

Dispersion Resulting from Flow through Spatially Periodic Porous Media II. Surface and Intraparticle Transport

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DISPERSION RESULTING FROM FLOW THROUGH SPATIALLY PERIODIC POROUS MEDIA II.† SURFACE AND INTRAPARTICLE TRANSPORT

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A rigorous theory of Brownian particle flow and dispersion phenomena in spatially periodic structures is presented within the context of generalized Taylor dispersion theory. The analysis expands upon a prior work, which was limited to transport within the continuous phase, to include convective and diffusive transport of the tracer particle within the interior of the discontinuous phase, as well as surface adsorption and transport along the phase boundary separating the discontinuous and continuous phases. Incorporated within the generalization are considerations of tracer particles of non-zero size, and situations wherein external forces act upon the tracer, the novel effect of each being to cause the tracer to move with a different velocity from that of the fluid in which it is suspended. Applications to various chromatographic separation phenomena are cited. Extensions of the analysis to heat-transfer problems and to situations involving homogeneous, first-order chemical reactions are also made. Both Eulerian and Lagrangian interpretations of the tracer transport phenomena are given.

1. INTRODUCTION

The previous paper in this series (Brenner 1980*a*; hereafter referred to as I) was devoted to a study of the mean velocity and Taylor dispersivity of a small Brownian tracer particle suspended in an incompressible fluid animated by a macroscopically homogeneous uniform Darcy flow through the interstices of a spatially periodic porous medium. That analysis was restricted to tracer particles that were (i) of point, or molecular, dimensions; (ii) subject to no net external forces; (iii) permanently confined to the interstitial fluid region (as was the fluid too) owing to the impenetrability of the discontinuous phase to passage of either the tracer or fluid through its interior. As a consequence of these assumptions, the Brownian corpuscle served the role of a passive tracer, essentially indistinguishable as regards its transport properties from a molecule of the interstitial fluid.

In this contribution restrictions (i)–(iii) will be removed. Thus the Brownian particle (assumed to be spherical in shape to avoid orientational issues) may possess a non-zero radius a relative to the characteristic interstitial linear pore size l . As a result of this non-vanishing a/l -value, hydrodynamic ‘wall effects’ arise owing to the proximity of the surfaces of the bed particles bounding the fluid internally to the Brownian sphere. The effect of these pore ‘walls’ is to retard the motion of the sphere centre relative to that of the neighbouring fluid in which it is instantaneously suspended. Simultaneously, however, the sphere centre is denied access to those points in the continuous phase near the bed particle surfaces lying closer than one sphere radius, a , though this region is accessible to a fluid molecule. The net effect of these two phenomena is that the mean velocity of the Brownian particle through the porous medium differs from that of the fluid.

A similar disparity between mean tracer and fluid velocities arises when external forces act upon the tracer particle. This is true even if the tracer particle is effectively of point dimensions, since such selective forces serve to distinguish the tracer particle from a fluid molecule. For a non-neutrally buoyant tracer, gravity provides a simple example of an external force.

Allowing the bed particles composing the discontinuous phase to be penetrable by the solute tracer molecule, including the possibility of fluid convection within their interiors (e.g. flow through a non-neutrally buoyant suspension of immiscible liquid droplets with internal circulation), greatly extends the domain of physical applicability of the analysis with surprisingly little additional effort. The resultant theory is then immediately applicable, for example, to transport processes in composite materials.

Cognizance is also given to the possibility of surface adsorption and transport of the tracer along the phase boundaries separating the continuous and discontinuous phases. Even if no tracer transport occurs through the bed-particle interiors, surface adsorption processes may play an important role in determining the mean velocity and dispersivity of the tracer. In effect, inclusion of surface transport processes permits the *implicit* incorporation of ultra-short-range forces (London–van der Waals, Debye double-layer, etc.) into the analysis without our having to treat them as *explicit* external forces exerted upon the tracer molecule in one or the other of the two ‘bulk’ phases (Brenner & Leal 1982).

In addition to the examination of such purely ‘mass-transfer’ phenomena, the analysis is extended to include heat-transfer processes. Apart from minor technical modifications, the novelty of this extension lies in the fact that it shows the general theory to be applicable not only to the transport of material entities such as mass, but also to abstract entities such as (internal) energy. In a similar context it is demonstrated that, in certain circumstances, the general concepts underlying the theoretical analysis are not strictly limited to the transport of *conserved* entities. This is done by considering the simple case of a homogeneous, first-order, irreversible chemical reaction taking place wholly within the interstitial fluid (in the absence of surface and intraparticle transport). The reactive species, rather than being conserved, is continuously depleted by the reaction.

The results of the analysis possess a variety of potential applications to fields other than conventional molecular convection–diffusion–reaction systems in porous or composite media. For example, the results are immediately applicable to the detailed analysis of various chromatographic separation processes, including hydrodynamic (Small 1974; Brenner & Gaydos 1977; Prieve & Hoyson 1978; Silebi & McHugh 1978, 1979; Giddings 1978), partition (Lee *et al.* 1977; Yau *et al.* 1979; Provder 1980) and adsorption (Ruckenstein & Prieve 1980;

Lightfoot *et al.* 1981) chromatography. Other obvious non-conventional applications of the theory arise in connection with, for example, deep-bed filtration (Ives 1975, 1978), hydrosol deposition in packed beds (Ruckenstein & Prieve 1980), transport in emulsions, and the sedimentation of particles through porous media (Bridgwater *et al.* 1969, 1971; Moore & Masliyah 1973; Masliyah & Bridgwater 1974).

The present paper is a natural outgrowth of a recent theory (Brenner 1980*b*, 1982) of generalized Taylor dispersion phenomena. In a fundamental sense, it differs from that theory only in that the ‘global’ (i.e. unbounded) variables, rather than being continuous, are now discrete. While this modification has a considerable effect upon the technical mathematical details, the physical precepts remain the same. Indeed, the final working formulas of the present contribution bear a striking resemblance to those of Dill & Brenner (1982), who have treated comparable surface transport for globally continuous Taylor dispersion.

The Introduction to I furnished a brief discussion of the philosophical relation between ‘real’ porous media and spatially periodic models thereof. To those remarks may be added the following supplement, defining the general criteria required of a satisfactory model. The role of any mathematical model is to capture the essence of the real physical phenomena in a simple, expeditious and mathematically unambiguous (inflexible) manner. Moreover, the subsequent analysis of the physical and mathematical principles defining the model needs to be rigorously performed. The model itself, however, need not attempt to mimic faithfully the detailed geometrical configuration of the system as it exists in Nature. Rather, it need do so only in some average or global sense.

Witness, for example, the so-called ‘hard-sphere’ model of an atom, oft-invoked in connection with statistical–mechanical theories of the macroscopic behaviour of monatomic gases and liquids. In the light of current knowledge of internal atomic structure, no one would seriously argue that the hard-sphere model represents an attempt at the faithful geometric portrayal of a real atom. Yet the model itself is extremely useful. For despite its simplicity and overidealization, this *microscopic* geometrical model captures the essence of many real *macroscopic* phenomena, on a length scale large compared with the mean distance between sphere centres. On such a length scale, the macroscopic predictions are insensitive to the fine-structure geometrical details. In particular, when rigorously treated, the hard-sphere model leads to a correct *qualitative* understanding of many equilibrium and non-equilibrium processes, as well as to at least a semi-*quantitative* description of such phenomena, including reasonable estimates of the magnitudes of the phenomenological coefficients appearing therein and their scaling laws.

It is hoped that the general line of reasoning embodied in the remarks of the preceding paragraph, intended to relate *microscopic* geometric models to *macroscopic* transport phenomena, will prove as fruitful in rationalizing macroscopic transport processes in real porous media as it has proved in modelling such processes in conventional fluid continua.

