag{5.3b}$$

to be satisfied by $\boldsymbol{\mu}_1$ on the cell faces. With $m = 1$ in equation (4.42) it therefore follows that

$$\frac{\mathrm{d}\boldsymbol{M}_1}{\mathrm{d}t} \simeq \frac{1}{\tau_{\mathrm{f}}}\sum_{j=1}^{3}\int_{s_{+j}} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}[\![\boldsymbol{r}]\!] + \mathrm{Exp}.$$

Use of the lemma (4.37) thereby yields

$$\frac{\mathrm{d}\boldsymbol{M}_1}{\mathrm{d}t} \simeq \frac{1}{\tau_{\mathrm{f}}}\int_{\partial\tau_0} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{r} + \mathrm{Exp},$$

or, upon integration,

$$\boldsymbol{M}_1 \simeq \left(\frac{1}{\tau_{\mathrm{f}}}\int_{\partial\tau_0} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{r}\right)t + \mathrm{const} + \mathrm{Exp}.$$

In view of equation (4.34) (with $m = 1$), this suggests an asymptotic trial solution for $\boldsymbol{\mu}_1$ (whose validity may be confirmed *a posteriori*) of the form

$$\boldsymbol{\mu}_1 \simeq \frac{1}{\tau_{\mathrm{f}}}[\boldsymbol{v}^* t + \boldsymbol{B}(\boldsymbol{r})] + \mathrm{Exp}, \tag{5.4}$$

wherein
$$\bar{\boldsymbol{v}}^* = \frac{1}{\tau_f}\int_{\partial\tau_o} \boldsymbol{r}\,\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v} = \text{const.} \tag{5.5}$$

The local function $\boldsymbol{B}(\boldsymbol{r})$ is the solution of the intracell boundary-value problem,

$$\bar{\boldsymbol{v}}^* = -\nabla\cdot(\boldsymbol{v}\boldsymbol{B}) + D\,\nabla^2\boldsymbol{B}, \tag{5.6a}$$

$$\nu\cdot\nabla\boldsymbol{B} = 0 \quad \text{on}\, s_p, \tag{5.6b}$$

$$\llbracket\boldsymbol{B}\rrbracket = -\llbracket\boldsymbol{r}\rrbracket, \quad \llbracket\nabla\boldsymbol{B}\rrbracket = 0, \tag{5.6c, d}$$

for $\boldsymbol{r}\in\tau_f$. Since $\boldsymbol{v}$ is presumably a known field, the constant $\bar{\boldsymbol{v}}^*$, defined by equation (5.5), is to be regarded as known.

From equation (4.34),
$$\boldsymbol{M}_1 \simeq \bar{\boldsymbol{v}}^* t + \bar{\boldsymbol{B}} + \text{Exp}, \tag{5.7}$$

where
$$\bar{\boldsymbol{B}} = \frac{1}{\tau_f}\int_{\tau_f} \boldsymbol{B}(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} = \text{const.} \tag{5.8}$$

Second-order moments

Equations (4.32*c*, *d*) in conjunction with the asymptotic expansions of μ_0 and $\boldsymbol{\mu}_1$ impose the following boundary conditions upon $\boldsymbol{\mu}_2$:

$$\llbracket\boldsymbol{\mu}_2\rrbracket = -\frac{1}{\tau_f}(\llbracket\boldsymbol{r}\rrbracket\bar{\boldsymbol{v}}^* t + \bar{\boldsymbol{v}}^*\llbracket\boldsymbol{r}\rrbracket t - \llbracket\boldsymbol{B}\boldsymbol{B}\rrbracket) + \text{Exp}, \tag{5.9a}$$

and‡
$$\llbracket\nabla\boldsymbol{\mu}_2\rrbracket = \frac{1}{\tau_f}(\llbracket(\nabla\boldsymbol{B})\,\boldsymbol{B}\rrbracket + \llbracket(\nabla\boldsymbol{B})\,\boldsymbol{B}^{\dagger}\rrbracket) + \text{Exp}. \tag{5.9b}$$

In principle, one may solve equations (4.32*a*) and (4.32*b*) for $\boldsymbol{\mu}_2$ so as to satisfy these asymptotic boundary conditions. However, subsequent calculations do not require explicit knowledge of $\boldsymbol{\mu}_2$, but rather only of $\boldsymbol{M}_2$ or, more precisely, of $\mathrm{d}\boldsymbol{M}_2/\mathrm{d}t$. And this function can be obtained directly from equations (4.42) and (5.9). By employing the jump lemmas (4.37) and (4.38) in their converse sense, this procedure ultimately gives rise to the relation (Brenner 1981)

$$\begin{aligned}\frac{\mathrm{d}\boldsymbol{M}_2}{\mathrm{d}t} \simeq \frac{1}{\tau_f}\bigg\{&\left(\int_{\partial\tau_o}\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{r}\right)\bar{\boldsymbol{v}}^* t + \bar{\boldsymbol{v}}^* t\int_{\partial\tau_o}\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{r}\\ &-\int_{\partial\tau_o}\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{B}\boldsymbol{B} + D\int_{\partial\tau_o}\mathrm{d}\boldsymbol{s}\cdot[(\nabla\boldsymbol{B})\,\boldsymbol{B} + (\nabla\boldsymbol{B})\,\boldsymbol{B}^{\dagger}]\bigg\} + \text{Exp}.\end{aligned} \tag{5.10}$$

From equation (5.5) the first two integrals are each $\tau_f\bar{\boldsymbol{v}}^*$. With use of boundary conditions (3.2) and (5.6*b*) on s_p, the last two surface integrals can be converted into comparable volume integrals over τ_f by application of the divergence theorem. In turn, the resulting volume integrals can be simplified by application of the identities

$$\nabla\cdot[(\nabla\boldsymbol{B})\,\boldsymbol{B} + (\nabla\boldsymbol{B})\,\boldsymbol{B}^{\dagger}] = \nabla^2(\boldsymbol{B}\boldsymbol{B}), \tag{5.11}$$

applicable to any vector field $\boldsymbol{B}$, and

$$\nabla\cdot(\boldsymbol{v}\boldsymbol{B}\boldsymbol{B}) = D[\nabla^2(\boldsymbol{B}\boldsymbol{B}) - 2\nabla\boldsymbol{B}^{\dagger}\cdot\nabla\boldsymbol{B}] - (\bar{\boldsymbol{v}}^*\boldsymbol{B} + \boldsymbol{B}\bar{\boldsymbol{v}}^*), \tag{5.12}$$

---

‡ The superscript † denotes a post-transposition operator, which for triadics (third-rank tensors) is defined as $(\boldsymbol{abc})^{\dagger} = \boldsymbol{acb}$, in which $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ are any vectors. Equivalently in Cartesian tensor notation $A^{\dagger}_{ijk} = A_{ikj}$.

derived by premultiplying (5.6*a*) by $\boldsymbol{B}$ and using equation (3.1). The transposition operator † appearing above has its usual dyadic interpretation. In this manner, there is obtained

$$\frac{\mathrm{d}\boldsymbol{M}_2}{\mathrm{d}t} \simeq 2\boldsymbol{v}^*\boldsymbol{v}^*t + \boldsymbol{v}^*\boldsymbol{B} + \boldsymbol{B}\boldsymbol{v}^* + \frac{2D}{\tau_{\mathrm{f}}}\int_{\tau_{\mathrm{f}}} \nabla\boldsymbol{B}^{\dagger}\cdot\nabla\boldsymbol{B}\,\mathrm{d}^3\boldsymbol{r} + \mathrm{Exp}, \tag{5.13}$$

with $\bar{\boldsymbol{B}}$ the constant vector defined in equation (5.8).

6. MEAN- AND MEAN-SQUARE DISPLACEMENTS

Mean displacement vector

From a 'macroscopic' or Darcy-scale viewpoint, the mean displacement of the Brownian particle at time t, from its initial position at time $t = 0$, is

$$\begin{aligned} \overline{\Delta\boldsymbol{R}} &\equiv \int_{V_{\mathrm{f}\infty}} (\boldsymbol{R}_n - \boldsymbol{R}'_n)\, P\, \mathrm{d}^3\boldsymbol{R} \\ &= \int_{\tau_{\mathrm{f}}} \sum_n (\boldsymbol{R}_n - \boldsymbol{R}'_n)\, P(\boldsymbol{R}_n - \boldsymbol{R}'_n, \boldsymbol{r}, t|\boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r}, \end{aligned} \tag{6.1}$$

with the use of equations (2.8) and (4.13). By 'macroscopic' is meant without regard to *local* positions $\boldsymbol{r}$ and $\boldsymbol{r}'$ within a unit cell (see equation (6.4)). From the definitions of $\boldsymbol{\mu}_1$ and $\boldsymbol{M}_1$ the above is formally equivalent to

$$\overline{\Delta\boldsymbol{R}} = \boldsymbol{M}_1. \tag{6.2}$$

In combination with equation (5.7) this yields the asymptotic result,

$$\overline{\Delta\boldsymbol{R}} \simeq \bar{\boldsymbol{v}}^* t \tag{6.3}$$

as $t \to \infty$. Thus, for sufficiently long times the mean displacement vector grows linearly with time.

Equation (6.2) may also be obtained asymptotically from a finer-grained viewpoint, by defining the mean displacement vector as

$$\overline{\Delta\boldsymbol{R}} \equiv \int_{V_{\mathrm{f}\infty}} (\boldsymbol{R} - \boldsymbol{R}')\, P(\boldsymbol{R}, t|\boldsymbol{R}')\, \mathrm{d}^3\boldsymbol{R}, \tag{6.4}$$

in place of the first of equations (6.1). With the use of equation (2.10) this is equivalent to

$$\overline{\Delta\boldsymbol{R}} = \int_{\tau_{\mathrm{f}}} \sum_n (\boldsymbol{R}_n - \boldsymbol{R}'_n)\, P(\boldsymbol{R}_n - \boldsymbol{R}'_n, \boldsymbol{r}, t|\boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r} + \int_{\tau_{\mathrm{f}}} (\boldsymbol{r} - \boldsymbol{r}') \sum_n P(\boldsymbol{R}_n - \boldsymbol{R}'_n, \boldsymbol{r}, t|\boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r},$$

or

$$\overline{\Delta\boldsymbol{R}} = \boldsymbol{M}_1 + \int_{\tau_{\mathrm{f}}} (\boldsymbol{r} - \boldsymbol{r}')\, \mu_0(\boldsymbol{r}, t|\boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r}.$$

However, from equation (5.1),

$$\int_{\tau_{\mathrm{f}}} (\boldsymbol{r} - \boldsymbol{r}')\, \mu_0\, \mathrm{d}^3\boldsymbol{r} \simeq \frac{1}{\tau_{\mathrm{f}}}\int_{\tau_{\mathrm{f}}} (\boldsymbol{r} - \boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r} + \mathrm{Exp}.$$

The right-hand integral tends to a constant (of $O(l)$), independent of time. Since $\boldsymbol{M}_1$ ultimately grows linearly with time, this time-independent constant ultimately becomes negligible compared with $\bar{\boldsymbol{v}}^* t$. Thus, we arrive at the same result as in equation (6.3).

From a Darcy-scale viewpoint the fluid-filled porous medium may be regarded as consisting of two interpenetrating continua – a particulate continuum and an interstitial fluid continuum. From the theory of Brownian motion (Brenner & Gaydos 1977) applied to the latter continuum, the mean velocity vector $\bar{\boldsymbol{U}}^*$ of the tracer through the interstitial fluid phase may be regarded as defined by the stochastic relation

$$\overline{\Delta \boldsymbol{R}} \simeq \bar{\boldsymbol{U}}^* t. \tag{6.5}$$

Hence, from equation (6.2),

$$\bar{\boldsymbol{U}}^* = \lim_{t\to\infty} \frac{\mathrm{d}\boldsymbol{M}_1}{\mathrm{d}t}. \tag{6.6}$$

Thus, it follows from equation (5.7), or more directly by comparing equation (6.5) with equation (6.3), that

$$\bar{\boldsymbol{U}}^* = \bar{\boldsymbol{v}}^*, \tag{6.7}$$

wherein $\bar{\boldsymbol{v}}^*$ is defined in equation (5.5).

It will be shown in § 7 that $\bar{\boldsymbol{v}}^*$ is the mean velocity of the *fluid* through the interstices. Thus, the physical significance of equation (6.7) resides in demonstrating that, on the average, the tracer moves at the same velocity as the fluid. In general, this would not be expected to be true (Brenner & Gaydos 1977). Equality of average tracer and fluid velocities in the present case arises from the fact the 'point' dimensions of the tracer corpuscle precludes the existence of retarding 'wall effects', arising from hydrodynamic interaction between it and the granules making up the porous bed. For the same reason, no 'excluded volume' (Brenner & Gaydos 1977) exists around each of the granules, from which the centre of the tracer particle is excluded by virtue of its finite size. Moreover, no external body forces act upon the tracer particle, which would cause it to move relative to the surrounding fluid. In effect, being free to sample all local interstitial positions $\boldsymbol{r} \in \tau_f$ within a unit cell (see § 7) with equal probability, the tracer molecule behaves no differently than a fluid molecule. Were the tracer particle, for example, able to freely diffuse through the bed granules, equation (6.7) would no longer obtain – even for tracer particles of point dimensions.

Mean-'square' displacement dyadic

In the same sense as equation (4.20), the 'macroscopic' mean-square displacement is defined as

$$\overline{(\Delta \boldsymbol{R} - \overline{\Delta \boldsymbol{R}})^2} \equiv \int_{V_{f\infty}} (\boldsymbol{R}_n - \boldsymbol{R}'_n - \overline{\Delta \boldsymbol{R}})^2 P \, \mathrm{d}^3\boldsymbol{R}, \tag{6.8}$$

with $\overline{\Delta \boldsymbol{R}}$ defined as in the first of equations (6.1). With use of equations (4.2) and (2.8) this makes

$$\overline{(\Delta \boldsymbol{R} - \overline{\Delta \boldsymbol{R}})^2} = \int_{\tau_f} \mathrm{d}^3\boldsymbol{r} \sum_n (\boldsymbol{R}_n - \boldsymbol{R}'_n)^2 P - (\overline{\Delta \boldsymbol{R}})^2. \tag{6.9}$$

The right-hand integral is $\boldsymbol{M}_2$. After the use of equation (6.2), the above is equivalent to

$$\overline{(\Delta \boldsymbol{R} - \overline{\Delta \boldsymbol{R}})^2} = \boldsymbol{M}_2 - \boldsymbol{M}_1 \boldsymbol{M}_1, \tag{6.10}$$

either exactly, or asymptotically, according as we employ $\boldsymbol{R}_n - \boldsymbol{R}'_n$ or $\boldsymbol{R} - \boldsymbol{R}'$, respectively, in the definitions of the mean displacement and mean-square displacement. This choice is without significance for sufficiently long times, which is the only condition of interest here.

Equations (6.10), (5.7), and (5.13) combine to show that the mean-square displacement varies linearly with t for sufficiently long times. This condition permits us to derive the dispersivity dyadic $\bar{\boldsymbol{D}}^*$ for the tracer corpuscle through the interstitial fluid since, from Einstein's generalized Brownian motion relation for continua (Brenner & Gaydos 1977),

$$\overline{(\Delta \boldsymbol{R} - \overline{\Delta \boldsymbol{R}})^2} \simeq 2\bar{\boldsymbol{D}}^* t. \tag{6.11}$$

That is, the dispersivity is defined as the proportionality constant between the asymptotic mean-square displacement and twice the time. Comparison of equations (6.10) and (6.11) thereby yields

$$\bar{\boldsymbol{D}}^* = \tfrac{1}{2}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{M}_2 - \boldsymbol{M}_1\boldsymbol{M}_1). \tag{6.12}$$

With the use of equations (5.13) and (5.7) this gives, explicitly,

$$\bar{\boldsymbol{D}}^* = \frac{D}{\tau_\mathrm{f}}\int_{\tau_\mathrm{f}} \nabla\boldsymbol{B}^\dagger\cdot\nabla\boldsymbol{B}\,\mathrm{d}^3\boldsymbol{r}. \tag{6.13}$$

Equivalently, in Cartesian tensor notation,

$$\bar{D}^*_{ij} = \frac{D}{\tau_\mathrm{f}}\int_{\tau_\mathrm{f}} B_{i,k}B_{j,k}\,\mathrm{d}^3\boldsymbol{r}. \tag{6.14}$$

The properties of the dispersion dyadic, given by equation (6.13), are discussed at length in § 8.

7. Darcy-scale tracer and fluid velocities

Equivalence of tracer and fluid mean velocities

According to the theory of Brownian movement, the constant vector $\bar{\boldsymbol{U}}^*$ appearing as the proportionality coefficient in the asymptotic relation (6.5), and defined generally by equation (6.6), is to be identified as the mean velocity of the tracer particle as it moves through the interstices of the porous medium. Quite independently of this, the constant vector $\bar{\boldsymbol{v}}^*$ defined by equation (5.5) represents the mean velocity of the fluid through the interstices, as will be made evident later on in this section. As discussed in the footnote pertaining to equation (6.7), and as will be elaborated upon at further length in subsequent paragraphs, these two velocities are equal in the present circumstances.