Notation

<i>a</i>	radius of Brownian tracer particle
A	tensor-valued field
b	vector field defined at the phase boundary <i>s</i>
B	vector field defined in the interiors of the continuous and discontinuous phases
$\bar{\mathbf{B}}$	constant vector representing the mean value of the B and b fields

C	constant defined in (8.20) and (8.44); heat capacity per unit volume (§ 12)
\bar{C}	mean volumetric heat capacity
\mathbf{d}	surface diffusion dyadic
\mathbf{D}	diffusion dyadic in a bulk phase
$\bar{\mathbf{D}}^*$	dispersion dyadic
Exp	terms of exponentially small order in time as $t \rightarrow \infty$
E	internal energy per unit volume
\mathbf{F}	any tensor-valued function, or external force exerted on the tracer
\mathbf{H}	surface dyadic defined in (5.11)
$(\mathbf{i}, \mathbf{j}, \mathbf{k})$	unit vectors along (x, y, z) -axes
\mathbf{l}	dyadic idemfactor
\mathbf{j}	surface-excess flux density vector
\mathbf{j}_m	m th moment of \mathbf{j}
\mathbf{J}	bulk-phase flux density vector
\mathbf{J}_m	m th moment of \mathbf{J}
k	adsorption coefficient or Boltzmann constant
K	interphase partition coefficient
l	characteristic linear unit cell dimension or pore size
\mathbf{l}_k	basic lattice vector ($k = 1, 2, 3$)
\mathbf{M}	mobility dyadic of the tracer
\mathbf{M}_m	m th-order total moment
n_k	integer taking on any positive or negative value, including zero ($k = 1, 2, 3$)
$\{\mathbf{n}\}$	the ‘coordinates’ of the n th cell, $\{n_1, n_2, n_3\}$
p	surface-excess probability density, or undisturbed fluid pressure
\mathbf{p}_m	m th local moment of p
P	bulk-phase probability density
\mathbf{P}_m	m th local moment of P
q_k	volumetric flow rate through face s_k of a unit cell
\mathbf{q}	heat flux vector
Q_k	time rate of tracer transport across face s_k of a unit cell
$d\bar{Q}_v$	time rate of tracer transport across the Darcy-scale surface element $d\bar{\mathbf{s}}_v$
\mathbf{r}	local position vector within a unit cell
r_o	superficial volume of a unit cell
$d\mathbf{r}$	differential volume element within a unit cell
∂r_o	external boundary of a unit cell, composed of its six faces
\mathbf{R}	generic position vector in the composite medium
\mathbf{R}_n	position cell of a lattice point
$\bar{\mathbf{R}}$	centroid of a unit cell or Darcy-scale position vector
$d\mathbf{R}$	differential element of volume in the composite medium
s	interphase boundary within a unit cell
s_k	face of a unit cell ($k = \pm 1, \pm 2, \pm 3$)
\mathbf{s}_k	directed vector of face s_k of a unit cell
ds	scalar element of surface area
$d\mathbf{s}$	directed vectorial element of surface area, $\mathbf{v} ds$
$d\bar{\mathbf{s}}_v$	Darcy-scale differential directed vectorial surface element, \mathbf{s}_k

S	surface area within a unit cell
sym	denotes symmetric portion of a dyadic
t	time
T	temperature
\mathbf{u}	local tracer velocity vector at a point on the phase boundary s
\mathbf{U}	local tracer velocity vector at a point in a bulk phase
\mathbf{U}'	local tracer velocity vector in the absence of external forces
$\bar{\mathbf{U}}$	constant vector defined in (4.38) or (4.39)
$\bar{\mathbf{U}}^*$	mean tracer velocity vector through the composite medium
\mathbf{v}	local undisturbed fluid velocity vector
$\bar{\mathbf{v}}$	Darcy-scale superficial velocity vector
$\bar{\mathbf{v}}^*$	mean interstitial fluid velocity vector
V	potential energy of the tracer in an internal force field
$V_{o\infty}$	entire volume of the composite medium
\mathbf{W}	dyadic field defined in (4.60)
(x, y, z)	cartesian coordinates
α	specific surface area
$\bar{\alpha}^*$	Darcy-scale thermal diffusivity dyadic
δ	Dirac δ -function
δ_{ij}	Kronecker δ
$\delta_{mn'}$	Kronecker δ for the pair of cells $\{\mathbf{n}\}$ and $\{\mathbf{n}'\}$
Δ	jump in value across the phase boundary s , or excluded volume (§11)
ϵ	porosity, $= \tau_c/\tau_o$
κ	velocity constant of chemical reaction
μ	fluid viscosity
Π	total probability
τ_o, τ_c, τ_d	superficial, continuous-phase and discontinuous-phase volumes within a unit cell
\mathbf{v}	unit normal vector to a surface
ψ	any spatially periodic function
∇	gradient operator; either $\partial/\partial\mathbf{R}$ or $\partial/\partial\mathbf{r}_{R_n}$
∇_s	surface gradient operator
$\bar{\nabla}$	Darcy-scale gradient operator, $\partial/\partial\bar{\mathbf{R}}$
$\llbracket \]$	difference between the values of the argument at geometrically equivalent points on opposite faces of a unit cell
<i>Subscripts</i>	
c	continuous phase
d	discontinuous phase
i	chemical species in a mixture ($i = 1, 2, \dots, N$)
k	summation index; either (1, 2, 3) or ($\pm 1, \pm 2, \pm 3$)
m	m th moment ($m = 0, 1, 2, \dots$)
n or \mathbf{n}	n th cell
o	superficial volume, consisting of both the continuous and discontinuous phases
r	chemically reactive
s	surface or interface between bulk phases

(x, y, z)	cartesian components
ν	unit normal to a Darcy-scale surface element
∞	entire infinite composite medium
\parallel	axial component
\perp	transverse component

Superscripts

(c)	continuous phase
(d)	discontinuous phase
e	external
i	internal
s	symmetric portion
'	initial value at $t = 0$
∞	asymptotic value as $t \rightarrow \infty$
\dagger	transposition operator
*	'effective' or Darcy-scale mean value

Marks over symbols

—	mean or Darcy-scale value
\subset	spatially periodic function

2. GEOMETRY AND PROBABILITY DENSITIES

Geometry

The geometrical description of the spatially periodic porous medium is the same as that in I. In the terminology of generalized Taylor dispersion theory (Brenner 1980*b*), \mathbf{R}_n plays the role of a (discrete) *global* variable, since it is unbounded. Here,†

$$\mathbf{R}_n = n_1 \mathbf{l}_1 + n_2 \mathbf{l}_2 + n_3 \mathbf{l}_3, \quad (2.1)$$

with $(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$ an appropriate set of basic lattice vectors, and

$$n_k = 0, \pm 1, \pm 2, \pm 3, \dots \quad (k = 1, 2, 3). \quad (2.2)$$

The parallelepiped whose edges are formed by the basic lattice vectors $(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$ constitutes a primitive unit cell of the array. The position vector \mathbf{R}_n , or equivalently the triplet of integers

$$\{\mathbf{n}\} = \{n_1, n_2, n_3\}, \quad (2.3)$$

serves to define the location of the n th unit cell of the array.

As in I, denote by \mathbf{r} the *local* position vector of a point within a given unit cell relative to an origin fixed in that cell. This vector is defined only within the cell interior \mathbf{r}_0 (designated in I by the symbol τ_0); i.e. $\mathbf{r} \in \mathbf{r}_0$. Being thus of bounded variation, \mathbf{r} plays the role of a *local* variable within the context of generalized Taylor dispersion theory (Brenner 1980*b*).

Relative to an arbitrary origin fixed in space, the position vector \mathbf{R} of any point within any cell may be written generally as the sum of a global and a local variable,

$$\mathbf{R} = \mathbf{R}_n + \mathbf{r}. \quad (2.4)$$

† If periodicity exists in only one or two spatial dimensions, rather than three, \mathbf{R}_n may then be reduced to a one- or two-dimensional vector field as appropriate.

(This decomposition is analogous to the generic decomposition of generalized Taylor dispersion theory (Brenner 1980*b*), $\chi = \mathbf{X} \oplus \mathbf{x}$, of the 'position vector' χ into global and local variables, \mathbf{X} and \mathbf{x} , respectively, except that \mathbf{X} is there regarded as a continuous variable.)

Let $V_{0\infty}$ denote the entire infinite domain of the composite medium, consisting of both the continuous (c) and the discontinuous (d) phase regions: for example, the interstitial fluid and the interiors of the bed particles, respectively. Symbolically,

$$V_{0\infty} = \sum_{\mathbf{n}} \mathbf{r}_0\{\mathbf{n}\}, \quad (2.5)$$

in which

$$\sum_{\mathbf{n}} = \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} \dots \quad (2.6)$$

Here, $\mathbf{r}_0\{\mathbf{n}\}$ denotes the entire superficial spatial domain contained within the n th unit cell. Similarly, with s_{∞} the total interfacial surface domain separating the continuous and discontinuous phases, $V_{0\infty}^{(c)}$ and $V_{0\infty}^{(d)}$, respectively, in $V_{0\infty}$ we have that

$$s_{\infty} = \sum_{\mathbf{n}} s\{\mathbf{n}\}, \quad (2.7)$$

where $s\{\mathbf{n}\}$ denotes the interfacial region (i.e. the surface(s) of the bed particle(s)) within the n th unit cell.

Probability densities

In contrast with I, where the tracer was confined exclusively to the (continuous) interstitial region, we allow here the possibility that the tracer (and fluid) may be transported through the discontinuous phase as well. Allowance is also made for the possibility of tracer adsorption on s , as well as transport of the adsorbed tracer along s ('surface-excess' diffusion and convection). In this manner we are led to introduce two probability density functions: (i) a volumetric or bulk probability density $P \equiv P(\mathbf{R}, t | \mathbf{R}')$ defined at each point $\mathbf{R} \in V_{0\infty}$; (ii) a surface-excess areal probability density $p \equiv p(\mathbf{R}, t | \mathbf{R}')$ defined only for those points $\mathbf{R} \equiv \mathbf{R}_s$ lying on s_{∞} . It will be assumed implicitly throughout the subsequent development that P and p are each non-negative functions for all $-\infty < t < \infty$, and for all current and initial positions, \mathbf{R} and \mathbf{R}' , respectively.

The two probability densities jointly serve to define the probability that the centre of the Brownian sphere will be at position \mathbf{R} at time t , given that it was initially at position \mathbf{R}' at $t = 0$. It will be assumed that \mathbf{R}' is contained within either the continuous or the discontinuous bulk phase, but does not lie on s_{∞} . The two densities will be assumed to satisfy conservation equations of the usual forms:

$$\partial P / \partial t + \nabla \cdot \mathbf{J} = \delta(\mathbf{R} - \mathbf{R}') \delta(t), \quad t > 0, \quad (2.8a)$$

$$P = 0, \quad t < 0, \quad (2.8b)$$

and (Scriven 1960, Brenner & Leal 1982)

$$\partial p / \partial t + \nabla_s \cdot \mathbf{j} = \Delta(\mathbf{v} \cdot \mathbf{J}), \quad t > 0, \quad (2.9a)$$

$$p = 0, \quad t < 0. \quad (2.9b)$$

In the first of these pairs of expressions δ is the Dirac δ -function and $\nabla \equiv \partial / \partial \mathbf{R}$ is the gradient operator. In the second of the pairs,

$$\nabla_s \equiv \mathbf{I}_s \cdot \nabla \quad (2.10)$$

is the surface gradient operator, wherein

$$\mathbf{I}_s = \mathbf{I} - \mathbf{v}\mathbf{v} \quad (2.11)$$

is the surface idemfactor dyadic. Here, \mathbf{I} is the three-dimensional dyadic idemfactor and \mathbf{v} denotes a unit normal vector on s_∞ . For definiteness, the sense of \mathbf{v} will be chosen to point from the discrete phase into the continuous phase. Finally, the operator Δ appearing in (2.9) denotes the 'jump' in the value of its argument at a point on s_∞ ; that is, for \mathbf{A} any tensor-valued field,

$$\Delta \mathbf{A} = \mathbf{A}^{(d)} - \mathbf{A}^{(c)}, \quad (2.12)$$

where $\mathbf{A}^{(d)}$ and $\mathbf{A}^{(c)}$ are respectively the values of \mathbf{A} in the discrete and continuous phases at contiguous points immediately adjoining the relevant surface point \mathbf{R}_s lying on s_∞ .

In general, in (2.8) the possibility is allowed that P may not be continuous across s_∞ . When it is necessary to make this fact notationally explicit, we shall introduce variables with appropriate superscripts, $(P^{(c)}, \mathbf{J}^{(c)})$ and $(P^{(d)}, \mathbf{J}^{(d)})$, in place of (P, \mathbf{J}) .

Fluxes

The flux density vector \mathbf{J} of the bulk-phase probability density P will be assumed to obey a convective–diffusive constitutive equation of the general form

$$\mathbf{J} = \mathbf{U}(\mathbf{r})P - \mathbf{D}(\mathbf{r}) \cdot \nabla P. \quad (2.13)$$

Likewise, the flux density vector \mathbf{j} of the surface-excess probability p is assumed to be given by a comparable constitutive equation (Scriven 1960; Brenner & Leal 1981)

$$\mathbf{j} = \mathbf{u}(\mathbf{r})p - \mathbf{d}(\mathbf{r}) \cdot \nabla_s p \quad (2.14)$$

on s_∞ . As indicated by their arguments (\mathbf{r}), the volumetric and surface tracer velocity vectors (\mathbf{U}, \mathbf{u}) and the diffusivity dyadics (\mathbf{D}, \mathbf{d}) are all assumed to be spatially periodic functions, and hence to be dependent only upon the local variable \mathbf{r} rather than upon \mathbf{R} . In particular they are independent of \mathbf{R}_n . In (2.13) we allow the implicit possibility that \mathbf{U} and \mathbf{D} may change discontinuously across the phase boundary s_∞ .

Spatially periodic phenomenological coefficients

The *physical* circumstances under which the four phenomenological coefficients appearing in these flux expressions will be spatially periodic, as supposed, are delineated in context at appropriate points in the subsequent text. However, the following general remarks are pertinent. The diffusion dyadics \mathbf{D} and \mathbf{d} are spatially periodic, in part, as a consequence of the *geometrical* periodicity of the array and, in part, as a consequence of the implicitly assumed periodicity of the *material* properties of the substances composing the array. Of course, the most important limiting case of such material-property periodicity occurs when these properties are constant throughout the array. If, for example, as in the Stokes–Einstein equation (see equation (11.6)), \mathbf{D} depends upon the local temperature and viscosity of the fluid, the last two are implicitly assumed everywhere constant to assure the spatial periodicity of \mathbf{D} .

Whereas \mathbf{D} and \mathbf{d} are generally intrinsic material properties of the system, dependent only upon its physical constitution and configuration, the velocities \mathbf{U} and \mathbf{u} are not. They generally derive from extrinsic external driving forces, be they external forces exerted on the tracer by its distant or immediate surroundings, or Darcy-scale external pressure gradients. Whatever the source of the driving forces, they must be of such nature as to assure the spatial periodicity of \mathbf{U} and \mathbf{u} .