That these two velocities may be expected to be equal on *a priori* grounds follows from the fact that the (passive) tracer molecule is kinematically and dynamically indistinguishable from a fluid molecule. Since $\bar{\boldsymbol{v}}^*$ represents the mean velocity of the fluid molecules through the interstices, then it must also represent the mean velocity of the tracer molecule. The logic behind this conclusion is as follows (Brenner & Gaydos 1977):

Provided that the time from the commencement of the tracer experiment is sufficiently long to satisfy the inequality (5.2), the tracer corpuscle will – as a result of its random Brownian movement – sample every *local* position $\boldsymbol{r}$ ($\in\tau_\mathrm{f}$) many times during the course of its interstitial travel through the pores of the medium. That the tracer may move from cell to cell during the course of sampling these local positions $\boldsymbol{r}$ is irrelevant, since for the same value of $\boldsymbol{r}$, all positions $\boldsymbol{R} = \boldsymbol{R}_n + \boldsymbol{r}$ are geometrically indistinguishable, irrespective of the value of $\{\boldsymbol{n}\}$ (see the further discussion of this point in § 11 in relation to the Taylor–Aris theory of dispersion in capillaries). Because of the point dimensions of the corpuscle, and in the absence of any external forces exerted upon it, every interstitial position $\boldsymbol{r}$ has equal *a priori* probability of being sampled by the tracer – provided that the time is sufficiently long for the particle to 'forget' its initial starting position $\boldsymbol{r}'$. Identical 'ergodic' characteristics describe the motion of fluid molecules. Hence, tracer and fluid mean velocities are expected to coincide in present circumstances, though not in general (Brenner & Gaydos 1977).

Though the expression (5.5) for the Darcy-scale interstitial fluid velocity has been derived by invoking Brownian motion theory for a passive tracer particle, the result is, of course, purely kinematical. In particular, as outlined in subsequent paragraphs, the same result can be derived by purely kinematical flux arguments. That this same result derives independently from both stochastic and deterministic arguments is very gratifying.

Seepage velocity kinematics

Define the seepage velocity vector as in equation (3.3). Since $\boldsymbol{v}$ is a spatially periodic function, for a prescribed cell shape the integral possesses the same value for all $\{\boldsymbol{n}\}$. It is therefore a constant throughout the porous medium. Accordingly, the affix $\{\boldsymbol{n}\}$ may be deleted, and the integral written as

$$\bar{\boldsymbol{v}} = \frac{1}{\tau_o}\int_{\tau_f} \boldsymbol{v}\,\mathrm{d}^3\boldsymbol{r} = \text{const.} \tag{7.1}$$

Superficial examination suggests that the numerical value of this integral depends upon the external shape $\partial\tau_o$ (bounding τ_f externally) chosen for the unit cell – for which infinitely-many choices exist for a specified array. Such a conclusion is physically unacceptable since a unit cell possesses no physical reality. Only the particles themselves, and their mode of arrangement possess objective (geometric) reality. Unit cells merely represent a convenient *mental* decomposition of the space into repetitive subunits. If $\bar{\boldsymbol{v}}$ is to possess physical significance it is therefore expedient to demonstrate that the integral (7.1) possesses the same (constant) numerical value for every consistent choice of cell shape. This is readily proved; for if $\breve{\boldsymbol{H}}(\boldsymbol{R})$ is any spatially-periodic tensor-valued function with period $\boldsymbol{R}_n$, the integral

$$\int_{\tau_f} \breve{\boldsymbol{H}}(\boldsymbol{R})\,\mathrm{d}^3\boldsymbol{r} = \tau_o\,\bar{\boldsymbol{H}}, \quad \text{say,} \tag{7.2}$$

possesses the same constant value for every curvilinear unit cell shape $\partial\tau_o$ consistent with the lattice (Brenner 1981). Thus, the constant vector $\bar{\boldsymbol{v}}$ defined by equation (7.1) is a macroscopic *invariant*.

[That equation (7.2) is independent of the explicit choice made for the external cell boundary $\partial\tau_o$ may be proved by reference to the comparable two-dimensional situation depicted in figure 9. For the integral over the domain τ_f bounded externally by $\partial\tau_0$, write

$$\int_{\tau_f} = \int_{\mathrm{I}} + \int_{\mathrm{II}}.$$

Similarly, for the integral over the domain τ_f' bounded externally by $\partial\tau_o'$, write

$$\int_{\tau_f'} = \int_{\mathrm{I}} + \int_{\mathrm{III}}.$$

Since domain I is common to both regions it follows upon subtraction that

$$\int_{\tau_f} \breve{\boldsymbol{H}}\,\mathrm{d}^3\boldsymbol{r} - \int_{\tau_f'} \breve{\boldsymbol{H}}\,\mathrm{d}^3\boldsymbol{r} = \int_{\mathrm{II}} \breve{\boldsymbol{H}}\,\mathrm{d}^3\boldsymbol{r} - \int_{\mathrm{III}} \breve{\boldsymbol{H}}\,\mathrm{d}^3\boldsymbol{r}.$$

Let $\boldsymbol{R}_{\mathrm{II}}$ and $\boldsymbol{R}_{\mathrm{III}}$ denote the position vectors of 'equivalent' points (cf. equation (2.13)) lying within interstitial fluid domains II and III, respectively. The spatial periodicity of $\breve{\boldsymbol{H}}$ requires that $\breve{\boldsymbol{H}}(\boldsymbol{R}_{\mathrm{II}}) = \breve{\boldsymbol{H}}(\boldsymbol{R}_{\mathrm{III}})$. Furthermore, since opposite pairs of cell faces are congruent it follows that the integration domains II and III are geometrically congruent. Hence,

$$\int_{\mathrm{II}} \breve{\boldsymbol{H}}(\boldsymbol{R}_{\mathrm{II}})\,\mathrm{d}^3\boldsymbol{r} = \int_{\mathrm{III}} \breve{\boldsymbol{H}}(\boldsymbol{R}_{\mathrm{III}})\,\mathrm{d}^3\boldsymbol{r},$$

whereupon

$$\int_{\tau_f} \breve{\boldsymbol{H}}\,\mathrm{d}^3\boldsymbol{r} = \int_{\tau_f'} \breve{\boldsymbol{H}}\,\mathrm{d}^3\boldsymbol{r}.$$

Consequently, $\bar{\boldsymbol{H}}' = \bar{\boldsymbol{H}}$. Q.E.D.]

It remains yet to demonstrate that $\bar{\boldsymbol{v}}$ possesses the *physical* attributes normally ascribed to the seepage velocity vector. Towards this end, use the general vector identity

$$\boldsymbol{v} = \nabla\cdot(\boldsymbol{v}\boldsymbol{R}) - \boldsymbol{R}\nabla\cdot\boldsymbol{v} \tag{7.3}$$

in conjunction with equation (3.1), the divergence theorem, and the boundary condition (3.2), to express equation (7.1) as the surface integral

$$\bar{\boldsymbol{v}} = \frac{1}{\tau_o}\int_{\partial\tau_o} \boldsymbol{R}\,\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v} \tag{7.4}$$

over the curvilinear cell boundaries, lying entirely in the fluid. The value of this integral is independent of the choice of origin from which $\boldsymbol{R}$ is measured, since this property is an attribute of equation (7.1) from which it derives. As such, it may be expressed entirely in terms of *local* variables in the form

$$\bar{\boldsymbol{v}} = \frac{1}{\tau_o}\int_{\partial\tau_o} \boldsymbol{r}\,\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}. \tag{7.5}$$

This can be proved by using equation (2.10) in conjunction with the facts that $\boldsymbol{R}_n$ is a constant within a unit cell, and

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v} = 0. \tag{7.6}$$

The latter is a consequence of equations (3.1) (in τ_f) and (3.2). (It also follows independently from equations (2.5), (4.39), and (4.40).)

Let

$$q_j = \int_{s_j} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v} \tag{7.7}$$

denote the volumetric flow rate of fluid through face s_j $(j = 1, 2, 3)$ of any curvilinear unit cell. Then the integral (7.4) defining $\bar{\boldsymbol{v}}$ possesses the fundamental property that

$$\boldsymbol{s}_j\cdot\bar{\boldsymbol{v}} = q_j. \tag{7.8}$$

To prove the latter, use equation (2.5) to write equation (7.5) as

$$\bar{\boldsymbol{v}} = \frac{1}{\tau_o}\sum_{i=1}^{3}\left[\int_{s_i} \boldsymbol{r}(P_{+i})\,\mathrm{d}\boldsymbol{s}(P_{+i})\cdot\boldsymbol{v}(P_{+i}) + \int_{s_i} \boldsymbol{r}(P_{-i})\,\mathrm{d}\boldsymbol{s}(P_{-i})\cdot\boldsymbol{v}(P_{-i})\right]$$

in the notation of figures 6 and 8. Since (cf. equation (2.13))

$$\boldsymbol{r}(P_{+i}) - \boldsymbol{r}(P_{-i}) = \boldsymbol{l}_i,$$

it follows that

$$\bar{\boldsymbol{v}} = \frac{1}{\tau_o}\sum_{i=1}^{3}\boldsymbol{l}_i\int_{s_i} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v} \tag{7.9}$$

upon using equations (4.39) and (4.40). Dot multiply both sides of the preceding by $\boldsymbol{s}_j$, and employ equation (2.12) to obtain

$$\boldsymbol{s}_j\cdot\bar{\boldsymbol{v}} = \int_{s_j} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}. \tag{7.10}$$

However, as in equation (7.7), the right-hand integral represents the volumetric flow rate q_j through face s_j. Thereby, theorem (7.8) is proved. As in equation (2.14), the areal vector $\boldsymbol{s}_j$ represents the directed area of the curvilinear face.

Introduce the notational equivalences

$$\boldsymbol{s}_j \equiv \mathrm{d}\bar{\boldsymbol{s}}_j, \quad q_j \equiv \mathrm{d}\bar{q}_j, \tag{7.11a, b}$$

reflecting the fact that whereas $\boldsymbol{s}_j$ and q_j are each finite in magnitude when viewed microscopically, they are to be regarded as only differential in magnitude when viewed from the macroscopic, Darcy-scale. The viewpoint implicit in this choice of notation is effectively tantamount to regarding the microscopically discrete field of vectors $\boldsymbol{R}_n$ as a continuous field of macroscopic, Darcy-scale position vectors $\overline{\boldsymbol{R}}$ (Brenner 1981) – and hence of regarding the volume element τ_0 of a unit cell as being equivalent to a differential volume element $\mathrm{d}^3\overline{\boldsymbol{R}}$ at the Darcy scale. From this same point of view, the 'differential' displacement vector $\mathrm{d}\overline{\boldsymbol{R}}$ at the Darcy scale is equivalent to one of the basic lattice vectors $\boldsymbol{l}_j$. Because the infinite field of such lattice vectors (cf. equation (2.3)) spans almost all possible directions in space, all orientations are accessible to these $\mathrm{d}\overline{\boldsymbol{R}}$ vectors.†

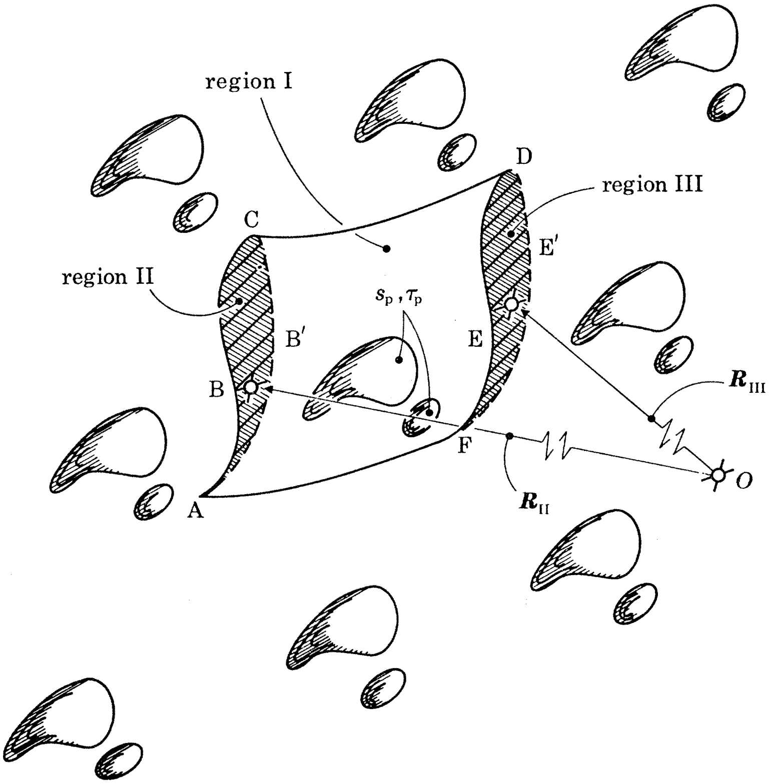

FIGURE 9. Two different, two-dimensional, curvilinear unit cells sharing the same lattice points. The four common lattice points are (A, C, D, F). The two unit cells, whose interstitial fluid domains will be designated as τ_f and τ_f', are those regions bounded externally by the closed curves $\partial\tau_0 \equiv$ ABCDEFA and $\partial\tau_0' \equiv$ AB′CDE′FA, respectively. Regions II and III, shown shaded, represent the interstitial fluid domains bounded by the closed curves ABCB′A and FEDE′F, respectively. Region I is the unshaded fluid domain in the centre, bounded externally by the closed curve AB′CDEFA, and internally by the particle surface(s) s_p. Thus, $\tau_f \equiv \mathrm{I}\oplus\mathrm{II}$ and $\tau_f' = \mathrm{I}\oplus\mathrm{III}$.

Equations (7.8) and (7.11) combine to yield

$$\mathrm{d}\bar{\boldsymbol{s}}_j \cdot \bar{\boldsymbol{v}} = \mathrm{d}\bar{q}_j. \tag{7.12}$$

As has been demonstrated, the vector $\bar{\boldsymbol{v}}$ defined in equation (7.1) is a Darcy-scale invariant, independent of the shape assigned to the unit cell. On the other hand, as discussed in § 2, the directed areas $\mathrm{d}\bar{\boldsymbol{s}}_j \equiv \boldsymbol{s}_j$ can be chosen, more or less arbitrarily, from an infinite field of orientations,

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† By employing multiple unit cells (Brenner 1981), all magnitudes for $|\mathrm{d}\overline{\boldsymbol{R}}|$ are essentially equally accessible. It is easily shown (Brenner 1981) that all Darcy-scale physical parameters, such as $\bar{\boldsymbol{v}}$, $\bar{\boldsymbol{v}}^*$ and $\boldsymbol{D}^*$ are independent of whether the requisite integrals defining these quantities are taken over a single, or multiple, unit cell.

according as which one of the infinitely many choices is made for the basic lattice vectors $(\boldsymbol{l}_1, \boldsymbol{l}_2, \boldsymbol{l}_3)$ describing the undeformed unit cell shape. Since equation (7.12) thus applies for an 'arbitrary' orientation of $\mathrm{d}\bar{\boldsymbol{s}}_j$, and since $\bar{\boldsymbol{v}}$ is independent of this 'orientation', the relation therefore represents the counterpart of the ordinary Eulierian definition of the fluid velocity vector $\boldsymbol{v}$ (Aris 1962, Batchelor 1967) for an incompressible fluid continuum, namely

$$\mathrm{d}\boldsymbol{s}_\upsilon \cdot \boldsymbol{v} = \mathrm{d}q_\upsilon. \tag{7.13}$$

As in figure 10, $\mathrm{d}\boldsymbol{s}_\upsilon$ is an arbitrarily-oriented microscopic directed element of surface area, parallel to the unit normal vector $\boldsymbol{\upsilon}$ to the areal element $\mathrm{d}s$, and $\mathrm{d}q_\upsilon$ is the volumetric flow rate through that area, in the direction of $\boldsymbol{\upsilon}$. The microscopic relation (7.13) is, in fact, the precursor of equation (7.7).

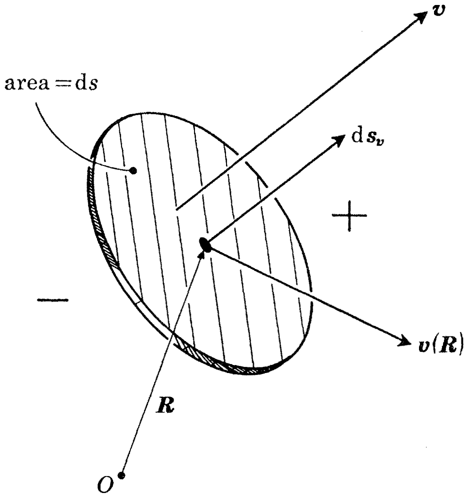

FIGURE 10. Flow through a differential element of surface area. The differential surface element is centred at the point $\boldsymbol{R}$. Here, $\mathrm{d}\boldsymbol{s}_\upsilon = \boldsymbol{\upsilon}\,\mathrm{d}s$, where $\mathrm{d}s = |\mathrm{d}\boldsymbol{s}_\upsilon|$ is the magnitude of the surface area. If $\boldsymbol{v}(\boldsymbol{R})$ is the local fluid velocity vector at $\boldsymbol{R}$, the volumetric flow rate $\mathrm{d}q_\upsilon$ (an algebraically signed scalar) across the elemental surface element in the direction in which $\boldsymbol{v}$ points is given by equation (7.19).