In applications, the most common external driving force is a homogeneous, uniform, Darcy-scale pressure gradient. As in I, this gives rise to a uniform Darcy-scale flow, characterized by

the constant seepage-velocity vector $\bar{\mathbf{v}}$ (see §9). In turn, this produces a spatially periodic local fluid velocity vector field $\mathbf{v}(\mathbf{r})$. While, in general, $\mathbf{U} \neq \mathbf{v}$ for a neutrally buoyant tracer immersed in the undisturbed flow \mathbf{v} (owing to ‘wall effects’ arising from the generally non-zero a/l -value; see §11), such hydrodynamic effects due to the proximity of the boundary are governed by the geometry of the system and hence are themselves spatially periodic. In conjunction with the periodicity of \mathbf{v} , this assures the periodicity of \mathbf{U} , at least for such uniform Darcy flows.

For non-neutrally buoyant particles, gravity provides a common example of a ‘distant’ external force field that results in a spatially periodic tracer velocity field \mathbf{U} , provided only that the fluid density is either everywhere constant or spatially periodic (for example, in emulsions). Likewise, external forces exerted upon the tracer by its immediate environment (e.g. London–van der Waals or Debye double-layer forces) will also be spatially periodic in consequence of the assumed geometric periodicity of the array in conjunction with a similar assumption regarding the periodic variation of material properties. Of course, such ultra-short-range forces may already have been implicitly incorporated into the surface adsorption and surface-excess flux at the phase boundary (Brenner & Leal 1982), which then accounts for the periodicity of \mathbf{u} (and \mathbf{d}). In this event such forces must not also be counted as external driving forces determining \mathbf{U} , since their inclusion would be redundant.

Normalization of the total probability

At any time $t > 0$ after its initial introduction into the system, the tracer has probability one of being somewhere within the infinite region $V_{\infty} \oplus s_{\infty}$; i.e. it must be present in either the continuous or the discontinuous phase, or else be adsorbed at the interface. This requires that, for all \mathbf{R}' ,

$$\int_{V_{\infty}} P \, d\mathbf{R} + \int_{s_{\infty}} p \, ds = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases} \quad (2.15)$$

in which $d\mathbf{R}$ denotes a volume element (denoted by $d^3\mathbf{R}$ in I) and ds a surface element. For these infinite integrals to converge it will be assumed that

$$(P, p) \rightarrow 0 \quad \text{as} \quad |\mathbf{R} - \mathbf{R}'| \rightarrow \infty. \quad (2.16)$$

Indeed, later on we shall require the stronger assertions that

$$|\mathbf{R} - \mathbf{R}'|^m (P, p) \rightarrow 0 \quad \text{as} \quad |\mathbf{R} - \mathbf{R}'| \rightarrow \infty, \quad (2.17)$$

for any integer $m \geq 0$. Similarly, it will be supposed that

$$|\mathbf{R} - \mathbf{R}'|^m (\mathbf{J}, \mathbf{j}) \rightarrow 0 \quad \text{as} \quad |\mathbf{R} - \mathbf{R}'| \rightarrow \infty. \quad (2.18)$$

The instantaneous source term appearing on the right-hand side of (2.8a) insures that condition (2.15) will automatically be satisfied. To demonstrate this fact, differentiate the integral

$$\Pi \stackrel{\text{def.}}{=} \int_{V_{\infty}} P \, d\mathbf{R} + \int_{s_{\infty}} p \, ds,$$

with respect to time, and use (2.8) and (2.9) to obtain

$$\frac{d\Pi}{dt} = - \int_{V_{\infty}} \nabla \cdot \mathbf{J} \, d\mathbf{R} + \delta(t) - \int_{s_{\infty}} \nabla_s \cdot \mathbf{j} \, ds + \int_{s_{\infty}} ds \Delta(\mathbf{v} \cdot \mathbf{J}),$$

in which it has been noted that

$$\int_{V_{\infty}} \delta(\mathbf{R} - \mathbf{R}') \, d\mathbf{R} = 1,$$

since \mathbf{R}' lies somewhere in $V_{0\infty}$. Since \mathbf{j} is assumed to be single-valued it follows that

$$\oint \nabla_s \cdot \mathbf{j} ds = 0$$

over any closed surface. Since s_∞ consists of a sum of closed surfaces (bounding each particle of the discontinuous phase externally) this surface integral over s_∞ is identically zero. Furthermore, if possible discontinuities of $\mathbf{v} \cdot \mathbf{J}$ at points \mathbf{R}_s on the surfaces composing the phase boundary s_∞ , are allowed for, the divergence theorem yields

$$\int_{\partial V_{0\infty}} ds \cdot \mathbf{J} = \int_{V_{0\infty}} \nabla \cdot \mathbf{J} d\mathbf{R} - \int_{s_\infty} ds \Delta(\mathbf{v} \cdot \mathbf{J}),$$

where $\partial V_{0\infty}$ denotes the indefinitely large closed surface bounding the volume $V_{0\infty}$ externally. However, in view of (2.18), the left-hand side of this equality is identically zero. Consequently

$$d\Pi/dt = \delta(t).$$

Integration, with the use of the unit integral property of the Dirac δ -function and the fact that $P = p = 0$ for $t < 0$, yields

$$\Pi = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases}$$

confirming (2.15).

Intracell probability densities

It will be convenient to regard $P(\mathbf{R}, t | \mathbf{R}')$ and $p(\mathbf{R}, t | \mathbf{R}')$ to be of the equivalent functional forms $P(\mathbf{R}_n, \mathbf{r}, t | \mathbf{R}'_n, \mathbf{r}')$ and $p(\mathbf{R}_n, \mathbf{r}, t | \mathbf{R}'_n, \mathbf{r}')$, respectively (see (2.4)). From (2.15), (2.5) and (2.7) these are required to satisfy the normalization condition

$$\sum_n \left(\int_{\mathbf{r}_o\{\mathbf{n}\}} P d\mathbf{r} + \int_{s\{\mathbf{n}\}} p ds \right) = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases} \quad (2.19)$$

for all \mathbf{R}'_n and \mathbf{r}' . For cellular emphasis the symbol $d\mathbf{r}$ has been used in place of $d\mathbf{R}$ for the volume element.

As in I, for a fixed cell \mathbf{R}_n , the bulk-phase probability density P may be regarded as satisfying the conservation law

$$\partial P / \partial t + \nabla \cdot \mathbf{J} = \delta_{nn'} \delta(\mathbf{r} - \mathbf{r}') \delta(t), \quad t > 0, \quad (2.20a)$$

$$P = 0, \quad t < 0, \quad (2.20b)$$

rather than (2.8). Here,†

$$\nabla \equiv (\partial / \partial \mathbf{r})_{\mathbf{R}_n} \quad (2.21)$$

is the \mathbf{r} -space gradient operator, and

$$\delta_{nn'} = \begin{cases} 1, & \{\mathbf{n}\} = \{\mathbf{n}'\}, \\ 0, & \{\mathbf{n}\} \neq \{\mathbf{n}'\} \end{cases} \quad (2.22a)$$

is a Kronecker δ . Explicitly,

$$\delta_{nn'} = \delta_{n_1 n'_1} \delta_{n_2 n'_2} \delta_{n_3 n'_3} \quad (2.22b)$$

with δ_{ij} the usual Kronecker δ with scalar indices. Similarly, with this new interpretation of the gradient operator (cf. (2.10)), the conservation equation (2.9) for surface-excess prob-

† In the general theory of Taylor dispersion (Brenner 1980*b*) in continuous systems it is necessary to distinguish clearly between the *global* gradient operator $\nabla_{\mathbf{X}} \equiv \partial / \partial \mathbf{X}$ and the *local* gradient operator $\nabla_{\mathbf{x}} \equiv \partial / \partial \mathbf{x}$. Consistency with this notation would have required that we use the symbols $\nabla_{\mathbf{R}} \equiv \partial / \partial \mathbf{R}$ and $\nabla_{\mathbf{r}} \equiv \partial / \partial \mathbf{r}$ to distinguish between the two types of gradient operators. However, since no confusion can result in the present discrete case, we have not appended any subscripts to ∇ to avoid a proliferation of offices.

ability density maintains its original form. The flux vectors \mathbf{J} and \mathbf{j} appearing in these new intracell conservation equations have the same constitutive forms as in (2.13) and (2.14), respectively, the altered interpretation of ∇ and ∇_s being borne in mind.

To complete the definitions of P and p we assume a linear adsorption ‘isotherm’ of the form

$$p = k(\mathbf{r}) P^{(c)} \quad \text{on } s, \quad (2.23)$$

where the adsorption coefficient k is a prescribed spatially periodic function at each point \mathbf{r} on s , and $P^{(c)}$ denotes the value of the continuous-phase bulk probability density at this point on s . It will be further supposed that local equilibrium prevails at each point on the interface s , and that this equilibrium state can be described by the linear relation

$$P^{(d)} = K(\mathbf{r}) P^{(c)} \quad \text{on } s, \quad (2.24)$$

with the equilibrium ‘constant’ (partition coefficient) K a spatially periodic function. The special case $K = 1$ corresponds to P being continuous across the interface.

(When no transport occurs through the interior of the discontinuous phase, equation (2.24) is replaced by the boundary condition

$$\mathbf{v} \cdot \mathbf{J}^{(d)} = 0 \quad \text{on } s, \quad (2.25)$$

so that on the right-hand side of (2.9a) there now appears $\Delta(\mathbf{v} \cdot \mathbf{J}) = -\mathbf{v} \cdot \mathbf{J}^{(c)}$. A complete discussion of this and other limiting cases, e.g. no surface adsorption or transport, is postponed until §8. Thus, conditions (2.23) and (2.24) will be assumed to prevail generally until then.)

The phenomenological-coefficient functions \mathbf{U} , \mathbf{u} , \mathbf{D} and \mathbf{d} appearing in the differential equations defining P and p , as well as the interphase-equilibrium-coefficient functions K and k appearing in the boundary conditions defining these fields, have been assumed spatially periodic and, hence, dependent only upon the local position \mathbf{r} , independent of the global position \mathbf{R}_n . It follows that, all other things being equal, P and p are each dependent only upon the linear displacement $\mathbf{R}_n - \mathbf{R}'_n$, rather than upon \mathbf{R}_n and \mathbf{R}'_n separately. Accordingly, P and p may be regarded to be of the functional forms

$$P \equiv P(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}') \quad (2.26)$$

and

$$p \equiv p(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}'), \quad (2.27)$$

respectively.

For specified values of both the initial cell location \mathbf{R}'_n or $\{\mathbf{n}'\}$ and the initial local position \mathbf{r}' of the tracer, and for prescribed phenomenological functions $(\mathbf{U}, \mathbf{D}, K)$ and $(\mathbf{u}, \mathbf{d}, k)$, equations (2.20) and (2.9) (with \mathbf{J} and \mathbf{j} given by (2.13) and (2.14), respectively) are to be solved for P and p (subject to the interphase boundary conditions (2.23) and (2.24)); that is P and p are to be determined as functions of the intracell coordinate \mathbf{r} for each unit cell $\{\mathbf{n}\}$. The infinite sequence of such intracell differential equations and interphase boundary conditions—one set for each $\{\mathbf{n}\}$ —are to be regarded as joined together by appropriate continuity requirements (to be discussed) imposed upon $(P, p, \mathbf{J}, \mathbf{j})$ across the faces of adjacent unit cells.

As has been demonstrated, the normalization condition (2.19) will automatically be satisfied in consequence of the appearance of the unit source term in (2.20) in conjunction with the convergence conditions (cf. (2.17), (2.18) and (2.4))

$$|\mathbf{R}_n - \mathbf{R}'_n|^m (P, p, \mathbf{J}, \mathbf{j}) \rightarrow 0 \quad \text{as } |\{\mathbf{n}\}| \rightarrow \infty \quad (2.28a-d)$$

for $\{\mathbf{n}'\}$ fixed. Thus, given appropriate continuity conditions on $(P, \mathbf{p}, \mathbf{J}, \mathbf{j})$ across adjacent unit cell faces, this procedure serves to determine (uniquely) P and \mathbf{p} at every point $\mathbf{R} = \mathbf{R}_n + \mathbf{r}$ within the entire infinite system $V_{\infty} \oplus s_{\infty}$.

Boundary conditions on the unit cell faces

Physically irrelevant *mathematical* questions of continuity may arise from possible real *physical* discontinuities across s in the event that the unit cell faces $\partial\mathbf{r}_0$ (bounding the unit cells \mathbf{r}_0 externally) coincide partly or wholly with the phase boundaries s . Such unnecessary mathematical complications can be avoided by reverting to the artifice adopted in I of imagining the unit cell faces to be drawn in such a way as to lie entirely within the *continuous* phase. This choice of 'curvilinear unit cell' insures complete continuity of all functions across the cell faces $\partial\mathbf{r}_0$ despite possible discontinuities across the phase boundaries s . From the point of view of the physics, the particular mathematical artifice adopted here is irrelevant since the unit cells and their boundaries are but imaginary mathematical constructions, devoid of physical reality. Indeed, ultimately we shall do away entirely with the concept of unit cells and revert wholly to a scheme based upon the introduction of spatially periodic functions satisfying boundary conditions only on the phase boundaries s (see §6). In such a scheme the unit cell boundaries play no role whatsoever.

As discussed in I, the continuity of P across the continuous-phase, curvilinear, unit cell faces, $\partial\mathbf{r}_0 \equiv \sum_{k=1}^3 s_{\pm k}$, requires that

$$P(\mathbf{R}_n - \mathbf{l}_k, \mathbf{r} + \mathbf{l}_k) = P(\mathbf{R}_n, \mathbf{r}) \quad (k = 1, 2, 3), \quad (2.29)$$

for each point \mathbf{r} on $\partial\mathbf{r}_0$. (For simplicity of notation, the fixed arguments \mathbf{R}' , \mathbf{r}' and t appearing in (2.26) have been temporarily suppressed in (2.29).) Similarly, from (2.13), the continuity of \mathbf{J} across the curvilinear cell faces is assured by the assumed continuity of P in conjunction with the requirement that ∇P be continuous. The latter condition requires that

$$\nabla P(\mathbf{R}_n - \mathbf{l}_k, \mathbf{r} + \mathbf{l}_k) = \nabla P(\mathbf{R}_n, \mathbf{r}) \quad (k = 1, 2, 3), \quad (2.30)$$

at all points \mathbf{r} lying on $\partial\mathbf{r}_0$.