The macroscopic Eulerian relation (7.12), considered in conjunction with the 'arbitrary' nature of $\mathrm{d}\bar{\boldsymbol{s}}_j$, the physical interpretation of $\mathrm{d}\bar{q}_j$, and the invariance of $\bar{\boldsymbol{v}}$, provides unequivocal confirmation of the interpretation of $\bar{\boldsymbol{v}}$, defined in equation (3.3) (or equation (7.1)), as being the seepage velocity vector (Bear 1972, Beran 1968, Scheidegger 1963, Whitaker 1966, 1967, 1969, 1971, 1973). Additional confirmation of this fact derives by adopting a Lagrangian point of view, as discussed in the penultimate subsection of the present section.

Mean interstitial fluid velocity

The Darcy-scale interstitial fluid velocity vector $\bar{\boldsymbol{v}}^*$ is defined as (Bear 1972)

$$\bar{\boldsymbol{v}}^* \equiv \bar{\boldsymbol{v}}/\epsilon, \tag{7.14}$$

where, as in equation (2.6), ϵ is the porosity, or fractional fluid-filled space, in the porous medium. Since both $\bar{\boldsymbol{v}}$ and ϵ are macroscopic invariants, independent of the mode of partitioning the bed into unit cells, the same property necessarily attached to $\bar{\boldsymbol{v}}^*$.

It follows from equations (2.6) and (7.5) that

$$\bar{\boldsymbol{v}}^* = \frac{1}{\tau_\mathrm{f}} \int_{\partial\tau_o} \boldsymbol{r}\,\mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}, \tag{7.15}$$

confirming that the integral (5.5) (which would ordinarily have been represented by the symbol $\bar{\boldsymbol{U}}^*$ – the mean interstitial tracer velocity) is indeed equal to the Darcy-scale interstitial fluid velocity. Alternatively, with the use of equation (7.1) in place of equation (7.5),

$$\bar{\boldsymbol{v}}^* = \frac{1}{\tau_f}\int_{\tau_f} \boldsymbol{v}\, \mathrm{d}^3\boldsymbol{r}. \tag{7.16}$$

In other words, the mean interstitial fluid velocity is equal to volume average of the local fluid velocity over the interstitial pore space.

Lagrangian kinematics

Independent confirmation of the physical interpretation of $\bar{\boldsymbol{v}}^*$ as the mean interstitial velocity derives by adopting a Lagrangian, rather than Eulerian, viewpoint.

In a homogeneous fluid continuum, one may follow over the course of time the trajectory, $\boldsymbol{R} \equiv \boldsymbol{R}(\boldsymbol{R}_o, t)$, of a material point $\boldsymbol{R}_o$. The Lagrangian velocity $\boldsymbol{v} \equiv \boldsymbol{v}(\boldsymbol{R}_o, t)$ of this material point is then (Aris 1962, Batchelor 1967)

$$\boldsymbol{v} = \mathrm{d}\boldsymbol{R}/\mathrm{d}t, \tag{7.17}$$

wherein the material derivative $\mathrm{d}/\mathrm{d}t$ is that for a mixed value of $\boldsymbol{R}_o$. As is well known (Aris 1962, Batchelor 1967), this velocity is identical to the Eulerian velocity $\boldsymbol{v} \equiv \boldsymbol{v}(\boldsymbol{R}, t)$ (defined as in equation (7.13), in terms of the flow through a fixed surface element) at the point $\boldsymbol{R}$ which happens to be occupied by the material particle $\boldsymbol{R}_o$ at time t. Here, we seek the analogue of equation (7.17) for the mean velocity through the interstices of the porous medium. At the same time we shall construct a proof that the Darcy-scale Lagrangian velocity thus defined is identical with the Darcy-scale Eulerian velocity $\bar{\boldsymbol{v}}^*$, defined by equations (7.12) and (7.14).

Let $\partial\tau_o(0)$ denote the external boundary of the incompressible fluid mass originally contained within any one curvilinear unit cell at time $t = 0$. Imagine that this material is instantaneously coloured with a non-diffusing dye, so as to be able to distinguish it from the remainder of the interstitial fluid filling the rest of the infinite pore space. One may now study the motion of this dyed domain with time as it is convected by the flowing fluid. In general, the external boundary $\partial\tau_o(t)$ of this advected fluid region at any time t itself qualifies as a unit cell in the usual sense (figure 11).

Though the coloured fluid mass, whose temporal movement is being studied, is finite in extent from a microscopic viewpoint, it is only 'infinitesimal' in extent when viewed at the Darcy-scale. Accordingly, this interstitial fluid mass qualifies as a *material 'point'* at the Darcy scale. Observe that since each point on the external boundary $\partial\tau_o(t)$ moves with the local fluid velocity $\boldsymbol{v}$ appropriate to that point, no mass crosses the boundary $\partial\tau_o(t)$ at any point. Hence, the fluid mass in the advected dyed unit cell remains constant in time. (Because of the assumed incompressibility of the fluid, the same is true of the volume $\tau_f(t)$ occupied by this fluid.) It is this constancy of mass which, *inter alia*, qualifies the dyed region as a Darcy-scale material point.

Of special interest is the motion of the centre of mass – or, equivalently, the centre of volume, $\bar{\boldsymbol{R}}^* \equiv \bar{\boldsymbol{R}}^*(t)$ – of the moving unit cell with time. Let $\tau_f(t)$ denote the interstitial domain occupied by this fluid mass at time t. The instantaneous location of its centre of mass is then given by

$$\bar{\boldsymbol{R}}^*(t) \equiv \frac{1}{\tau_f}\int_{\tau_f} \boldsymbol{R}\, \mathrm{d}^3\boldsymbol{r}, \tag{7.18}$$

where $\boldsymbol{R}$ denotes the position vector of a point in $\tau_f(t)$, measured relative to the same fixed origin as is $\bar{\boldsymbol{R}}^*$. From a Lagrangian viewpoint the time derivative (cf. equation (7.17))

$$\mathrm{d}\bar{\boldsymbol{R}}^*/\mathrm{d}t \equiv \bar{\boldsymbol{v}}^*, \quad \text{say}, \tag{7.19}$$

gives the Darcy-scale Lagrangian velocity of the macroscopic material 'point'. Hence, by definition of this vector $\bar{\boldsymbol{v}}^*$,

$$\bar{\boldsymbol{v}}^* = \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{1}{\tau_f}\int_{\tau_f(t)} \boldsymbol{R}\,\mathrm{d}^3\boldsymbol{r}\right]. \tag{7.20}$$

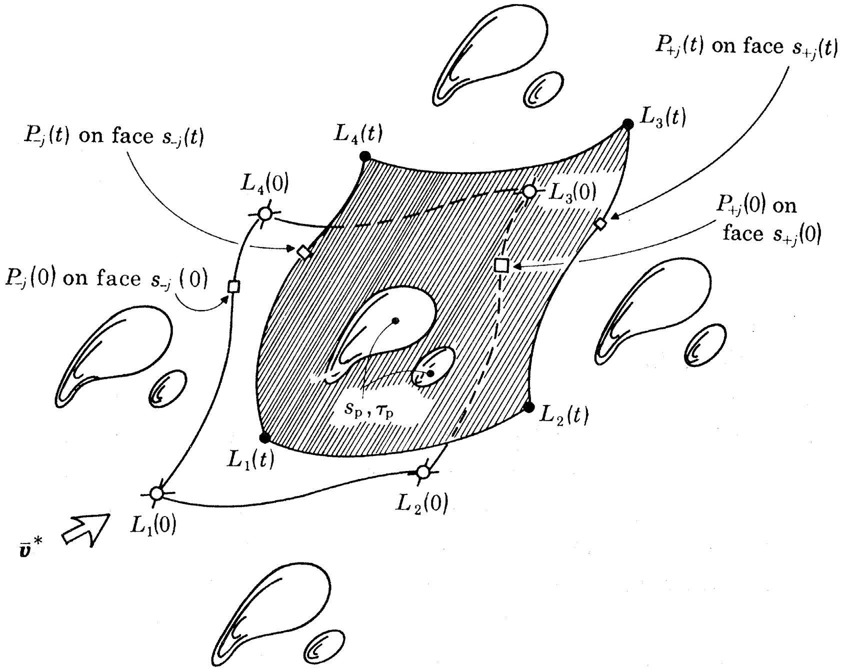

FIGURE 11. Motion of the fluid contents of a two-dimensional unit cell with time. Initially, at time $t = 0$, the curvilinear unit cell is that containing the four lattice points $L_i(0)$ $(i = 1, 2, 3, 4)$. After a period of time t, the fluid contents of the advected unit cell – corresponding to the shaded region – is that containing the four lattice points $L_i(t)$. The external shape $\partial\tau_o(t)$ of the curvilinear unit cell at time t will generally differ from the external shape $\partial\tau_o(0)$ of the original cell from which it derives. That $\partial\tau_o(t)$ fulfills the criteria demanded of a unit cell may be demonstrated by using the local Lagrangian relation (7.17) in conjunction with the spatial periodicity condition (3.4). This permits calculation of the trajectory $\boldsymbol{R}(\boldsymbol{R}_o, t)$ of each material point $\boldsymbol{R}_o$. In particular, it is readily proved that the vector $\{L_i(0) \rightarrow L_i(t)\}$ has the same value for each i. Moreover, if $P_{\pm j}(0)$ denote an equivalent pair of material points (in the sense of equation (2.13)) on the opposite pair of faces $s_{\pm j}(0)$, and if $P_{\pm j}(t)$ represent these same material points on the surfaces $s_{\pm j}(t)$, then it can be shown that $\{P_{-j}(0) \rightarrow P_{-j}(t)\} = \{P_{+j}(0) \rightarrow P_{+j}(t)\}$. Hence, the opposite pair of surfaces $s_{\pm j}(t)$ are congruent in the sense described in the text preceding equation (2.13). It is these facts that show $\partial\tau_o(t)$ to be a unit cell.

According to Reynolds' transport theorem (Aris 1962, Batchelor 1967),

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\tau_f(t)} \psi\,\mathrm{d}^3\boldsymbol{r} = \int_{\tau_f(t)} \frac{\partial\psi}{\partial t}\,\mathrm{d}^3\boldsymbol{r} + \oint_{\partial\tau_o(t)+s_p} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}\psi, \tag{7.21}$$

for ψ any tensor-valued field. In the present instance choose $\psi = 1$, and employ equations (3.2) and (7.6) to obtain

$$\mathrm{d}\tau_f(t)/\mathrm{d}t = 0. \tag{7.22}$$

Hence, the interstitial volume occupied by the moving unit cell is a constant, τ_f, say, independent of time. This is, of course, an immediate consequence of the constancy of the mass contained in $\tau_f(t)$, considered in conjunction with the incompressibility of the fluid.

Equation (7.20) may thus be written as

$$\bar{\boldsymbol{v}}^* = \frac{1}{\tau_f}\left[\frac{d}{dt}\int_{\tau_f(t)} \boldsymbol{R}\, d^3\boldsymbol{r}\right]. \tag{7.23}$$

The term in square brackets may be evaluated by putting $\psi = \boldsymbol{R}$ in Reynolds' transport theorem [7.21] to obtain

$$\bar{\boldsymbol{v}}^* = \frac{1}{\tau_f}\left[\int_{\tau_f(t)} \frac{\partial \boldsymbol{R}}{\partial t}\, d^3\boldsymbol{r} + \oint_{\partial\tau_o(t)+s_p} d\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{R}\right].$$

However, $\partial\boldsymbol{R}/\partial t = 0$ since the partial time differentiation is to be performed with $\boldsymbol{R}$ held fixed. Furthermore, equation (3.2) shows that the above surface integral vanishes on s_p. Consequently,

$$\bar{\boldsymbol{v}}^* = \frac{1}{\tau_f}\int_{\partial\tau_o(t)} d\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{R}. \tag{7.24}$$

The preceding relation provides a prescription whereby the Darcy-scale Lagrangian velocity $\bar{\boldsymbol{v}}^*$, defined by equation (7.19), may be computed from knowledge of the local interstitial field $\boldsymbol{v}$. However, from equations (7.14), (7.4), and (2.6), the integral on the right-hand side of the above also defines the Darcy-scale *Eulerian* velocity. Thereby, the formal equivalence of the Lagrangian and Eulerian velocities is demonstrated.

Beginning with definition of the centre of volume of the *entire* unit cell,

$$\bar{\boldsymbol{R}}(t) \equiv \frac{1}{\tau_o}\int_{\tau_o(t)} \boldsymbol{R}\, d^3\boldsymbol{r}, \tag{7.25}$$

in place of equation (7.18), it can be similarly demonstrated that the Lagrangian vector $\bar{\boldsymbol{v}}$, defined as

$$\bar{\boldsymbol{v}} \equiv d\bar{\boldsymbol{R}}/dt, \tag{7.26}$$

is given by

$$\bar{\boldsymbol{v}} = \frac{1}{\tau_o}\int_{\partial\tau_o(t)} d\boldsymbol{s}\cdot\boldsymbol{v}\boldsymbol{R}, \tag{7.27}$$

and so is identical to the (Eulerian) seepage velocity vector (7.4). [The proof requires use of the fact that the domain of integration in equation (7.25) may be written as $\tau_o(t) \equiv \tau_f(t) \oplus \tau_p$. Furthermore, $d\tau_p/dt = 0$, since τ_p is independent of time.]

'Areal' versus 'volumetric' porosity

Equation (2.12) may be written in Darcy-scale notation as

$$d\bar{\boldsymbol{R}}_i \cdot d\bar{\boldsymbol{s}}_j = \delta_{ij}\,\tau_o, \tag{7.28}$$

with $\tau_o \equiv d^3\bar{\boldsymbol{R}}$ the Darcy-scale volume element. Analogously, one may define the mean interstitial directed surface element $d\bar{\boldsymbol{s}}_j^*$ via the relation

$$d\bar{\boldsymbol{R}}_i \cdot d\bar{\boldsymbol{s}}_j^* = \delta_{ij}\,\tau_f. \tag{7.29}$$

Define the 'areal' porosity ϵ^* as the proportionality coefficient in the expression

$$d\bar{\boldsymbol{s}}_v^* = \epsilon^* d\bar{\boldsymbol{s}}_v, \tag{7.30}$$

which serves to relate the interstitial and superficial areas. It follows from these three relations that $\epsilon^* = \tau_f/\tau_o$. Comparison of the latter with equation (2.6) shows that

$$\epsilon^* = \epsilon. \tag{7.31}$$

Hence the areal porosity is identical with the 'volumetric' porosity ϵ. This equality also holds for random porous media (Bear 1972, Whitaker 1966, 1967, 1969, 1971, 1973).

It is this circumstance that accounts for the appearance in equation (7.14) of the volumetric, rather than areal, porosity, since the natural *Eulerian* definition of $\bar{\boldsymbol{v}}^*$ is

$$\mathrm{d}\bar{q}_v = \mathrm{d}\bar{\boldsymbol{s}}_v^* \cdot \bar{\boldsymbol{v}}^*, \tag{7.32}$$

whence it follows from equations (7.13) and (7.30) that

$$\bar{\boldsymbol{v}}^* = \bar{\boldsymbol{v}}/\epsilon^*. \tag{7.33}$$

8. PROPERTIES OF THE DISPERSION DYADIC

Symmetry and positive-definiteness

The dispersion dyadic, defined in equation (6.14), is symmetric, in the sense that

$$\bar{D}^*_{ij} = \bar{D}^*_{ji}. \tag{8.1}$$

Moreover, $\bar{\boldsymbol{D}}^*$ = a positive-definite dyadic. (8.2)

To prove this, let $\boldsymbol{\chi}$ be any arbitrary, position-independent vector. It follows that

$$\chi_i \bar{D}^*_{ij} \chi_j = \frac{D}{\tau_f} \int_{\tau_f} \psi_k^2 \, \mathrm{d}^3\boldsymbol{r}, \tag{8.3}$$

where $\boldsymbol{\psi}$ is the vector $\psi_k = \chi_l B_{l,k}$. The integrand is non-negative definite at all points $\boldsymbol{r}$, and vanishes at all $\boldsymbol{r}$ for an arbitrary vector $\boldsymbol{\chi}$ if, and only if, $\boldsymbol{B}$ is constant for all $\boldsymbol{r} \in \tau_f$. However, the value $\boldsymbol{B}$ = constant is incompatible with the system of equations (5.6) defining $\boldsymbol{B}$. Hence, ψ_k^2 cannot vanish for all $\boldsymbol{r} \in \tau_f$. In conjunction with the positive-definite nature of the scalars D and τ_f, this shows that $\boldsymbol{\chi} \cdot \bar{\boldsymbol{D}}^* \cdot \boldsymbol{\chi} > 0$, which proves equation (8.2).

Invariance of $\bar{\boldsymbol{D}}^*$ to external unit cell shape

Superficially, it would appear that the integral (6.13), and hence $\bar{\boldsymbol{D}}^*$ depends upon the external shape $\partial\tau_o$ of the curvilinear unit cell bounding the fluid volume τ_f for two reasons: (i) the $\boldsymbol{B}$ field entering into the integrand appears to depend upon cell shape, since the basic lattice vectors $\boldsymbol{l}_j$ $(j = 1, 2, 3)$ appear explicitly in boundary condition (5.6*c*) (i.e., as in the equation immediately preceding equation (7.9), $[\![\boldsymbol{r}]\!] = \boldsymbol{l}_j$), and there exist infinitely many ways in which these may be selected; (ii) the integration domain τ_f appearing in equation (6.13) depends upon cell shape.