3. MOMENTS OF THE PROBABILITY DENSITIES

Local moments

Define the m th local polyadic moments of the distribution functions P and \mathbf{p} within a unit cell as

$$\mathbf{P}_m(\mathbf{r}, t | \mathbf{r}') = \sum_{\mathbf{n}} (\mathbf{R}_n - \mathbf{R}'_n)^m P(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}') \quad (3.1a)$$

and

$$\mathbf{p}_m(\mathbf{r}, t | \mathbf{r}') = \sum_{\mathbf{n}} (\mathbf{R}_n - \mathbf{R}'_n)^m \mathbf{p}(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}') \quad (m = 0, 1, 2, \dots). \quad (3.1b)$$

In accordance with (2.28) these sums are expected to be convergent. The summation operator (2.6) is global in character and hence commutes with all \mathbf{r} -space operations in (2.20), (2.9), (2.13) and (2.14) (with the ∇ operator given as in (2.21)). Thereby it is readily established that the local volumetric moments \mathbf{P}_m and surface moments \mathbf{p}_m satisfy the following differential equations:

$$\partial \mathbf{P}_m / \partial t + \nabla \cdot \mathbf{J}_m = \delta_{m0} \delta(\mathbf{r} - \mathbf{r}') \delta(t), \quad t > 0, \quad (3.2a)$$

$$\mathbf{P}_m = 0, \quad t < 0, \quad (3.2b)$$

$$\text{and} \quad \partial \mathbf{p}_m / \partial t + \nabla_s \cdot \mathbf{j}_m = \Delta(\mathbf{v} \cdot \mathbf{J}_m), \quad t > 0, \quad (3.3a)$$

$$\mathbf{p}_m = 0, \quad t < 0, \quad (3.3b)$$

for each m . Here, \mathbf{J}_m and \mathbf{j}_m are polyadics of order $m+1$ defined, respectively, as

$$\mathbf{J}_m = \mathbf{U} \mathbf{P}_m - \mathbf{D} \cdot \nabla \mathbf{P}_m \quad (3.4)$$

$$\text{and} \quad \mathbf{j}_m = \mathbf{u} \mathbf{p}_m - \mathbf{d} \cdot \nabla_s \mathbf{p}_m. \quad (3.5)$$

These may be termed the fluxes of the corresponding moments.

Interfacial continuity conditions (2.23) and (2.24) require that

$$\mathbf{p}_m = k \mathbf{P}_m^{(c)} \quad \text{on } s \quad (3.6)$$

$$\text{and} \quad \mathbf{P}_m^{(d)} = K \mathbf{P}_m^{(c)} \quad \text{on } s \quad (3.7)$$

as immediate consequences of the definitions (3.1).

The boundary conditions imposed upon \mathbf{P}_m (referred to as $\boldsymbol{\mu}_m$ in I) across the unit cell faces are given in I. In particular, let \mathbf{F} be any tensor-valued field, which may be either global or local with respect to its functional dependence upon position. Define the ‘jump’ $[[\mathbf{F}]]$ in the value of this function at geometrically equivalent points, $\mathbf{r}(s_{+k}) = \mathbf{r}(s_{-k}) + \mathbf{l}_k$, lying on the opposite faces, s_{-k} and s_{+k} , respectively, of the surface $\partial \mathbf{r}_0\{\mathbf{n}\}$ of cell $\mathbf{r}_0\{\mathbf{n}\}$ as

$$[[\mathbf{F}]] = \begin{cases} \mathbf{F}(\mathbf{R}_n, \mathbf{r} + \mathbf{l}_j) - \mathbf{F}(\mathbf{R}_n, \mathbf{r}), \\ \text{or} \\ \mathbf{F}(\mathbf{r} + \mathbf{l}_j) - \mathbf{F}(\mathbf{r}), \end{cases} \quad (3.8)$$

according as the character of \mathbf{F} is global or local, respectively. In terms of this generic jump function, the cell-surface boundary conditions arising from the cellular continuity conditions (2.29) and (2.30) are, respectively, for the first few moments (cf. I):

$$m = 0: \quad [[\mathbf{P}_0]] = 0, \quad [[\nabla \mathbf{P}_0]] = 0; \quad (3.9a, b)$$

$$m = 1: \quad [[\mathbf{P}_1]] = -[[\mathbf{r} \mathbf{P}_0]], \quad [[\nabla \mathbf{P}_1]] = -[[\nabla(\mathbf{r} \mathbf{P}_0)]]; \quad (3.10a, b)$$

$$m = 2: \quad [[\mathbf{P}_2]] = [[\mathbf{P}_1 \mathbf{P}_1 / P_0]], \quad [[\nabla \mathbf{P}_2]] = [[\nabla(\mathbf{P}_1 \mathbf{P}_1 / P_0)]]. \quad (3.11a, b)$$

These jump boundary conditions ultimately play a role in the present theory analogous to the role of integration by parts in generalized Taylor dispersion theory (Brenner 1980b).

The preceding systems of differential equations and boundary conditions, defining each pair of local-moment fields $(\mathbf{P}_m, \mathbf{p}_m)$ within a unit cell $\mathbf{r} \in \mathbf{r}_0$, can, in principle, be solved successively for $(\mathbf{P}_0, \mathbf{p}_0)$, $(\mathbf{P}_1, \mathbf{p}_1)$, $(\mathbf{P}_2, \mathbf{p}_2)$, ..., as functions of \mathbf{r} , t and \mathbf{r}' . Each such intracell field pair $(\mathbf{P}_m, \mathbf{p}_m)$ can be shown to possess a unique solution independent of which of the infinitely many compatible unit-cell shapes for a specified lattice (cf. I) are selected for application of the cellular boundary conditions (3.9)–(3.11) *et seq.*

Note that the normalization condition

$$\int_{\mathbf{r}_0} \mathbf{P}_0 d\mathbf{r} + \int_s \mathbf{p}_0 ds = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases} \quad (3.12)$$

follows as a consequence of (2.19) and (3.1) (for $m = 0$), and is valid for all \mathbf{r}' . It can be demonstrated (cf. the comments regarding \mathbf{M}_0 in the final paragraph of this section) that this condition will automatically be satisfied by (3.2) and (3.3) (for $m = 0$) as a consequence of the appearance of the unit-source term on the right-hand side of (3.2a).

Total moments

In addition to the local moments $(\mathbf{P}_m, \mathbf{p}_m)$, define the m -adic total moments

$$\mathbf{M}_m(t | \mathbf{r}') = \int_{\mathbf{r}_o} \mathbf{P}_m d\mathbf{r} + \int_s \mathbf{p}_m ds, \quad t > 0, \quad (3.13a)$$

$$\text{and} \quad \mathbf{M}_m = 0, \quad t < 0 \quad (m = 0, 1, 2, \dots). \quad (3.13b)$$

In particular, for $m = 0$ it follows from (3.12) that

$$M_0 = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases} \quad (3.14)$$

independently of the value of \mathbf{r}' .

A formula that will prove to be very useful in the subsequent analysis may be derived as follows. Differentiate (3.13) with respect to t (for a fixed value of \mathbf{r}') and use (3.2) and (3.3) to obtain,

$$\begin{aligned} \frac{d\mathbf{M}_m}{dt} &= \int_{\mathbf{r}_o} \frac{\partial \mathbf{P}_m}{\partial t} d\mathbf{r} + \int_s \frac{\partial \mathbf{p}_m}{\partial t} ds \\ &= - \int_{\mathbf{r}_o} \nabla \cdot \mathbf{J}_m d\mathbf{r} + \delta_{m0} \delta(t) - \int_s \nabla_s \cdot \mathbf{j}_m ds + \int_s ds \Delta(\mathbf{v} \cdot \mathbf{J}_m), \end{aligned} \quad (3.15)$$

in which we have used the identity

$$\int_{\mathbf{r}_o} \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} = 1,$$

whose validity is a consequence of the fact that \mathbf{r}' lies somewhere within \mathbf{r}_o . However, if

$$\partial \mathbf{r}_o \equiv \sum_{k=1}^3 s_{\pm k} \quad (3.16)$$

denotes the closed surface composed of the six faces of the (curvilinear) unit cell \mathbf{r}_o , the divergence theorem for any tensor-valued field \mathbf{A} applied to the domain $\mathbf{r}_o \oplus s$ possesses the form

$$\int_{\partial \mathbf{r}_o} ds \cdot \mathbf{A} = \int_{\mathbf{r}_o} \nabla \cdot \mathbf{A} d\mathbf{r} - \int_s ds \Delta(\mathbf{v} \cdot \mathbf{A}). \quad (3.17)$$