For the same physical reasons discussed in connection with $\bar{\boldsymbol{v}}$ (and $\bar{\boldsymbol{v}}^*$) it behoves us, therefore, to demonstrate that $\bar{\boldsymbol{D}}^*$ is independent of the external cell shape $\partial\tau_o$, and is therefore a macroscopic invariant. This will be done in two steps: (i) the field $\boldsymbol{B}(\boldsymbol{r})$ will be demonstrated to be independent of cell shape; (ii) the value of the integral (6.13) will be shown to possess a similar invariance with respect to explicit choice of cell shape.

*Invariance of **B**-field to external unit cell shape*

Equations (5.6), governing transport of the vector quantity $\boldsymbol{B}$ within the interstices of a unit cell, correspond physically to a steady-state convective–diffusive transport process characterized by a position-independent volumetric source density $-\bar{\boldsymbol{v}}^*$, zero normal diffusion flux across the surfaces bounding τ_f, and a difference $\boldsymbol{l}_j$ $(j = 1, 2, 3)$ in the density of $\boldsymbol{B}$ across the cell faces. For a *prescribed cell shape*, it is shown in appendix A that the solution $\boldsymbol{B}$ of these equations is uniquely defined to within an arbitrary additive constant vector. The latter is physically irrelevant insofar as the integral (6.13) is concerned

The field $\boldsymbol{B}(\boldsymbol{r})$ is defined only within the interior of a unit cell It is possible, however, to introduce a comparable continuous field $\boldsymbol{B}(\boldsymbol{R})$, defined globally on the entire porous medium, such that it is identical to $\boldsymbol{B}(\boldsymbol{r})$ within any given cell, albeit to within an additive constant vector In particular, consider the vector field $\boldsymbol{B}(\boldsymbol{R})$ $(\boldsymbol{R} \in V_{f\infty})$, defined as the solution of the system of equations

$$\bar{\boldsymbol{v}}^* = -\boldsymbol{v}\cdot\nabla\boldsymbol{B} + D\,\nabla^2\boldsymbol{B}, \tag{8.4a}$$

$$\boldsymbol{v}\cdot\nabla\boldsymbol{B} = 0 \quad \text{on } s_p, \tag{8.4b}$$

$$\nabla\boldsymbol{B} = \text{spatially periodic}, \tag{8.4c}$$

$$\frac{1}{\tau_o}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\boldsymbol{B} = -\boldsymbol{I}, \tag{8.4d}$$

with $\boldsymbol{I}$ the dyadic idemfactor. By spatial periodicity of $\nabla\boldsymbol{B}$ is meant $\nabla\boldsymbol{B}(\boldsymbol{R}+\boldsymbol{R}_n) = \nabla\boldsymbol{B}(\boldsymbol{R})$.

Appearances to the contrary notwithstanding, the solution $\boldsymbol{B}(\boldsymbol{R})$ of this system of equations is independent of the external cell shape $\partial\tau_o$. This may be demonstrated by observing that the curvilinear cell shape enters only via its appearance as the domain of integration in boundary condition (8.4*d*). However, by application of the generalized divergence theorem to the fluid volume τ_f, this integral can be written as

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\boldsymbol{B} = \int_{\tau_f} \nabla\boldsymbol{B}\,\mathrm{d}^3\boldsymbol{r} - \int_{s_p} \mathrm{d}\boldsymbol{s}\boldsymbol{B}.$$

Since $\nabla\boldsymbol{B}$ is a spatially periodic function, the theorem pertaining to equation (7.2) shows that the integral over τ_f is independent of external cell shape. The same is obviously true of the integral over s_p too. Hence, the value of the intergal in equation (8.4*d*) is invariant to the particular choice made for $\partial\tau_o$, whence the same property necessarily attaches to $\boldsymbol{B}(\boldsymbol{R})$.

That $\partial\tau_o$ rather than $\partial\tau_o\{\boldsymbol{n}\}$ appears as the domain of integration in the boundary condition (8.4*d*) is a reflection of the fact that this integral possesses the same value for every cell $\{\boldsymbol{n}\}$ in the array as a consequence of the spatial-periodicity condition (8.4*c*) (Brenner 1981). [This can be proved, for example, by utilizing the decomposition theorem (8.7) in conjunction with the fact that

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\breve{\boldsymbol{B}} = 0$$

(cf. equation (B 7) of appendix B).]

If $\boldsymbol{u}(\boldsymbol{R})$ is any global tensor-valued field possessing a spatially periodic gradient, then the following fundamental 'decomposition' theorem obtains (Brenner 1981):

$$\boldsymbol{u}(\boldsymbol{R}) = \breve{\boldsymbol{u}}(\boldsymbol{R}) + \boldsymbol{R}\cdot\bar{\boldsymbol{G}}, \tag{8.5}$$

in which $\breve{\boldsymbol{u}}$ is a spatially periodic function, and

$$\bar{\boldsymbol{G}} = \frac{1}{\tau_o}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\boldsymbol{u} \tag{8.6}$$

is a constant tensor (whose rank is one order higher than $\boldsymbol{u}$), independent of the external shape $\partial\tau_o$ of the cell over which the surface integration is to be performed, and possessing the same value for every cell $\{\boldsymbol{n}\}$ in the array. In view of equation (8.4*c*) this theorem may be applied to the function $\boldsymbol{B}(\boldsymbol{R})$, with the result that the latter can be expressed in the form

$$\boldsymbol{B}(\boldsymbol{R}) = \breve{\boldsymbol{B}} - \boldsymbol{R}, \tag{8.7}$$

since

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\boldsymbol{R} = \boldsymbol{I}. \tag{8.8}$$

Here, $\breve{\boldsymbol{B}}$ is a spatially periodic function,

$$\breve{\boldsymbol{B}}(\boldsymbol{R}_n + \boldsymbol{R}) = \breve{\boldsymbol{B}}(\boldsymbol{R}). \tag{8.9}$$

As demonstrated in appendix B, the system of equations (8.4) defining the global field $\boldsymbol{B}(\boldsymbol{R})$ possesses a solution which is unique to within an arbitrary additive constant vector, whose value is physically irrelevant.

It is an immediate consequence of equations (8.7), (2.10), and of the spatial periodicity of $\breve{\boldsymbol{B}}$, that

$$[\![\boldsymbol{B}]\!] = -[\![\boldsymbol{r}]\!]. \tag{8.10}$$

Moreover, it follows from equation (8.4*c*) that

$$[\![\nabla\boldsymbol{B}]\!] = 0. \tag{8.11}$$

The system of equations (8.4*a*, *b*), (8.10), and (8.11) satisfied by the global function $\boldsymbol{B}(\boldsymbol{R})$ is identical to the comparable system (5.6) satisfied by the local function $\boldsymbol{B}(\boldsymbol{r})$. Since each has separately been shown to be unique to within an arbitrary additive constant, it necessarily follows that

$$\boldsymbol{B}(\boldsymbol{R}) = \boldsymbol{B}(\boldsymbol{r}) + \boldsymbol{f}(\boldsymbol{R}_n), \tag{8.12}$$

with $\boldsymbol{f}$ a vector function, functionally dependent only upon $\boldsymbol{R}_n$. Within any one cell (i.e. $\boldsymbol{R} \in \tau_f\{\boldsymbol{n}\}$) this function is a constant. The value of this function may be obtained from equations (2.10) and (8.7) as $\boldsymbol{f}(\boldsymbol{R}_n) = -\boldsymbol{R}_n$. Thus,

$$\boldsymbol{B}(\boldsymbol{R}) = \boldsymbol{B}(\boldsymbol{r}) - \boldsymbol{R}_n, \tag{8.13}$$

in addition to

$$\breve{\boldsymbol{B}} = \boldsymbol{B}(\boldsymbol{r}) + \boldsymbol{r} + \text{const.} \tag{8.14}$$

The arbitrary constant in the latter expression possesses the same numerical value for every cell in the array. Equation (8.13) shows that the global and local $\boldsymbol{B}$ fields coincide within any cell to within the local position-independent constant $\boldsymbol{R}_n$ defining the particular cell within which the comparison is being made.

Since $\boldsymbol{B}(\boldsymbol{R})$ is independent of the external cell shape $\partial\tau_o$, and since the vector $\boldsymbol{R}_n$ is also independent of cell shape (depending only upon the locations of the lattice points characterizing the array), this same property must also be an attribute of $\boldsymbol{B}(\boldsymbol{r})$ in consequence of equation (8.13).

In view of equation (8.13), the field $\boldsymbol{B}$, required in the computation of the dispersivity integral (6.13), may be regarded as being unambigously defined (to within an arbitrary constant vector) by either of the systems of equations (5.6) or (8.4), whichever proves more convenient. Whereas the boundary-value problem posed by equation (5.6) is purely local in nature, and need be solved only within the interior of a single unit cell, the comparable boundary-value problem posed by equation (8.4) is global in nature, and must be solved at every interstitial point in the entire porous medium.

Yet another alternative is to solve instead the system of global equations,

$$\nabla\cdot(\boldsymbol{v}\breve{\boldsymbol{B}})-D\,\nabla^2\breve{\boldsymbol{B}}=\boldsymbol{v}-\boldsymbol{v}^*, \tag{8.15a}$$

$$\boldsymbol{\nu}\cdot\nabla\breve{\boldsymbol{B}}=\boldsymbol{\nu}\quad\text{on}\quad s_{\mathrm{p}}, \tag{8.15b}$$

$$\breve{\boldsymbol{B}}=\text{spatially periodic}, \tag{8.15c}$$

derived either from the pair of equations (8.7) and (8.4), or from equations (5.6) and (8.14). The solution $\breve{\boldsymbol{B}}(\boldsymbol{R})$ of these equations is easily shown to be unique to within an arbitrary additive constant, which possesses the same value throughout the array. In principle, this represents perhaps the simplest system of $\boldsymbol{B}$ equations to solve, since no boundary conditions are imposed on any external cell boundaries $\partial\tau_o$. Moreover, since $\breve{\boldsymbol{B}}$ and $\boldsymbol{v}$ are both spatially periodic, each may be expanded in Bloch functions (Brillouin 1953, Sachs 1963) possessing the translational symmetry of the lattice.

The demonstrated invariance of $\boldsymbol{B}$ to cell shape shows that the integrand of equation (6.13), from which $\bar{\boldsymbol{D}}^*$ is to be computed, displays this same invariance. Moreover, it is a consequence of equation (8.4c) that the integrand,

$$\nabla\boldsymbol{B}^{\dagger}\cdot\nabla\boldsymbol{B}=\text{spatially periodic}. \tag{8.16}$$

As in the general discussion pertaining to equation (7.2), it may therefore be concluded that the Darcy-scale constant $\bar{\boldsymbol{D}}^*$ is an invariant, independent of the external shape selected for the unit cell. Such a conclusion is, of course, gratifying in terms of the physical significance of the dispersivity dyadic.

Longitudinal dispersion

The dispersion dyadic (6.13) is composed of *longitudinal* dispersion, parallel to the direction of the mean flow, and *transverse* or lateral dispersion, normal to the mean flow. The former may be treated wholly independently of the latter by the following procedure. Let

$$\boldsymbol{\lambda}=\bar{\boldsymbol{v}}^*/\bar{v}^*, \tag{8.17}$$

with

$$\bar{v}^*=|\bar{\boldsymbol{v}}^*|, \tag{8.18}$$

be a unit vector parallel to the direction of the Darcy-scale flow. Then the (scalar) longitudinal dispersion coefficient is defined as

$$D_{\mathrm{L}}\equiv\boldsymbol{\lambda}\cdot\bar{\boldsymbol{D}}^*\cdot\boldsymbol{\lambda}. \tag{8.19}$$

Hence, from equation (6.13),

$$D_{\mathrm{L}}=\frac{D}{\tau_{\mathrm{f}}}\int_{\tau_{\mathrm{f}}}\nabla B\cdot\nabla B\,\mathrm{d}^3\boldsymbol{r}, \tag{8.20}$$

where B is the *scalar* field,

$$B=\boldsymbol{\lambda}\cdot\boldsymbol{B}. \tag{8.21}$$

In view of the non-negative nature of the integrand in equation (8.20) it follows that $D_{\mathrm{L}}\geqslant 0$, in accord with expectations.

The scalar B field required in the evaluation of equation (8.20) may be regarded as either local or global in character. From a *local* viewpoint, $B(\boldsymbol{r})$ may be regarded as defined by the following system of equations, derived from equation (5.6) (see figure 8):

$$\boldsymbol{v}\cdot\nabla B-D\,\nabla^2 B=-\bar{v}^*, \tag{8.22a}$$

$$\boldsymbol{\nu}\cdot\nabla B=0\quad\text{on}\quad s_{\mathrm{p}}, \tag{8.22b}$$

$$B(P_{+j}) = B(P_{-j}) - l_j \cos\theta_j \quad (j = 1, 2, 3), \tag{8.22c}$$

$$\nabla B(P_{+j}) = \nabla B(P_{-j}) \quad (j = 1, 2, 3), \tag{8.22d}$$

with $l_j = |\boldsymbol{l}_j|$, and θ_j the constant angle between the directions of $\boldsymbol{l}_j$ and the mean flow.

These correspond physically to a conventional scalar convective-diffusion transport process with a constant sink of volumetric strength $\bar{v}^*$. As such, B may be interpreted as a local 'solute' concentration. It follows from these equations that the net convective flow, $-\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}B$, of solute into the cell through the external boundaries $\partial\tau_o$ is exactly sufficient to account for the total rate of solute annihilation $\bar{v}^*\tau_f$ occurring within the interstitial fluid.

Despite the ease with which these equations lend themselves to physical interpretation, integration is obviously a matter of great analytical difficulty owing to the formidable structure of the local velocity field $\boldsymbol{v}$. It is hoped to be able to report upon the outcome of such numerical computations in a subsequent publication.

Pure molecular diffusion. The case of no convection

In the limiting case where $\bar{\boldsymbol{v}}^* = 0$ – and, hence, $\boldsymbol{v} = 0$, everywhere – solute transport in the interstices occurs solely by the mechanism of molecular diffusion. In such circumstances equation (6.13) yields

$$\bar{\boldsymbol{D}}_o^* = \frac{D}{\tau_f}\int_{\tau_f} \nabla \boldsymbol{B}_o^\dagger \cdot \nabla \boldsymbol{B}_o \, \mathrm{d}^3\boldsymbol{r} \tag{8.23}$$

for the Darcy-scale *diffusivity* dyadic. Here, $\boldsymbol{B}_o$ is the solution of the system of equations (5.6), or any of its equivalent global invariants, with $\bar{\boldsymbol{v}}^* = \boldsymbol{v} = 0$. For definiteness we shall regard $\boldsymbol{B}_o$ as the global field derived from equations (8.4), namely

$$\nabla^2 \boldsymbol{B}_o = 0, \quad \boldsymbol{\nu}\cdot\nabla\boldsymbol{B}_o = 0 \quad \text{on} \quad s_p, \tag{8.24a, b}$$

$$\nabla\boldsymbol{B}_o = \text{spatially periodic}, \tag{8.24c}$$

and

$$\frac{1}{\tau_o}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\boldsymbol{B}_o = -\boldsymbol{I}. \tag{8.24d}$$

Equation (8.23), derived by an *unsteady-state* tracer analysis, may also be obtained by a wholly independent method (Brenner 1981), based upon a *steady-state*, macroscopically homogeneous and unidirectional, analysis of the molecular diffusion process occurring in the interstices.

At steady state, the local solute flux vector $\boldsymbol{j} \equiv \boldsymbol{j}(\boldsymbol{R})$ at any point $\boldsymbol{R}$ within the interstices satisfies the conservation equation,

$$\nabla\cdot\boldsymbol{j} = 0. \tag{8.25}$$

Additionally, the condition that the bed particles are impermeable to solute requires that

$$\boldsymbol{\nu}\cdot\boldsymbol{j} = 0 \quad \text{on} \quad s_p. \tag{8.26}$$

These conditions are analogous to equations (3.1) and (3.2). As in the case of the velocity field, it is therefore assumed that

$$\boldsymbol{j} = \text{spatially periodic} \tag{8.27}$$

in the subsequent steady-state analysis.

Let $\bar{\boldsymbol{j}}$ be the *superficial* Darcy-scale solute flux vector, defined as (cf. equations (7.8) and (7.7))

$$q_k \equiv \boldsymbol{s}_k\cdot\bar{\boldsymbol{j}}, \tag{8.28}$$

with

$$q_k = \int_{s_k} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{j} \tag{8.29}$$

the time rate of solute transport across face s_k of a curvilinear unit cell. Hence, analogous to equations (7.4) and (7.1), it follows that

$$\bar{\boldsymbol{j}} = \frac{1}{\tau_o}\int_{\partial\tau_o} \boldsymbol{R}\, \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{j} = \frac{1}{\tau_o}\int_{\tau_f} \boldsymbol{j}\,\mathrm{d}^3\boldsymbol{r}. \tag{8.30}$$

This vector is independent of $\{\boldsymbol{n}\}$, and hence constant throughout the porous medium. (Moreover, its numerical value is independent of the explicit choice made for the external cell shape $\partial\tau_o$.) The constancy of $\bar{\boldsymbol{j}}$ or, equivalently, of the Darcy-scale *interstitial* solute flux vector (cf. equation (7.14)),

$$\bar{\boldsymbol{j}}^* \equiv \bar{\boldsymbol{j}}/\epsilon = \frac{1}{\tau_f}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{j}\boldsymbol{R}, \tag{8.31}$$

corresponds physically to a macroscopically homogeneous, rectilinear, Darcy-scale solute transport process.

With $c \equiv c(\boldsymbol{R})$ the local volumetric solute concentration, it will be assumed that

$$\boldsymbol{j} = -D\nabla c, \tag{8.32}$$

corresponding to Fick's law of diffusion. For a prescribed value of $\bar{\boldsymbol{j}}$ or $\bar{\boldsymbol{j}}^*$, the system of equations (8.25)–(8.27), (8.30) or (8.31), and (8.32) can be shown (Brenner 1981, Cone 1971) to yield a unique solution for the field pair $(\boldsymbol{j}, c)$ at each point $\boldsymbol{R} \in V_{f\infty}$, though c itself is unique only to within a physically irrelevant, arbitrary additive constant.

In combination, equations (8.27) and (8.32) reveal that ∇c is spatially periodic. Hence, theorem (8.5)–(8.6) shows that c possesses a decomposition of the form

$$c = \breve{c} + \boldsymbol{R}\cdot\bar{\boldsymbol{G}}^*, \tag{8.33}$$

with $\breve{c} \equiv \breve{c}(\boldsymbol{R})$ a spatially periodic function, and

$$\bar{\boldsymbol{G}}^* \equiv \frac{1}{\tau_o}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\, c \tag{8.34}$$

a constant vector throughout the porous medium. In particular, it is independent of $\{\boldsymbol{n}\}$, and invariant to choice of external cell shape $\partial\tau_o$. Physically, this macroscopic vector plays the role of the Darcy-scale solute concentration gradient, a fact that may be demonstrated as follows:

Define the Darcy-scale interstitial solute concentration at a 'macroscopic point' $\boldsymbol{R}_n$ as

$$\bar{c}(\boldsymbol{R}_n) \equiv \frac{1}{\tau_f}\int_{\tau_f\{\boldsymbol{n}\}} c\,\mathrm{d}^3\boldsymbol{r}. \tag{8.35}$$

It is then a consequence of equation (8.33) that

$$\bar{c}(\boldsymbol{R}_n) = \bar{c}(\boldsymbol{0}) + \boldsymbol{R}_n\cdot\bar{\boldsymbol{G}}^*, \tag{8.36}$$

wherein we have arbitrarily put $\boldsymbol{R}_o = \boldsymbol{0}$. In addition, define the Darcy-scale 'gradient operator' $\bar{\nabla}$ such that, for $\boldsymbol{l}_k$ any one of the infinite number of allowable basic lattice vectors,

$$\bar{\boldsymbol{f}}(\boldsymbol{R}_n + \boldsymbol{l}_k) - \bar{\boldsymbol{f}}(\boldsymbol{R}_n) = \boldsymbol{l}_k\cdot\bar{\nabla}\bar{\boldsymbol{f}}. \tag{8.37}$$

Here, $\bar{\boldsymbol{f}} \equiv \bar{\boldsymbol{f}}(\boldsymbol{R}_n)$ is any Darcy-scale tensor-valued function, dependent upon the position of the 'macroscopic point' $\boldsymbol{R}_n$. (A special case of this relation is $\bar{\nabla}\boldsymbol{R}_n = \boldsymbol{I}$, which serves as the Darcy-scale analogue of the continuous-field relation $\nabla\boldsymbol{R} = \boldsymbol{I}$.) The vector 'operator' $\bar{\nabla}$ defined by equation (8.37) is an invariant, independent of the choice of $\boldsymbol{l}_k$ (Brenner 1981).

[The relation between the Darcy-scale gradient operator $\bar{\nabla}$, defined by equation (8.37), and the ordinary gradient operator ∇ is most readily grasped by adopting the Darcy-scale notation, $\bar{\boldsymbol{R}} \equiv \boldsymbol{R}_n$ and $\mathrm{d}\bar{\boldsymbol{R}} \equiv \boldsymbol{l}_k$. Consequently, equation (8.37) may be written as

$$\mathrm{d}\bar{f} = \mathrm{d}\bar{\boldsymbol{R}}\cdot\bar{\nabla}\bar{f},$$

wherein

$$\mathrm{d}\bar{f} \equiv \bar{f}(\bar{\boldsymbol{R}}+\mathrm{d}\bar{\boldsymbol{R}})-\bar{f}(\bar{\boldsymbol{R}})$$

is the difference in the value of the function $\bar{f}(\bar{\boldsymbol{R}})$ between the two 'adjacent' macropoints, $\bar{\boldsymbol{R}}$ and $\bar{\boldsymbol{R}}+\mathrm{d}\bar{\boldsymbol{R}}$. The suggestive notational equivalence, $\mathrm{d}\bar{\boldsymbol{R}} \equiv \boldsymbol{l}_k$, hinges upon the fact 'almost all' orientations in space can be represented by the infinite set of orientations $\boldsymbol{v}_k = \boldsymbol{l}_k/|\boldsymbol{l}_k|$.

The first of the displayed relations in this parenthetical remark is the obvious analogue of the continuous field relation

$$\mathrm{d}f = \mathrm{d}\boldsymbol{R}\cdot\nabla f,$$

where $f \equiv f(\boldsymbol{R})$. This relation constitutes the definition of the gradient operator.]

It is an immediate consequence of equation (8.36) that

$$\bar{c}(\boldsymbol{R}_n+\boldsymbol{l}_k)-\bar{c}(\boldsymbol{R}_n) = \boldsymbol{l}_k\cdot\bar{\boldsymbol{G}}^*, \tag{8.38}$$

Comparison of this with the generic relation (8.37) thereby yields

$$\bar{\boldsymbol{G}}^* = \bar{\nabla}\bar{c}. \tag{8.39}$$

This equation is to be understood as providing confirmation of the fact that the vector $\bar{\boldsymbol{G}}^*$, defined by equation (8.34), physically represents the Darcy-scale solute concentration gradient.

In applications, either the Darcy-scale flux $\bar{\boldsymbol{j}}^*$ (cf. equation (8.31)) or the Darcy-scale concentration gradient $\bar{\boldsymbol{G}}^*$ (cf. equation (8.34)) may be regarded as the prescribed *physical* parameter. Specification of either, in conjunction with the system of equations (8.25)–(8.27) and (8.32), leads to a unique solution (Brenner 1981, Cone 1971) for the field pair $(\boldsymbol{j}, c)$ at each point $\boldsymbol{R}$. Hence, $\bar{\boldsymbol{j}}^*$ may be regarded as uniquely determined by $\bar{\boldsymbol{G}}^*$ and conversely. The former case, wherein $\bar{\boldsymbol{G}}^*$ is specified and $\bar{\boldsymbol{j}}^*$ is subsequently calculated, represents the most commonly encountered physical situation.

For a specified value of the Darcy-scale concentration gradient $\bar{\boldsymbol{G}}^*$, define a vector 'concentration' field $\boldsymbol{C} \equiv \boldsymbol{C}(\boldsymbol{R})$ by the relation

$$c = \boldsymbol{C}\cdot\bar{\boldsymbol{G}}^*. \tag{8.40}$$

Since the direction and magnitude of $\bar{\boldsymbol{G}}^*$ may be arbitrarily specified, it readily follows from equations (8.32), (8.25)–(8.27), and (8.34) that $\boldsymbol{C}$ is the solution of the system of equations

$$\nabla^2\boldsymbol{C} = 0, \quad \boldsymbol{v}\cdot\nabla\boldsymbol{C} = 0 \quad \text{on} \quad s_{\mathrm{p}}, \tag{8.41 a, b}$$

$$\nabla\boldsymbol{C} = \text{spatially periodic}, \tag{8.42 a}$$

and

$$\frac{1}{\tau_o}\int_{\partial\tau_o}\mathrm{d}\boldsymbol{s}\boldsymbol{C} = \boldsymbol{I}. \tag{8.42 b}$$

The (unique, to within an arbitrary constant vector) solution $\boldsymbol{C}$ of this system of equations depends only upon the geometrical configuration of the porous medium. In particular, this intrinsic field is independent of the physical parameters of the problem, namely $\bar{\boldsymbol{G}}^*$ (or $\bar{\boldsymbol{j}}^*$) and D. In terms of $\boldsymbol{C}$, the local solute flux (8.32) is given by

$$\boldsymbol{j} = -D(\nabla\boldsymbol{C})\cdot\bar{\boldsymbol{G}}^*. \tag{8.43}$$

Equation (8.31) may be employed to calculate $\bar{\boldsymbol{j}}^*$ from the prescribed value of $\bar{\boldsymbol{G}}^*$. Equations (8.40) and (8.33) show that $\boldsymbol{C}$ possesses the decomposition

$$\boldsymbol{C} = \check{\boldsymbol{C}} + \boldsymbol{R}, \tag{8.44}$$

a result that also follows more directly from (8.42*a*) and (8.42*b*) by application of the theorem (8.5)–(8.6). Here, $\check{\boldsymbol{C}}$ is a spatially-periodic vector field. Elimination of $\boldsymbol{R}$ between equations (8.31) and (8.44) yields

$$\bar{\boldsymbol{j}}^* = \frac{1}{\tau_{\mathrm{f}}}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{j}\boldsymbol{C} - \frac{1}{\tau_{\mathrm{f}}}\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{j}\check{\boldsymbol{C}}. \tag{8.45}$$

Since $\boldsymbol{j}$ and $\check{\boldsymbol{C}}$ are each spatially periodic the same is true of their product. It thereby follows from equation (4.38) (see also (B 7) of appendix B) that the last integral in equation (8.45) is identically zero. In addition, the boundary condition (8.26) permits the first integral in equation (8.45) to be extended over s_{p} too. Consequently,

$$\bar{\boldsymbol{j}}^* = \frac{1}{\tau_{\mathrm{f}}}\int_{\partial\tau_o+s_{\mathrm{p}}} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{j}\boldsymbol{C} = \frac{1}{\tau_{\mathrm{f}}}\int_{\tau_{\mathrm{f}}} \nabla\cdot(\boldsymbol{j}\boldsymbol{C})\,\mathrm{d}^3\boldsymbol{r} \tag{8.46}$$

upon application of the divergence theorem. However, by vector identity,

$$\nabla\cdot(\boldsymbol{j}\boldsymbol{C}) = (\nabla\cdot\boldsymbol{j})\,\boldsymbol{C} + (\nabla\boldsymbol{C})^{\dagger}\cdot\boldsymbol{j}, \tag{8.47}$$

valid for $\boldsymbol{j}$ and $\boldsymbol{C}$ any vector fields. Use of equations (8.25) and (8.44) thereby yields

$$\bar{\boldsymbol{j}}^* = -\bar{\boldsymbol{D}}_o^*\cdot\bar{\boldsymbol{G}}^*, \tag{8.48}$$

wherein

$$\bar{\boldsymbol{D}}_o^* \equiv \frac{D}{\tau_{\mathrm{f}}}\int_{\tau_{\mathrm{f}}} \nabla\boldsymbol{C}^{\dagger}\cdot\nabla\boldsymbol{C}\,\mathrm{d}^3\boldsymbol{r}. \tag{8.49}$$

Since the intrinsic field $\boldsymbol{C}$ is a purely geometric field, independent of $\bar{\boldsymbol{j}}^*$ and $\bar{\boldsymbol{G}}^*$, the same is true of $\bar{\boldsymbol{D}}_o^*$. Hence, equation (8.48) is to be interpreted as a linear Darcy-scale constitutive equation, furnishing the flux $\bar{\boldsymbol{j}}^*$ for a prescribed value of $\bar{\boldsymbol{G}}^*$. In particular, since $\bar{\boldsymbol{G}}^*$ has been shown in equation (8.39) to be the Darcy-scale solute concentration gradient, equation (8.48) may be regarded as the Darcy-scale form of Fick's law. It constitutes the macroscopic analogue of the microscopic relation (8.32).

The phenomenological dyadic $\bar{\boldsymbol{D}}_o^*$ appearing in equation (8.48), and defined in equation (8.49), represents the Darcy-scale diffusion dyadic. It is easily shown, analogous to equations (8.1) and (8.2), to be both positive-definite and symmetric.

Comparison of the system of equations (8.24) defining $\boldsymbol{B}_o$ with the system (8.41)-(8.42) defining $\boldsymbol{C}$, considered in conjunction with the uniqueness (Brenner 1981, Cone 1971) of these fields, show that

$$\boldsymbol{C}(\boldsymbol{R}) = -\boldsymbol{B}_o(\boldsymbol{R}) + \mathrm{const} \tag{8.50}$$

for all $\boldsymbol{R}\in V_{\mathrm{f}\infty}$. Equation (8.49) may therefore be written as

$$\bar{\boldsymbol{D}}_o^* = \frac{D}{\tau_{\mathrm{f}}}\int_{\tau_{\mathrm{f}}} \nabla\boldsymbol{B}_o^{\dagger}\cdot\nabla\boldsymbol{B}_o\,\mathrm{d}^3\boldsymbol{r}. \tag{8.51}$$

This is identical to equation (8.23), which is the formula for the Darcy-scale diffusivity obtained from the unsteady-state dispersion analysis in the limiting case of no convection. Thus, the unsteady-state tracer analysis leads to precisely the same result as the steady-state flux/gradient analysis. Agreement of these two very different modes of analysis is, of course, a very gratifying conclusion.

Similar steady-state modes of analysis (Brenner 1981, Cone 1971) have been used to extend the calculations to include: (i) conduction through the particle interiors; (ii) surface diffusion; (iii) anisotropic molecular conduction; (iv) first-order irreversible chemical reactions in the pore space, etc.

9. Relation of Brownian-motion theory to conventional dispersion phenomena

The unique solution P of the differential equation (4.8) satisfying the boundary conditions (4.7) and (4.3) may be regarded as furnishing the fundamental source solution for the local solute concentration in ordinary convective–diffusion transport processes in spatially periodic porous media. In particular, in a system containing N independently acting tracer (solute) molecules, initially distributed throughout the interstitial fluid in an arbitrary manner, let $c(\boldsymbol{R}, t)$ denote the local number density of solute molecules arising from some arbitrary initial solute distribution $c(\boldsymbol{R}, 0)$, $(\boldsymbol{R} \in V_{\mathrm{f}\infty})$. It will be supposed that

$$c(\boldsymbol{R}, t) \to 0 \quad \text{as} \quad |\boldsymbol{R}| \to \infty \tag{9.1}$$

sufficiently rapidly, such that the integral

$$\int_{V_{\mathrm{f}\infty}} c(\boldsymbol{R}, t)\, \mathrm{d}^3\boldsymbol{R} = N \tag{9.2}$$

is convergent. As is easily proved, the number N of solute molecules in the interstitial fluid remains constant in time since the bed granules are impervious to solute.

By the linear superposition principle, $c(\boldsymbol{R}, t)$ may be expressed in terms of the initial condition $c(\boldsymbol{R}, 0)$ and the fundamental solution P as

$$c(\boldsymbol{R}, t) = \int_{V'_{\mathrm{f}\infty}} c(\boldsymbol{R}', 0)\, P(\boldsymbol{R}, t | \boldsymbol{R}')\, \mathrm{d}^3\boldsymbol{R}'. \tag{9.3}$$

As is readily shown, the solute concentration derived from this relation satisfies the differential equation (cf. equation (4.8)),

$$\partial c/\partial t + \boldsymbol{v} \cdot \nabla c = D\, \nabla^2 c, \tag{9.4}$$

the boundary conditions (cf. equations (4.7) and (4.3)),

$$\boldsymbol{\nu} \cdot \nabla c = 0 \quad \text{on} \quad s_{\mathrm{p}}, \tag{9.5}$$

and

$$c \to 0 \quad \text{as} \quad |\boldsymbol{R}| \to \infty, \tag{9.6}$$

the initial condition,

$$c = c(\boldsymbol{R}, 0) \quad \text{at} \quad t = 0, \tag{9.7}$$

and the normalization condition (9.2) (for all $t > 0$).

From a cellular viewpoint, equation (9.3) may be written alternatively as

$$c(\boldsymbol{R}_n, \boldsymbol{r}, t) = \sum_{n'} \int_{\tau_{\mathrm{f}}\{n'\}} c(\boldsymbol{R}'_n, \boldsymbol{r}', 0)\, P(\boldsymbol{R}_n - \boldsymbol{R}'_n, \boldsymbol{r}, t | \boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r}', \tag{9.8}$$

with c the solute concentration at a (local) point $\boldsymbol{r}$ in cell $\{\boldsymbol{n}\}$. Define the average interstitial solute concentration in cell $\{\boldsymbol{n}\}$ as (cf. equation (8.35))

$$\bar{c}(\boldsymbol{R}_n, t) = \frac{1}{\tau_{\mathrm{f}}} \int_{\tau_{\mathrm{f}}\{n\}} c(\boldsymbol{R}_n, \boldsymbol{r}, t)\, \mathrm{d}^3\boldsymbol{r}. \tag{9.9}$$

From a global viewpoint, this function changes discontinuously as we pass from one cell to the next.

In addition, define the moments,

$$\bar{\boldsymbol{M}}_m(t) = \tau_{\mathrm{f}} \sum_n \boldsymbol{R}_n^m \bar{c}(\boldsymbol{R}_n, t) \quad (m = 0, 1, 2, \ldots), \tag{9.10}$$

of this discontinuous solute number density. In particular, it is readily shown that

$$\bar{M}_0 = N, \tag{9.11}$$

expressing the conservation of solute molecules. Furthermore, as $t \to \infty$ (cf. equation (5.2)) it can be shown (Brenner 1981) that

$$\bar{\boldsymbol{M}}_m(t) \simeq N \boldsymbol{M}_m(t|\boldsymbol{r}'), \tag{9.12}$$

independently of the value of $\boldsymbol{r}'$. Here, $\boldsymbol{M}_m$ are the moments defined in equation (4.34).