Here, the directed element of surface area ds on $\partial \mathbf{r}_o$ is chosen to point outward from the unit-cell domain \mathbf{r}_o ; moreover, $\Delta(\mathbf{v} \cdot \mathbf{A})$ is defined as in (2.12). In present circumstances choose $\mathbf{A} = \mathbf{J}_m$ and substitute the resulting identity into (3.15) to obtain

$$\frac{d\mathbf{M}_m}{dt} = - \int_{\partial \mathbf{r}_o} ds \cdot \mathbf{J}_m + \delta_{m0} \delta(t). \quad (3.18)$$

In deriving this relation we have used the single-valuedness of \mathbf{j}_m in conjunction with the fact that s is a closed surface to conclude that

$$\int_s \nabla_s \cdot \mathbf{j}_m ds = 0.$$

For ψ any spatially periodic tensor-valued function, it follows by definition that

$$[\psi] = 0. \quad (3.19)$$

With the jump-function brackets $[[\]]$ defined as in (3.8) for any tensor field \mathbf{F} , it is proved in I that

$$\int_{\partial r_o} d\mathbf{s} \psi \mathbf{F} = \sum_{k=1}^3 \int_{s_{+k}} d\mathbf{s} \psi [[\mathbf{F}]]. \quad (3.20)$$

Various special cases arise, for example by choosing $\psi = 1$. Applied to the function $\mathbf{F} = \cdot \mathbf{J}_m$ this yields

$$\int_{\partial r_o} d\mathbf{s} \cdot \mathbf{J}_m = \sum_{k=1}^3 \int_{s_{+k}} d\mathbf{s} \cdot [[\mathbf{J}_m]]. \quad (3.21)$$

Consequently, (3.18) may be written alternatively as

$$\frac{d\mathbf{M}_m}{dt} = - \sum_{k=1}^3 \int_{s_{+k}} d\mathbf{s} \cdot [[\mathbf{J}_m]] + \delta_{m0} \delta(t). \quad (3.22)$$

As a consequence of the spatially periodic character of \mathbf{U} and \mathbf{D} , they possess the same values at geometrically equivalent points on opposite pairs of cell faces, s_{-k} and s_{+k} , respectively. Thus, (3.4) yields the jump-function condition

$$[[\mathbf{J}_m]] = \mathbf{U}[[\mathbf{P}_m]] - \mathbf{D} \cdot [[\nabla \mathbf{P}_m]], \quad (3.23)$$

in which \mathbf{U} and \mathbf{D} refer to their values on s_{+k} , say. Hence (3.22) becomes

$$\frac{d\mathbf{M}_m}{dt} = - \sum_{k=1}^3 \int_{s_{+k}} d\mathbf{s} \cdot \mathbf{U}[[\mathbf{P}_m]] + \sum_{k=1}^3 \int_{s_{+k}} d\mathbf{s} \cdot \mathbf{D} \cdot [[\nabla \mathbf{P}_m]] + \delta_{m0} \delta(t). \quad (3.24)$$

Since the boundary conditions (3.9)–(3.11) *et seq.*, imposed upon \mathbf{P}_m at the cell faces, permit $[[\mathbf{P}_m]]$ and $[[\nabla \mathbf{P}_m]]$ to be expressed entirely in terms of the lower-order volumetric moments $\mathbf{P}_{m-1}, \mathbf{P}_{m-2}, \dots, \mathbf{P}_1, \mathbf{P}_0$, the integration scheme implicit in (3.24) permits the calculation of \mathbf{M}_m solely from knowledge of these lower-order volumetric moments. This will prove useful in what follows.

As an immediate application of (3.24) consider the case for $m = 0$. With use of (3.9) this yields $d\mathbf{M}_0/dt = \delta(t)$. Integration, subject to the condition (3.13 *b*), immediately gives (3.14).

4. ASYMPTOTIC, LONG-TIME MOMENTS

Zero-order moments

The zero-order local moments (P_0, \mathbf{p}_0) are defined by the system of differential equations (for $t > 0$)

$$\partial P_0 / \partial t + \nabla \cdot \mathbf{J}_0 = \delta(\mathbf{r} - \mathbf{r}') \delta(t), \quad (4.1)$$

$$\mathbf{J}_0 = \mathbf{U}P_0 - \mathbf{D} \cdot \nabla P_0, \quad (4.2)$$

$$\partial \mathbf{p}_0 / \partial t + \nabla_s \cdot \mathbf{j}_0 = \Delta(\mathbf{v} \cdot \mathbf{J}_0), \quad (4.3)$$

$$\mathbf{j}_0 = \mathbf{u}\mathbf{p}_0 - \mathbf{d} \cdot \nabla_s \mathbf{p}_0, \quad (4.4)$$

along with the boundary conditions

$$[[P_0]] = 0, \quad [[\nabla P_0]] = 0 \quad \text{on} \quad \partial r_o \quad (4.5a, b)$$

at the cell surfaces, and the interphase boundary conditions

$$\mathbf{p}_0 = kP_0^{(c)} \quad \text{on} \quad s \quad (4.6)$$

and

$$P_0^{(d)} = KP_0^{(c)} \quad \text{on} \quad s. \quad (4.7)$$

The steady-state solution of this system of equations, achieved at infinite time, will be denoted by the functions

$$P_0^\infty(\mathbf{r}) = \lim_{t \rightarrow \infty} P_0(\mathbf{r}, t | \mathbf{r}') \quad (4.8a)$$

and

$$\mathbf{p}_0^\infty(\mathbf{r}) = \lim_{t \rightarrow \infty} \mathbf{p}_0(\mathbf{r}, t | \mathbf{r}'). \quad (4.8b)$$

These represent the solution of the differential equations

$$\nabla \cdot \mathbf{J}_0^\infty = 0, \quad (4.9)$$

$$\mathbf{J}_0^\infty = \mathbf{U}P_0^\infty - \mathbf{D} \cdot \nabla P_0^\infty, \quad (4.10)$$

$$\nabla_s \cdot \mathbf{j}_0^\infty = \Delta(\mathbf{v} \cdot \mathbf{J}_0^\infty), \quad (4.11)$$

$$\mathbf{j}_0^\infty = \mathbf{u}p_0^\infty - \mathbf{d} \cdot \nabla_s p_0^\infty, \quad (4.12)$$

and boundary conditions

$$[[P_0^\infty]] = 0, \quad [[\nabla P_0^\infty]] = 0 \quad \text{on } \partial \mathbf{r}_0 \quad (4.13 a, b)$$

and

$$p_0^\infty = kP_0^{\infty(c)}, \quad p_0^{\infty(d)} = KP_0^{\infty(c)} \quad \text{on } s. \quad (4.14 a, b)$$

Moreover, since the initial-condition source term in (4.1) has been 'lost' from these steady-state equations, it is now necessary to reimpose the normalization condition (cf. (3.12))

$$\int_{\mathbf{r}_0} P_0^\infty d\mathbf{r} + \int_s p_0^\infty ds = 1, \quad (4.15)$$

which is no longer automatically satisfied.

Despite the apparent complexity of the system of equations (4.9)–(4.15), in commonly encountered physical situations these equations often possess simple solutions (see §§8–14). In the following it will therefore be assumed that the solutions (P_0^∞, p_0^∞) and $(\mathbf{J}_0^\infty, \mathbf{j}_0^\infty)$ of these equations can be found. In any event they will henceforth be regarded as known functions.