For sufficiently long times after commencement of the experiment, the discontinuous solute concentration field $\bar{c}(\boldsymbol{R}_n, t)$ can be put into a 'one-to-one correspondence' with a *continuous* field $\bar{c}(\bar{\boldsymbol{R}}, t)$ satisfying the differential equation

$$\partial\bar{c}/\partial t + \bar{\boldsymbol{v}}^{\bullet} \cdot \bar{\nabla}\bar{c} = \bar{\boldsymbol{D}}^{\bullet} : \bar{\nabla}\bar{\nabla}\bar{c}, \tag{9.13}$$

in which $\bar{\boldsymbol{v}}^{\bullet}$ and $\bar{\boldsymbol{D}}^{\bullet}$ are, respectively, a constant vector and constant (symmetric) dyadic, to be chosen so as to effect this 'correspondence'. Here, $\bar{\boldsymbol{R}}$ is a continuous field of position vectors, defined throughout all of space, $-\infty < |\bar{\boldsymbol{R}}| < \infty$, and $\bar{\nabla} \equiv \partial/\partial\bar{\boldsymbol{R}}$.

[The right-hand side of this expression would normally be written as $\bar{\nabla} \cdot (\bar{\boldsymbol{D}}^{\bullet} \cdot \bar{\nabla}\bar{c})$. Since $\bar{\boldsymbol{D}}^{\bullet}$ is constant, it may be written in the form (9.13) in which, however, $\bar{\boldsymbol{D}}^{\bullet}$ is strictly only the *symmetric* portion of the dispersivity dyadic, in the event that the latter is not generally symmetric.]

The continuous concentration field will be chosen to satisfy the conditions

$$\bar{c}(\bar{\boldsymbol{R}}, t) \to 0 \quad \text{as} \quad |\boldsymbol{R}| \to \infty, \tag{9.14}$$

and

$$\epsilon \int_{\bar{V}_\infty} \bar{c}(\bar{\boldsymbol{R}}, t)\, \mathrm{d}^3\bar{\boldsymbol{R}} = N, \tag{9.15}$$

wherein N has the same value as before, and $\bar{V}_\infty$ denotes all of space – not just the interstitial space $V_{\mathrm{f}\infty}$. Equation (9.15) represents the initial condition imposed upon $\bar{c}$, since it is readily demonstrated from the solute conservation law (9.13) and the boundary condition (9.14), that if equation (9.15) is satisfied at $t = 0$ then it will automatically be satisfied for all $t > 0$.

There are, of course, no boundary conditions to be imposed *vis-a-vis* the bed granules, which possess no explicit existence at the level of description of the Darcy-scale continuum relations defining $\bar{c}(\bar{\boldsymbol{R}}, t)$. Rather, their existence is *implicit* in the numerical values of the phenomenological coefficients $\bar{\boldsymbol{v}}^{\bullet}$ and $\bar{\boldsymbol{D}}^{\bullet}$, as well as in the porosity factor multiplying equation (9.15).

Define the moments $\bar{\boldsymbol{M}}_m^{\bullet}$ of equation (9.13) as

$$\bar{\boldsymbol{M}}_m^{\bullet}(t) = \epsilon \int_{\bar{V}_\infty} \bar{\boldsymbol{R}}^m \bar{c}(\bar{\boldsymbol{R}}, t)\, \mathrm{d}^3\bar{\boldsymbol{R}} \quad (m = 0, 1, 2, \ldots). \tag{9.16}$$

It follows immediately from equation (9.15) that

$$\bar{M}_0^{\bullet} = N \tag{9.17}$$

for all $t > 0$.

By physical interpretation, the quantity

$$\mathrm{d}\overline{m}(\bar{\boldsymbol{R}}, t) \equiv \epsilon\bar{c}(\bar{\boldsymbol{R}}, t)\,\mathrm{d}^3\bar{\boldsymbol{R}}, \tag{9.18}$$

represents the number of solute molecules present within the volume element $\mathrm{d}^3\bar{\boldsymbol{R}}$ centred at $\bar{\boldsymbol{R}}$, as given by the continuum theory. On the other hand, the discretized quantity

$$\overline{m}(\boldsymbol{R}_n, t) \equiv \tau_{\mathrm{f}}\,\bar{c}(\boldsymbol{R}_n, t) \tag{9.19}$$

physically represents the number of solute molecules contained (in the fluid) within the superficial volume $\tau_o\{\boldsymbol{n}\}$ of cell $\{\boldsymbol{n}\}$. As discussed in § 7, the volumes $\mathrm{d}^3\bar{\boldsymbol{R}}$ and τ_o are to be identified as equivalent Darcy-scale volume elements in the continuum and discrete descriptions, respectively, of the transport processes. Accordingly, it is natural to define the 'one-to-one correspondence' of $\bar{c}(\bar{\boldsymbol{R}}, t)$ and $\bar{c}(\boldsymbol{R}_n, t)$ by requiring that the respective moments,

$$\bar{\boldsymbol{M}}^{\bullet}(t) \equiv \int_{\bar{V}_\infty} \bar{\boldsymbol{R}}^m\,\mathrm{d}\overline{m}(\bar{\boldsymbol{R}}, t), \tag{9.20}$$

and

$$\bar{\boldsymbol{M}}_m(t) \equiv \sum_{\boldsymbol{n}} \boldsymbol{R}_n^m\,\overline{m}(\boldsymbol{R}_n, t), \tag{9.21}$$

of the continuous and discrete solute number densities be asymptotically equal at sufficiently long times for each m:

$$\bar{\boldsymbol{M}}_m^{\bullet}(t) \simeq \bar{\boldsymbol{M}}_m(t). \tag{9.22}$$

(The index m should not be confused with $\overline{m}$.)

It can be shown (Brenner 1981) that if these moments are asymptotically matched only in the special cases $m = 1$ and 2, they will automatically be matched for all higher-order m. (In view of equations (9.11) and (9.17) the moments are already matched for $m = 0$.) The momental matching criterion (9.22) of 'equivalence' between $\bar{c}(\bar{\boldsymbol{R}}, t)$ and $\bar{c}(\boldsymbol{R}_n, t)$ ultimately furnishes the formulas by means of which the macroscopic phenomenological coefficients $\bar{\boldsymbol{v}}^{\bullet}$ and $\bar{\boldsymbol{D}}^{\bullet}$ appearing in the continuum model (9.13) are to be derived from knowledge of the microscopic quantities $\boldsymbol{v}$, D, and the geometrical structure of the porous medium.

Comparison of equations (9.22) and (9.12) yields

$$\bar{\boldsymbol{M}}_m^{\bullet} \simeq N\boldsymbol{M}_m(t). \tag{9.23}$$

In consequence of this it follows that formulas (6.6) and (6.12) may be expressed alternatively as (cf. equation (6.7))

$$\bar{\boldsymbol{v}}^* = \lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\bar{\boldsymbol{M}}_1^{\bullet}}{N}\right), \quad \bar{\boldsymbol{D}}^* = \tfrac{1}{2}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\bar{\boldsymbol{M}}_2^{\bullet}}{N} - \frac{\bar{\boldsymbol{M}}_1^{\bullet}\,\bar{\boldsymbol{M}}_1^{\bullet}}{N^2}\right). \tag{9.24a, b}$$

On the other hand (analogous to the steps leading to equation (4.36)), differentiation of equation (9.16) with respect to t, and use of equation (9.13) for $\partial\bar{c}/\partial t$, coupled with the divergence theorem in $\bar{\boldsymbol{R}}$-space, and integration by parts in the light of equation (9.14), eventually gives (Brenner 1981, Brenner & Gaydos 1977)

$$\mathrm{d}\bar{M}_0^{\bullet}/\mathrm{d}t = 0, \quad \Rightarrow \bar{M}_0^{\bullet} = N, \tag{9.25}$$

and

$$\mathrm{d}\bar{\boldsymbol{M}}_1^{\bullet}/\mathrm{d}t = \bar{M}_0^{\bullet}\,\bar{\boldsymbol{v}}^{\bullet}, \tag{9.26}$$

in addition to

$$\mathrm{d}\bar{\boldsymbol{M}}_2^{\bullet}/\mathrm{d}t = \bar{\boldsymbol{M}}_1^{\bullet}\,\bar{\boldsymbol{v}}^{\bullet} + \bar{\boldsymbol{v}}^{\bullet}\bar{\boldsymbol{M}}_1^{\bullet} + (\bar{\boldsymbol{D}}^{\bullet} + \bar{\boldsymbol{D}}^{\bullet\dagger})\,\bar{M}_0^{\bullet}. \tag{9.27}$$

These three equations combine to yield

$$\bar{\boldsymbol{v}}^{\bullet} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\bar{\boldsymbol{M}}_1^{\bullet}}{N}\right), \quad \bar{\boldsymbol{D}}^{\bullet} = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\bar{\boldsymbol{M}}_2^{\bullet}}{N} - \frac{\bar{\boldsymbol{M}}_1^{\bullet}\bar{\boldsymbol{M}}_1^{\bullet}}{N^2}\right), \tag{9.28a, b}$$

the latter being based upon the assumed symmetry of $\bar{\boldsymbol{D}}^{\bullet}$.

Comparison of equations (9.28) and (9.24) thereby shows that

$$\bar{\boldsymbol{v}}^{\bullet} = \bar{\boldsymbol{v}}^{*}, \quad \bar{\boldsymbol{D}}^{\bullet} = \bar{\boldsymbol{D}}^{*}. \tag{9.29a, b}$$

This demonstrates that the mean solute or fluid velocity $\bar{\boldsymbol{v}}^{\bullet}$, and the dispersivity $\bar{\boldsymbol{D}}^{\bullet}$, required in equation (9.13) to being about an equivalence between $\bar{c}(\bar{\boldsymbol{R}}, t)$ and $\bar{c}(\bar{\boldsymbol{R}}_n, t)$ are precisely those quantities $\bar{\boldsymbol{v}}^{*}$ and $\bar{\boldsymbol{D}}^{*}$ already derived from Brownian motion theory, and given explicitly by equations (7.15) (or (7.16)) and (6.13), respectively.

In light of the relationship between Brownian motion and diffusion theory at the microscopic level, such a conclusion appears perfectly reasonable (Brenner & Gaydos 1977), entirely in accord with expectations.

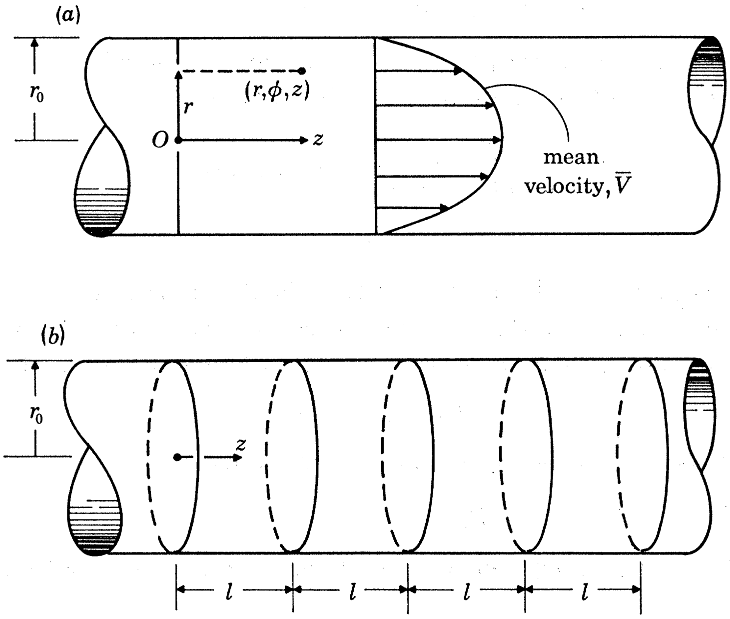

FIGURE 12. (*a*) Poiseuille flow in a circular cylindrical capillary tube. (*b*) Decomposition of the capillary tube into 'unit cells' of length l. The distance z may be regarded as either the local variable, $0 \leqslant z \leqslant l$, or the global variable, $-\infty < z < \infty$.

10. REDUCTION TO TAYLOR–ARIS DISPERSION IN A CAPILLARY TUBE

The complex chain of reasoning leading to equation (5.5) for $\bar{\boldsymbol{v}}^{*}$, and equation (6.13) for $\bar{\boldsymbol{D}}^{*}$, suggests the desirability of illuminating and confirming these expressions by reference to a simple example in which the resnlts are already known independently via an alternative method of calculation. Accordingly, we shall derive from these two integrals the well-known Taylor–Aris results for dispersion of a passive solute in a circular capillary tube. That these general three-dimensional formulas may be applied to the problem of one-dimensional flow in a tube is consistent with the discussion of consolidated porous media in § 2, wherein it was pointed out that such capillary-type transport may be regarded as deriving in a limiting case from comparable transport phenomena through the interstices of an unconsolidated spatially periodic array (see figure 3).

Consider the Poiseuille flow of a Newtonian liquid at mean velocity $\bar{V}$ through a circular capillary of radius r_0 (figure 12), with (r, ϕ, z) a system of circular cylindrical coordinates. This problem may be brought within the realm of spatially periodic flows by imagining the capillary to be decomposed into segments of length l (figure 12). The Poiseuille velocity distribution is given by

$$\boldsymbol{v} = \hat{\boldsymbol{z}}v(r), \tag{10.1}$$

with $\hat{\boldsymbol{z}}$ a unit vector in the z-direction, and

$$v(r) = 2\bar{V}[1-(r/r_0)^2]. \tag{10.2}$$

Since this flow is locally rectilinear its 'period' l is of arbitrary length. Hence, the parameter l cannot (and does not) appear in the final expressions for the phenomenal coefficients $\bar{\boldsymbol{v}}^*$ and $\bar{\boldsymbol{D}}^*$. The interior τ_f of a 'unit cell' is defined by the finite circular cylindrical region,

$$0 \leqslant r \leqslant r_0, \quad 0 \leqslant \phi \leqslant 2\pi, \quad 0 \leqslant z \leqslant l, \tag{10.3}$$

whose boundaries are defined by the planes $z = 0$ and l, and by the cylinder wall $r = r_0$.

Since $\tau_f = \pi r_0^2 l$, equation (7.16) becomes $\bar{\boldsymbol{v}}^* = \hat{\boldsymbol{z}}\bar{v}^*$, where

$$\bar{v}^* = \frac{1}{\pi r_0^2 l}\int_{z=0}^{l}\int_{\phi=0}^{2\pi}\int_{r=0}^{r_0} v(r)\, r\, \mathrm{d}r\, \mathrm{d}\phi\, \mathrm{d}z = \bar{V}. \tag{10.4}$$

Hence,

$$\bar{\boldsymbol{v}}^* = \hat{\boldsymbol{z}}\bar{V}, \tag{10.5}$$

as was to be expected, since $\bar{V}$ is the mean velocity of the Poiseuille flow.

In present circumstances we need only be concerned with spatial periodicity in the z-direction. Consequently, the boundary condition (5.6*c*) (with $[\![\boldsymbol{r}]\!] = \boldsymbol{l}_j$) adopts the form†

$$\boldsymbol{B}(z=l, r) - \boldsymbol{B}(z=0, r) = -\hat{\boldsymbol{z}}l \tag{10.6}$$

for all $0 \leqslant r \leqslant r_0$. Likewise, the boundary condition (5.6*b*) becomes

$$\partial \boldsymbol{B}/\partial r = 0 \quad \text{at} \quad r = r_0, \tag{10.7}$$

since the solid wall r_0 is clearly to be identified with the solid surface s_p, and $\boldsymbol{\nu} = \hat{\boldsymbol{r}}$ is a unit vector in the radial direction.

The system of equations (5.6) defining the $\boldsymbol{B}$ field admits of the solution

$$\boldsymbol{B} = \hat{\boldsymbol{z}}B(z, r), \tag{10.8}$$

where the *scalar* field B is the solution of the boundary-value problem

$$\bar{V} = -v(r)\frac{\partial B}{\partial z} + D\left[\frac{\partial^2 B}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial B}{\partial r}\right)\right], \tag{10.9a}$$

$$\partial B/\partial r = 0 \quad \text{at} \quad r = r_0, \tag{10.9b}$$

$$B(z=l, r) - B(z=0, r) = -l, \tag{10.9c}$$

$$\partial B/\partial z|_{z=l,\, r} = \partial B/\partial z|_{z=0,\, r}. \tag{10.9d}$$

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† For simplicity, we are here solving only the axisymmetric case, where $\boldsymbol{B}$ is independent of ϕ. The relation between this and the more general asymmetric case is discussed by Brenner & Gaydos (1977).

In turn, these admit of a solution of the form (cf. equations (8.7) and (8.13))

$$B(z,r) = \breve{B}(r) - z, \tag{10.10}$$

with $\breve{B}(r)$ a function to be determined. This form automatically satisfies the boundary conditions (10.9*c*) and (10.9*d*). The function $\breve{B}(r)$ is thus determined by the two remaining equations,

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\breve{B}}{\mathrm{d}r}\right) = \frac{\bar{V}-v(r)}{D}, \tag{10.11}$$

and

$$\mathrm{d}\breve{B}/\mathrm{d}r = 0 \quad \text{at} \quad r = r_0. \tag{10.12}$$

The solution is readily found to be

$$\breve{B}(r) = \frac{\bar{V}r_0^2}{8D}\left[\left(\frac{r}{r_0}\right)^4 - 2\left(\frac{r}{r_0}\right)^2\right] + C. \tag{10.13}$$

The appearance of the arbitrary constant of integration C is consistent with the prior observation that the $\boldsymbol{B}$ field is uniquely determined only to within an arbitrary additive constant vector.

[The field

$$\boldsymbol{B} = \hat{\boldsymbol{z}}\left\{\frac{\bar{V}r_0^2}{8D}\left[\left(\frac{r}{r_0}\right)^4 - 2\left(\frac{r}{r_0}\right)^2\right] - z + C\right\},$$

may be regarded as furnishing either the locally-defined field $\boldsymbol{B}(\boldsymbol{r})$ or the globally-defined field $\boldsymbol{B}(\boldsymbol{R})$, respectively, according as z is restricted to the cellular range $0 \leqslant z \leqslant l$, or the global range $-\infty < z < \infty$. This is consistent with equation (8.13), since in present circumstances, $\boldsymbol{R}_n = \hat{\boldsymbol{z}}nl$, where n is the cell number ($n = 0, \pm 1, \pm 2, \ldots$) in which the local field $\boldsymbol{B}(\boldsymbol{r})$ is defined. In turn, this is consistent with equation (8.14), which in present circumstances is equivalent to

$$\boldsymbol{B}(\boldsymbol{r}) = \breve{\boldsymbol{B}}(\boldsymbol{r}) - \hat{\boldsymbol{z}}z + \text{const.}]$$

Equation (6.13) reduces in this case to

$$\bar{\boldsymbol{D}}^* = \hat{\boldsymbol{z}}\hat{\boldsymbol{z}}\bar{D}^*, \tag{10.14}$$

with the scalar (longitudinal) dispersivity given by

$$\bar{D}^* = \frac{D}{\pi r_0^2 l}\int_{z=0}^{l}\int_{r=0}^{r_0}\left[\left(\frac{\partial B}{\partial z}\right)^2 + \left(\frac{\partial B}{\partial r}\right)^2\right] 2\pi r\,\mathrm{d}r\,\mathrm{d}z.$$

From equations (10.10) and (10.13) this yields

$$\bar{D}^* = D + \frac{\bar{V}^2 r_0^2}{48D}, \tag{10.15}$$

in accord with the Taylor–Aris result (Aris 1956, Taylor 1953, 1954*b*).

As was to be expected, these results for $\bar{\boldsymbol{v}}^*$ and $\bar{\boldsymbol{D}}^*$ are independent of the arbitrary length unit l defining the spatial 'period'.

11. Discussion

Formal analogies with Taylor dispersion

Despite the obvious physical differences between one-dimensional Taylor–Aris (T–A) dispersion in capillary tubes, and three-dimensional dispersion phenomena in spatially periodic (s.p.) porous media, formal mathematical analogies exist (Brenner & Gaydos 1977). Perhaps the major analogy is that existing between the (z, r) variables in T–A theory, and the respective $(\boldsymbol{R}_n, \boldsymbol{r})$ variables in s.p. theory. In particular, z and $\boldsymbol{R}_n$ (or $\{\boldsymbol{n}\}$) constitute analogous *global* variables, whereas r and $\boldsymbol{r}$ constitute analogous *local* variables. The mutual independence or 'orthogonality' (Horn 1971) of z and r in T–A theory is analogous to the independence of $\boldsymbol{R}_n$ and $\boldsymbol{r}$ in s.p. theory.

Success of the T–A theory hinges critically upon the fact that the local Poiseuille velocity field $v(r)$ (cf. equation (10.1)) is functionally dependent only upon the local variable r. Analogous to the success of the s.p. theory is the fact the local interstitial velocity vector $\boldsymbol{v}$ is functionally dependent only upon the local variable $\boldsymbol{r}$, as in equation (3.5).

Averages over the local variable r in T–A theory play roles analogous to comparable averages of the local variable $\boldsymbol{r}$ in s.p. theory. Finally, we remark that in the course of forming local moments $\mu_m(r, t|r')$ in T–A theory (Brenner & Gaydos 1977) one integrates over the global variable z^m, and uses integration by parts to then recursively relate moments of different orders. These steps are respectively analogous to forming the local moments $\boldsymbol{\mu}_m(\boldsymbol{r}, t|\boldsymbol{r}')$ in the s.p. theory, summing over the global variable $\boldsymbol{R}_n^m$, and using the technique of 'summation by parts' to recursively relate the moments of different orders, as in equations (4.29).

The s.p. calculations of the present paper are but an example of the deep and abstract generalized analysis of classes of dispersion phenomena by Horn (1971).

Random porous media

The principal geometric characteristic of a 'random' porous medium is that it is identical to itself under an infinitesimal translation $\mathrm{d}\boldsymbol{R}$ in any direction, at least in a statistical sense. In contrast, a spatially periodic porous medium is identical to itself only under the group of finite translations $\boldsymbol{l}_j$ ($\equiv \mathrm{d}\bar{\boldsymbol{R}}$) in specific directions. However, viewed from the Darcy-scale, the distance $|\boldsymbol{l}_j|$ is only 'infinitesimal' in magnitude. Moreover, because of the non-uniqueness of the $\boldsymbol{l}_j$, the infinite set of directions $\boldsymbol{v}_j \equiv \boldsymbol{l}_j/|\boldsymbol{l}_j|$ for which the porous medium maps into itself encompasses virtually all possible directions in space.

Accordingly, Darcy-scale transport phenomena occurring within the interstices of these two different classes of porous media are unlikely to manifest major differences. This strongly suggests the potential applicability of specific results gleaned from the present spatially periodic analysis to random media. The extent to which these hopes are borne out by experience remains to be established by comparison of numerical values predicted from the theory with experimental data. Comparison of experimental *pressure drop* data for real media with theoretical predictions based upon the spatially-periodic model is encouraging in this regard (Brenner 1981).

Longitudinal and transverse dispersion

That the dispersivity is a second-rank tensor, rather than a scalar, accords with experience (Bear 1969, 1972, de Jong 1958, 1972, Fried & Combarnous 1971, Gunn 1969, Whitaker 1967, 1969, 1971, 1973) for real, geometrically isotropic porous media. Such media are transversely isotropic with regard to the direction, $\boldsymbol{\lambda} = \bar{\boldsymbol{v}}/|\bar{\boldsymbol{v}}|$, of the mean flow (cf equation (8.17)). Hence, the dispersion dyadic is necessarily of the general form

$$\bar{\boldsymbol{D}}^* = \boldsymbol{\lambda\lambda} D_{\mathrm{L}} + (\boldsymbol{I} - \boldsymbol{\lambda\lambda})\, D_{\mathrm{T}}, \tag{11.1}$$

with D_{L} the longitudinal or axial dispersivity, and D_{T} the transverse or radial dispersivity. Transverse isotropy with respect to second-rank tensors would not be expected to prevail generally for spatially-periodic media, although it will arise – for example – in the special case where the mean flow is parallel to the 'crystallographic axes' of a simple cubic array (Brenner 1981).

'Mechanical' dispersion in the absence of molecular diffusion

Superficial examination of equation (8.20) suggests that no longitudinal dispersion will occur in the limiting case where the molecular diffusivity tends to zero, since D occurs as the multiplier of the integral. Such, however, is not the case owing to the singular nature of the B field in this limit – as is clearly revealed by the Taylor–Aris example (cf. equation (10.13)). More generally, equation (8.22*a*) reveals the singular nature of the limiting process $D \rightarrow 0$. Discarding the diffusive term would reduce the differential equation describing the transport of B from second- to first-order. As is well known in related problems (Acrivos 1971, Acrivos & Goddard 1965, Acrivos & Taylor 1962, Brenner 1970, Fedkiw & Newman 1977, Frankel & Acrivos 1968, Hinch & Leal 1972, Leal & Hinch 1971, Sih & Newman 1967, Van Dyke 1975) this gives rise to a singular perturbation problem (Van Dyke 1975), requiring rather special limit techniques for its resolution.

In dimensionless terms, this limiting case corresponds to the situation where the Péclet number, $Pe = \bar{v}l/D$, tends to infinity Here, $\bar{v} = |\bar{\boldsymbol{v}}|$, and l is a characteristic particle, pore, or cell size. The Péclet number describes the global ratio of convective to diffusive solute transport. Apart from the fact that the streamline configuration, and hence $\boldsymbol{v}/\bar{v}$, may change as the mean velocity is changed (owing to the effects of inertia upon the viscous fluid motion), the limit $D \rightarrow 0$ corresponds to $\bar{v} \rightarrow \infty$ in terms of the Péclet number criterion.

Experimental dispersion data (Bear 1972, Fried & Combarnous 1971) pertaining to situations in which $Pe \rightarrow \infty$ reveal that the longitudinal dispersivity tends to an non-zero limiting value given by

$$D_{\mathrm{L}} = kl\bar{v}, \tag{11.2}$$

at least in low Reynolds number, Darcy-flow, situations, where the laminar streamline configuration around the individual particles is independent of the mean velocity of flow. Here, k is a non-dimensional constant of order unity. The dispersion occurring in this limiting case is termed 'mechanical' dispersion in the literature (Bear 1972, Fried & Combarnous 1971), since equation (11.2) depends upon the purely hydromechanical factor $\bar{v}$. In particular, the molecular diffusivity does not enter explicitly into the numerical value of D_{L}.

The formula (11.2) has been rationalized (Bear 1972) by assuming that since D does not appear *explicitly* in the limiting formula for D_{L}, it cannot enter *implicitly* into the dispersion mechanism either. Thus, the dispersion mechanism leading to equation (11.2) is presumed to be purely hydromechanical in origin. Since dispersion is, by definition, regarded phenomenologically as a *stochastic* process, the source of such 'mechanical' dispersion has been attributed exclusively to the 'random' geometry of the particle arrangement, and hence to the random interstitial pore space too – with molecular diffusion given no role to play in the stochastic process. Were this general argument correct, in the limit $D \rightarrow 0$ no dispersion could occur in perfectly ordered arrays of the type considered herein, since such media are wholly lacking in stochastic features (and the flow is locally laminar). However, singular perturbation theory applied to the system of equations (8.22) suggests that equation (8.20) will almost certainly yield a nonzero value for D_{L} in the limit where $Pe \rightarrow \infty$.

Thus, in our view, 'mechanical' dispersion is a misnomer. The phenomenon appears conceptually unrelated to the possibly stochastic geometrical structure of the porous medium; nor is it a purely hydromechanical phenomenon. Molecular diffusivity, no matter how small, must be accounted for in its calculation, despite the fact that it does not appear explicitly in the ultimate expression (11.2) for the resulting dispersivity.

The highly singular nature of the limiting process $D \to 0$ is, perhaps, best understood by analogy to the comparable, purely hydrodynamic, problem of the drag force experienced by an isolated sphere immersed in a streaming flow, in the limit where the kinematic viscosity $v \to 0$.

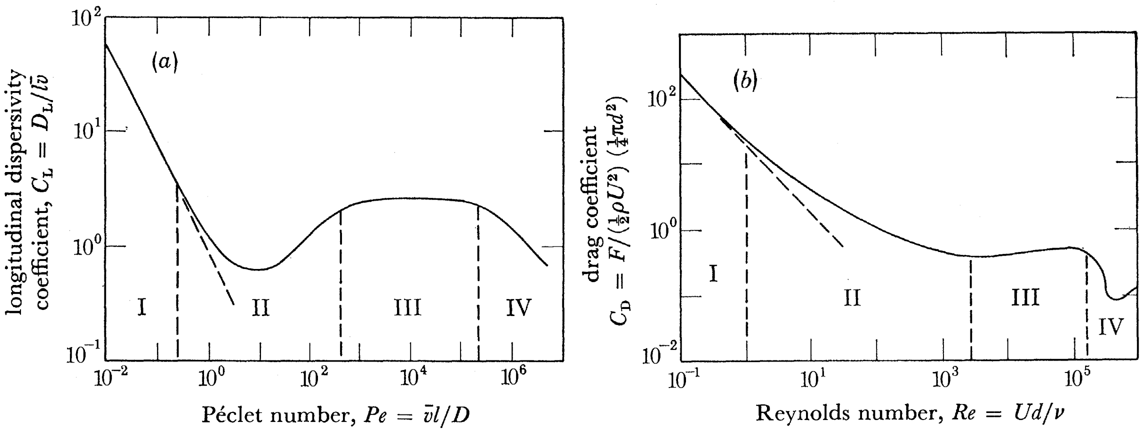

FIGURE 13 (*a*). Summary of experimental data on the longitudinal dispersion coefficient in natural porous media (Bear 1972, Fried & Combarnous 1971). The physical significance of the different régimes is as follows: I, molecular diffusion dominant; II, superposition of molecular diffusion and mechanical dispersion effects; III, mechanical dispersion dominant; IV, dispersion outside the Darcy-flow domain. Fluid inertial effects and/or turbulence cannot be neglected. In general, this régime cannot strictly be represented by a single curve; rather, a series of curves must obtain, one for each value of the Schmidt number ν/D. (*b*) Summary of experimental data on the drag coefficient against Reynolds number for an isolated sphere in a streaming flow (Zenz & Othmer 1960). The physical significance of the different régimes is as follows: I, Stokes law region, viscous effects dominant; II, superposition of viscous and inertial (convective) effects; III, Newton's law region, inertial effects dominant (laminar boundary layer); IV, turbulent boundary layer.

Figure 13*a*, taken from the graphical data compilations of Fried & Combarnous (1971) and Bear (1972), is a dimensionless plot of the experimental longitudinal dispersivity coefficient, $C_D = D_L/\bar{v}l$, against the Péclet number. Essentially four different 'régimes' are found. This plot bears a remarkable resemblance to figure 13*b* (Zenz & Othmer 1960), which is a dimensionless plot of the drag coefficient $C_D = F/(\frac{1}{2}\rho U^2)\ (\frac{1}{4}\pi d^2)$ against the Reynolds number $Re = Ud/\nu$, (F is drag force, ρ fluid density, U stream velocity, and d sphere diameter) for the force on an isolated sphere. Of special interest is a comparison of the 'purely mechanical' dispersion régime III in figure 13*a* – characterized by $C_L = k \approx$ constant, with the 'Newton's law' régime III in figure 13*b* – characterized by $C_D \approx$ constant. Each corresponds to the dominance of convective effects over molecular effects.

The main characteristic of the Newton's law region lies in the fact that the force on the sphere is explicitly independent of the kinematic viscosity ν. Despite this independence, it is well known from boundary-layer theory that the kinematic viscosity contributes importantly to the mechanism whereby the drag force is created. In particular, putting $\nu = 0$ in the Navier–Stokes equations, in an attempt to derive the curve of C_D against Re, which characterizes region III, is known to be theoreticaly incorrect owing to the singular nature of the limiting process $\nu \to 0$ (Van Dyke 1975).

For precisely analogous reasons, one cannot set $D = 0$ in equation (8.22*a*) (nor any of its global variants), and hope to reproduce the C_L against Pe curve characterizing region III of the dispersion plot. Rather, the singular nature of the limiting process $D \to 0$ must be accounted for (cf. the discussions of Saffman (1959*b*, 1960) and Beran (1968) for this limiting case).

This analogy makes it highly unlikely that 'mechanical' dispersion is a purely hydromechanical phenomenon. If confirmed by more detailed considerations, random-walk models of mechanical dispersion would thereby be shown to be devoid of physical content.

Similar remarks apply to the *transverse* dispersivity in the limit as $D \to 0$. Indeed, a curve analogous to figure 13*a* is presented by Fried & Combarnous (1971) for $C_T = D_T/\bar{v}l$ against Pe, showing the same four regions.

Appendix A. Uniqueness of the local field $\boldsymbol{B}(\boldsymbol{r})$

Let $\boldsymbol{B}'(\boldsymbol{r})$ and $\boldsymbol{B}''(\boldsymbol{r})$ each be solutions of the system of equations (5.6). The difference,

$$\boldsymbol{B}^o(\boldsymbol{r}) \equiv \boldsymbol{B}'(\boldsymbol{r}) - \boldsymbol{B}''(\boldsymbol{r}), \tag{A 1}$$

then satisfies the following system of *homogeneous* equations:

$$\nabla \cdot (\boldsymbol{v}\boldsymbol{B}^o) - D\,\nabla^2 \boldsymbol{B}^o = 0, \tag{A 2}$$

$$\boldsymbol{v} \cdot \nabla \boldsymbol{B}^o = 0 \quad \text{on} \quad s_p, \tag{A 3}$$

$$[\![\boldsymbol{B}^o]\!] = 0, \quad [\![\nabla \boldsymbol{B}^o]\!] = 0. \tag{A 4a, b}$$

Dot multiply the first of these by $\boldsymbol{B}^o$, multiply by a volume element $d^3\boldsymbol{r}$, integrate over the interstitial volume τ_f, and employ the divergence theorem to obtain

$$D\int_{\tau_f} \nabla \boldsymbol{B}^o : \nabla \boldsymbol{B}^{o\dagger}\, d^3\boldsymbol{r} = -\frac{1}{2}\int_{\partial\tau_o + s_p} d\boldsymbol{s} \cdot \boldsymbol{v}(B^o)^2 + D\int_{\partial\tau_o + s_p} d\boldsymbol{s} \cdot (\nabla \boldsymbol{B}^o) \cdot \boldsymbol{B}^o, \tag{A 5}$$

with $(B^o)^2 = \boldsymbol{B}^o \cdot \boldsymbol{B}^o$. Boundary conditions (3.2) and (A 3) show that the above surface integrals vanish on s_p. Furthermore, it is a consequence of (A 4) that $[\![(B^o)^2]\!] = 0$ and $[\![(\nabla \boldsymbol{B}^o) \cdot \boldsymbol{B}^o]\!] = 0$. Hence, lemmas (4.37) and (4.38) may be invoked to demonstrate that the surface integrals vanish over $\partial\tau_o$ too. Consequently,

$$\int_{\tau_f} \nabla \boldsymbol{B}^o : \nabla \boldsymbol{B}^{o\dagger}\, d^3\boldsymbol{r} = 0. \tag{A 6}$$

The integrand is a non-negative definite form, from which it may be concluded that

$$\boldsymbol{B}^o(\boldsymbol{r}) = \text{const} \tag{A 7}$$

for all $\boldsymbol{r} \in \tau_f$. Hence, equation (A 1) shows that the solution $\boldsymbol{B}(\boldsymbol{r})$ of the system of equations (5.6) is unique to within an arbitrary additive constant. Q.E.D.

Appendix B. Uniqueness of the global field $\boldsymbol{B}(\boldsymbol{R})$

Let $\boldsymbol{B}'(\boldsymbol{R})$ and $\boldsymbol{B}''(\boldsymbol{R})$ each represent solutions of the system of equations (8.4). The difference,

$$\boldsymbol{B}^o(\boldsymbol{R}) \equiv \boldsymbol{B}'(\boldsymbol{R}) - \boldsymbol{B}''(\boldsymbol{R}), \tag{B 1}$$

then satisfies the following system of *homogeneous* equations:

$$\nabla \cdot (\boldsymbol{v}\boldsymbol{B}^o) - D\,\nabla^2 \boldsymbol{B}^o = 0, \tag{B 2}$$

$$\boldsymbol{v} \cdot \nabla \boldsymbol{B}^o = 0 \quad \text{on} \quad s_p, \tag{B 3}$$

$$\nabla \boldsymbol{B}^o = \text{spatially periodic}, \tag{B 4}$$

$$\int_{\partial\tau_o} d\boldsymbol{s}\, \boldsymbol{B}^o = 0. \tag{B 5}$$

Equation (B 4) in conjunction with theorem (8.5)–(8.6) shows that

$$\boldsymbol{B}^o(\boldsymbol{R}) = \text{spatially periodic} \tag{B 6}$$

upon the use of equation (B 5).

Dot multiply equation (B 2) by $\boldsymbol{B}^o(\boldsymbol{R})$. Proceeding as in the derivation of equation (A 5) from equation (A 2), we eventually obtain a relation identical to (A 5), but with $\boldsymbol{B}^o(\boldsymbol{r})$ replaced by $\boldsymbol{B}^o(\boldsymbol{R})$. Equations (3.2) and (B 3) then show, as before, that the surface integrals vanish over s_p. Now, if $\breve{\boldsymbol{H}}(\boldsymbol{R})$ is any spatially periodic tensor-valued field, it follows that $[\![\breve{\boldsymbol{H}}]\!] = 0$, with the bracketed function defined generically by equation (4.27). Hence, lemma (4.38), which remains valid if the dot-product symbol is removed from both sides of the equality, shows that

$$\int_{\partial\tau_o} \mathrm{d}\boldsymbol{s}\breve{\boldsymbol{H}} = 0. \tag{B 7}$$

Inasmuch as $\boldsymbol{v}$, $\boldsymbol{B}^o(\boldsymbol{R})$ and $\nabla\boldsymbol{B}^o(\boldsymbol{R})$ are each spatially periodic fields, the same is true of any combinations of their products. Hence, theorem (B 7) shows that the surface integrals over $\partial\tau_o$ in equation (A 5) vanish.

Equation (A 6) therefore applies with $\boldsymbol{B}^o(\boldsymbol{R})$ appearing in place of $\boldsymbol{B}^o(\boldsymbol{r})$. Hence, analogous to equation (A 7),

$$\boldsymbol{B}^o(\boldsymbol{R}) = \text{const} \tag{B 8}$$

for all $\boldsymbol{R} \in V_{\mathrm{f}\infty}$. In turn, from equation (B 1), this demonstrates the uniqueness of $\boldsymbol{B}(\boldsymbol{R})$ to within an arbitrary additive constant. Q.E.D.

Appendix C. Derivation of equation (5.1)

Subject to *a posteriori* verification, assume an eigenfunction expansion of the system of equations (4.30) having the form

$$\mu_0(\boldsymbol{r}, t|\boldsymbol{r}') = \frac{1}{\tau_\mathrm{f}} + \sum_{k=1}^{\infty} y_k(\boldsymbol{r}|\boldsymbol{r}') \exp(\lambda_k t). \tag{C 1}$$

The eigenfunctions y_k and eigenvalues λ_k are determined by the system of equations

$$\lambda_k y_k = -\nabla\cdot(\boldsymbol{v}y_k) + D\,\nabla^2 y_k, \tag{C 2a}$$

$$\boldsymbol{v}\cdot\nabla y_k = 0 \quad \text{on} \quad s_p, \tag{C 2b}$$

$$[\![y_k]\!] = 0, \quad [\![\nabla y_k]\!] = 0, \tag{C 2c, d}$$

for $k = 1, 2, 3, \ldots$. In addition, it is required that

$$\sum_{k=1}^{\infty} y_k(\boldsymbol{r}|\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') - \frac{1}{\tau_\mathrm{f}} \tag{C 2e}$$

so as to satisfy the initial condition $\mu_0(\boldsymbol{r}, 0|\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}')$ (cf. equation (C 1) with $t = 0$). The latter initial condition is formally used in place of the equivalent instantaneous source term $\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t)$ appearing explicitly in equation (4.30a). Since, from the properties of the delta function,

$$\int_{\tau_\mathrm{f}} \delta(\boldsymbol{r}-\boldsymbol{r}')\,\mathrm{d}^3\boldsymbol{r} = 1,$$

the condition (C 2e) assures that equation (4.33) is satisfied for all time.

Multiply equation (C 2a) by y_k and integrate over the interstitial fluid volume τ_f within a unit cell to obtain, with use of some obvious identities,

$$\lambda_k \int_{\tau_\mathrm{f}} y_k^2\,\mathrm{d}^3\boldsymbol{r} = -\frac{1}{2}\oint_{\partial\tau_o+s_p} \mathrm{d}\boldsymbol{s}\cdot\boldsymbol{v}y_k^2 + D\oint_{\partial\tau_o+s_p} \mathrm{d}\boldsymbol{s}\cdot(\nabla y_k)\,y_k - D\int_{\tau_\mathrm{f}} \nabla y_k\cdot\nabla y_k\,\mathrm{d}^3\boldsymbol{r}, \tag{C 3}$$

upon application of the divergence theorem. Equations (3.2) and (C 2*b*) show that the two surface integrals on the right-hand side vanish on s_p. Furthermore, lemmas (4.37) and (4.38), when considered in conjunction with the facts that $[\![y_k^2]\!] = 0$ and $[\![y_k \nabla y_k]\!] = 0$ – which follow as a consequence of equations (C 2*c*, *d*) – show that the surface integrals in equation (C 3) vanish over $\partial\tau_o$ too. Consequently,

$$\lambda_k = -D \int_{\tau_f} (\nabla y_k)^2 \, \mathrm{d}^3\boldsymbol{r} \Big/ \int_{\tau_f} y_k^2 \, \mathrm{d}^3\boldsymbol{r}. \tag{C 4}$$

Except possibly for the trivial case $y_k = \text{const}$, for which $\lambda_k = 0$, the non-negative nature of these integrands shows that $\lambda_k < 0$. This fact confirms the error estimate in equation (5.1).

The *physical* interpretation of the asymptotic solution (5.1) is as follows: since $\mu_0(\boldsymbol{r}, t|\boldsymbol{r}')$ satisfies the convective-diffusion equation (4.30*a*), it may be interpreted as the instantaneous local concentration of the 'zeroth moment solute' (within the domain $\boldsymbol{r} \in \tau_f$), resulting from a unit input of this solute at the position $\boldsymbol{r} = \boldsymbol{r}'$ at $t = 0$. The boundary conditions (4.30*b*–*d*) ensure that no *net* flow of this solute occurs across the boundaries, s_p and $\partial\tau_o$, of the system. Hence, the unit amount of solute initially charged remains permanently within the interstitial region τ_f for all time. By the mechanism of molecular diffusion, this solute ultimately becomes uniformly distributed throughout the system. Indeed, as may be formally verified, the steady-state solution, $\mu_0 = 1/\tau_f$, is an *exact* solution of the system of equations (4.30) and (4.33).

This manuscript is dedicated to the late Professor F. J. M. Horn. He shared in the inception of this research during his sabbatical leave at Carnegie–Mellon University during the academic year 1969–70, where I was in residence in the Chemical Engineering Department. To him goes the credit for recognizing that spatially-periodic porous media provided a proper 'orthogonal space', $(\boldsymbol{R}_n, \boldsymbol{r})$, such as to constitute a special example of his profound general analysis (Horn 1971) of dispersion phenomena in such spaces. The ensuing dispersion analysis, albeit in a non-invariant, cell-shape dependent form, forms a portion of the doctoral dissertation (Cone 1971) of Dr E. J. Cone, carried out under my supervision.

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REFERENCES

Acrivos, A. 1971 Heat transfer at high Péclet number from a small sphere freely rotating in a simple shear field. *J. Fluid Mech.* **46**, 233–240.

Acrivos, A. & Goddard, J. D. 1965 Asymptotic expansions for laminar forced-convection heat and mass transfer. Part 1. Low speed flows. *J. Fluid Mech.* **23**, 273–291.

Acrivos, A. & Taylor, T. D. 1962 Heat and mass transfer from single spheres in Stokes flow. *Phys. Fluids* **5**, 387–394.

Aris, R. 1956 On the dispersion of a solute in a fluid flowing through a tube. *Proc. R. Soc. Lond.* A **235**, 67–77.

Aris, R. & Amundson, N. R. 1957 Some remarks on longitudinal mixing or diffusion in packed beds. *Am. Inst. chem. Engrs J.* **3**, 280–282.

Aris, R. 1962 *Vectors, tensors, and the basic equations of fluid mechanics*. Englewood Cliffs, New Jersey: Prentice-Hall.

Batchelor, G. K. 1967 *An introduction to fluid dynamics*. Cambridge University Press.

Bear, J. 1969 Hydrodynamic dispersion. *Flow through porous media (ed. R. J. M. de Weist)*, pp. 109–199. New York and London: Academic Press.

Bear, J. 1972 *Dynamics of fluids in porous media*. New York. London and Amsterdam: American Elsevier.

Beran, M. J. 1968 *Statistical continuum theories*, ch. 6. New York: Wiley–Interscience.

Brenner, H. 1970 Orientation-space boundary layers in problems of rotational diffusion and convection at large rotary Péclet numbers. *J. Colloid Interface Sci.* **34**, 103–125.

Brenner, H. 1981 *Transport processes in porous media*. New York: Hemisphere/McGraw-Hill. (In the press).

Brenner, H. & Gaydos, L. J. 1977 The constrained Brownian movement of spherical particles in cylindrical pores of comparable radius: Models of the diffusive and convective transport of solute molecules in membranes and porous media. *J. Colloid Interface Sci.* **58**, 312–356.

Brillouin, L. 1953 *Wave propagation in periodic structures*, 2nd edn. New York: Dover.

Cone, E. J. 1971 Transport phenomena in periodic porous media. Ph.D. dissertation. Carnegie-Mellon University, Pittsburgh, Pennsylvania.

De Jong, G. de J. 1958 Longitudinal and transverse diffusion in granular deposits. *Trans. Am. geophys. Union* **39**, 67–74; discussion, pp. 1160–1161.

De Jong, G. de J. 1972 The tensor character of the dispersion coefficient in anisotropic porous media. *Fundamentals of transport phenomena in porous media*, pp. 259–267. Amsterdam, London and New York: Elsevier.

De Ligny, C. L. 1970 Coupling between diffusion and convection in radial dispersion of matter by fluid flow through packed beds. *Chem. engng Sci.* **25**, 1177–1181.

Edwards, M. F. & Richardson, J. F. 1968 Gas dispersion in packed beds. *Chem. engng Sci.* **23**, 109–123.

Fedkiw, P. & Newman, J. 1977 Mass transfer at high Péclet numbers for creeping flow in a packed-bed reactor. *Am. Inst. chem. Engrs J.* **23**, 255–263.

Frankel, N. A. & Acrivos, A. 1968 Heat and mass transfer from small spheres and cylinders freely suspended in shear flow. *Phys. Fluids* **11**, 1913–1918.

Fried, J. J. & Combarnous, M. A. 1971 Dispersion in porous media. *Advances in hydroscience* (ed. V. T. Chow), vol. 7, pp. 169–282. New York and London: Academic Press.

Gunn, D. J. 1969 Theory of axial and radial dispersion in packed beds. *Trans. Instn chem. Engrs* **47**, T351–T359.

Gunn, D. J. & De Souza, J. F. C. 1974 Heat transfer and axial dispersion in packed beds. *Chem. engng Sci.* **29**, 1363–1371.

Gunn, D. J. & England, R. 1971 Dispersion and diffusion in beds of porous particles. *Chem. engng Sci.* **26**, 1413–1423.

Gunn, D. J. & Khalid, M. 1975 Thermal dispersion and wall heat transfer in packed beds. *Chem. engng Sci.* **30**, 261–267.

Gunn, D. J. & Pryce, C. 1969 Dispersion in packed beds. *Trans. Instn chem. Engrs* **47**, T341–T350.

Hashin, Z. 1970 *Theory of fiber reinfroced materials*. N.A.S.A. (Contract NAS 1-8818), Langley Research Center, Hampton, Virginia.

Hilton, H. 1963 *Mathematical crystallography and the theory of groups of movements*. New York: Dover.

Hinch, E. J. & Leal, L. G. 1972 The effect of Brownian motion on the rheological properties of a suspension of non-spherical particles. *J. Fluid Mech.* **52**, 683–712.

Horn, F. J. M. 1971 Calculation of dispersion coefficients by means of moments. *Am. Inst. chem. Engrs J.* **17**, 613–620.

Leal, L. G. & Hinch, E. J. 1971 The effect of weak Brownian rotations on particles in shear flow. *J. Fluid Mech.* **46**, 685–703.

Nikolaevskii, V. N. 1959 Convective diffusion in porous media. *Prikl. Mat. Mekh.* **23**, 1042–1050.

Rumer, R. R. Jr. 1972 On the derivation of a convective-dispersion equation by spatial averaging. *Fundamentals of transport phenomena in porous media*, pp. 268–275. Amsterdam, London and New York: Elsevier.

Sachs, M. 1963 *Solid state theory*. New York: McGraw-Hill.

Saffman, P. G. 1959*a* A theory of dispersion in a porous medium. *J. Fluid Mech.* **6**, 321–349.

Saffman, P. G. 1959*b* Dispersion in flow through a network of capillaries. *Chem. engng Sci.* **11**, 125–129.

Saffman, P. G. 1960 Dispersion due to molecular diffusion and macroscopic mixing in flow through a network of capillaries. *J. Fluid Mech.* **7**, 194–208.

Scheidegger, A. E. 1963 *The physics of flow through porous media*, 2nd edn. Toronto University Press.

Sih, P. H. & Newman, J. 1967 Mass transfer to the rear of a sphere in Stokes flow. *Int. J. Heat Mass Transfer* **10**, 1749–1756.

Simpson, E. S. 1969 Velocity and the longitudinal dispersion coefficient in flow through porous media. *Flow through porous media* (ed. R. J. M. De Wiest), pp. 201–214. New York and London: Academic Press.

Taylor, G. I. 1953 Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. Lond.* A **219**, 186–203.

Taylor, G. I. 1954*a* The dispersion of matter in turbulent flow through a pipe. *Proc. R. Soc. Lond.* A **223**, 446–468.

Taylor, G. I. 1954*b* Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion. *Proc. R. Soc. Lond.* A **225**, 473–477.

Urban, J. C. & Gomezplata, A. 1969 Axial dispersion coefficients in packed beds at low Reynolds numbers. *Can. J. chem. Engng* **47**, 353–359.

Van Dyke, M. 1975 *Perturbation methods in fluid mechanics* (annotated edn). Stanford, California: Parabolic Press.

Vortmeyer, D. 1975 Axial heat dispersion in packed beds. *Chem. engng Sci.* **30**, 999–1001.

Votruba, J., Hlaváček, V. & Marek, M. 1972 Packed bed axial thermal conductivity. *Chem. engng Sci.* **27**, 1845–1851.

Whitaker, S. 1966 The equations of motion in porous media. *Chem. engng Sci.* **21**, 291–300.

Whitaker, S. 1967 Diffusion and dispersion in porous media. *Am. Inst. chem. Engrs J.* **13**, 420–427; errata, p. 1237.

Whitaker, S. 1969 Advances in theory of fluid motion in porous media. *Ind. engng Chem.* **61**, 14–28.

Whitaker, S. 1971 On the functional dependence of the dispersion vector for scalar transport in porous media. *Chem. engng Sci.* **26**, 1893–1899.

Whitaker, S. 1973 The transport equations for multi-phase systems. *Chem. engng Sci.* **28**, 139–147; errata, 1974, **29**, 640.

Zenz, F. A. & Othmer, D. F. 1960 *Fluidization and fluid-particle systems*, pp. 202–3. New York: Reinhold.