For sufficiently long times it can be shown that the asymptotic approach to this steady state is exponentially rapid with time; i.e.

$$P_0(\mathbf{r}, t | \mathbf{r}') \simeq P_0^\infty(\mathbf{r}) + \text{Exp} \quad (4.16 a)$$

and

$$p_0(\mathbf{r}, t | \mathbf{r}') \simeq p_0^\infty(\mathbf{r}) + \text{Exp}, \quad (4.16 b)$$

where Exp denotes terms in \mathbf{r}, t and \mathbf{r}' that are attenuated exponentially with time. By 'long times' is meant, more precisely,

$$\|\mathcal{D}\| t/l^2 \gg 1, \quad (4.17)$$

in which $\mathcal{D} = \min(\mathbf{D}, \mathbf{d})$. The modulus bars indicate some norm of the function, and l denotes some characteristic linear unit cell dimension, e.g. the cube root of the superficial cell volume τ_0 . Physically, the phrase 'long time' refers simply to sufficient time for the Brownian tracer particle to sample all (accessible) positions within \mathbf{r}_0 and on s often enough to achieve effectively a steady state with respect to the local \mathbf{r} -space transport processes in the bounded region \mathbf{r}_0 , but not with respect to the global \mathbf{R}_n -space transport processes in the entire unbounded region $V_{0\infty}$.

From (4.16), (4.2) and (4.4) it follows that

$$\mathbf{J}_0(\mathbf{r}, t | \mathbf{r}') \simeq \mathbf{J}_0^\infty(\mathbf{r}) + \text{Exp} \quad (4.18 a)$$

and

$$\mathbf{j}_0(\mathbf{r}, t | \mathbf{r}') \simeq \mathbf{j}_0^\infty(\mathbf{r}) + \text{Exp}. \quad (4.18 b)$$

First-order moments

The local first-order vector moments $(\mathbf{P}_1, \mathbf{p}_1)$ are defined by the system of equations ($t > 0$)

$$\partial \mathbf{P}_1 / \partial t + \nabla \cdot \mathbf{J}_1 = 0, \quad (4.19)$$

$$\mathbf{J}_1 = \mathbf{U}\mathbf{P}_1 - \mathbf{D} \cdot \nabla \mathbf{P}_1, \quad (4.20)$$

$$\partial \mathbf{p}_1 / \partial t + \nabla_s \cdot \mathbf{j}_1 = \Delta(\mathbf{v} \cdot \mathbf{J}_1), \quad (4.21)$$

$$\mathbf{j}_1 = \mathbf{u}\mathbf{p}_1 - \mathbf{d} \cdot \nabla_s \mathbf{p}_1, \quad (4.22)$$

along with boundary conditions on the cell surfaces

$$[[\mathbf{P}_1]] = -[[\mathbf{r}P_0]], \quad [[\nabla\mathbf{P}_1]] = -[[\nabla(\mathbf{r}P_0)]] \quad \text{on } \partial\mathbf{r}_o, \quad (4.23 a, b)$$

and interphase boundary conditions

$$\mathbf{p}_1 = k\mathbf{P}_1^{(c)}, \quad \mathbf{P}_1^{(d)} = K\mathbf{P}_1^{(c)} \quad \text{on } s. \quad (4.24 a, b)$$

An asymptotic solution for $(\mathbf{P}_1, \mathbf{p}_1)$ analogous to that for (P_0, p_0) may be developed by pursuing the following line of reasoning. Putting $m = 1$ in (3.23) gives

$$[[\mathbf{J}_1]] = \mathbf{U}[[\mathbf{P}_1]] - \mathbf{D} \cdot [[\nabla\mathbf{P}_1]]. \quad (4.25)$$

As a consequence of (4.5a), P_0 possesses the same values at geometrically equivalent points on opposite pairs of cell faces on $\partial\mathbf{r}_o$. Consequently, (4.23a) may be written as

$$[[\mathbf{P}_1]] = -P_0[[\mathbf{r}]]. \quad (4.26)$$

By an obvious identity applied to the right-hand side of (4.23b),

$$[[\nabla\mathbf{P}_1]] = -\mathbf{I}[[P_0]] - [[(\nabla P_0) \mathbf{r}]],$$

with $\mathbf{I} = \nabla\mathbf{r}$ the dyadic idemfactor. Upon using (4.5a, b) it follows that

$$[[\nabla\mathbf{P}_1]] = -\nabla P_0[[\mathbf{r}]]. \quad (4.27)$$

Introduction of (4.26) and (4.27) into (4.25) yields

$$[[\mathbf{J}_1]] = -\mathbf{J}_0[[\mathbf{r}]], \quad (4.28)$$

with \mathbf{J}_0 given by (4.2). Note from (3.23) (for $m = 1$) and (4.5) that

$$[[\mathbf{J}_0]] = 0, \quad (4.29)$$

so that \mathbf{J}_0 possesses the same values at equivalent points \mathbf{r} and $\mathbf{r} + \mathbf{l}_k$ lying on opposite faces s_{-k} and s_{+k} of $\partial\mathbf{r}_o$.

For $m = 1$, equation (3.22) combines with (4.28) to give

$$\frac{d\mathbf{M}_1}{dt} = \sum_{k=1}^3 \int_{s_{+k}} ds \cdot \mathbf{J}_0[[\mathbf{r}]]. \quad (4.30)$$

Hence, in view of (4.29), one obtains

$$\frac{d\mathbf{M}_1}{dt} = \int_{\partial\mathbf{r}_o} ds \cdot \mathbf{J}_0 \mathbf{r}, \quad (4.31)$$

upon applying theorem (3.19), (3.20) in its converse sense. This constitutes an exact relation.

Substitution of (4.18a) into (4.31) gives the asymptotic relation

$$\frac{d\mathbf{M}_1}{dt} \simeq \int_{\partial\mathbf{r}_o} ds \cdot \mathbf{J}_0^\infty \mathbf{r} + \text{Exp.} \quad (4.32)$$

The generalized divergence theorem (3.17) with $\mathbf{A} = \mathbf{J}_0^\infty \mathbf{r}$ is

$$\int_{\partial\mathbf{r}_o} ds \cdot \mathbf{J}_0^\infty \mathbf{r} = \int_{\mathbf{r}_o} \nabla \cdot (\mathbf{J}_0^\infty \mathbf{r}) d\mathbf{r} - \int_s ds \Delta(\mathbf{v} \cdot \mathbf{J}_0^\infty \mathbf{r}). \quad (4.33)$$

$$\text{However, in view of (4.9),} \quad \nabla \cdot (\mathbf{J}_0^\infty \mathbf{r}) = \mathbf{J}_0^\infty. \quad (4.34)$$

Furthermore, since \mathbf{r} is continuous across s ,

$$\Delta(\mathbf{v} \cdot \mathbf{J}_0^\infty \mathbf{r}) = [\Delta(\mathbf{v} \cdot \mathbf{J}_0^\infty)] \mathbf{r} = (\nabla_s \cdot \mathbf{j}_0^\infty) \mathbf{r}$$

upon using (4.11). By identity,

$$(\nabla_s \cdot \mathbf{j}_0^\infty) \mathbf{r} = \nabla_s \cdot (\mathbf{j}_0^\infty \mathbf{r}) - \mathbf{j}_0^\infty.$$

However, on *any* closed surface,

$$\oint ds \nabla_s \cdot (\mathbf{j}_0^\infty \mathbf{r}) = 0,$$

since $\mathbf{j}_0^\infty \mathbf{r}$ is a single-valued function. Consequently,

$$\int_s ds \Delta(\mathbf{v} \cdot \mathbf{J}_0^\infty \mathbf{r}) = \int_s \mathbf{j}_0^\infty ds. \quad (4.35)$$

Introduction of (4.34) and (4.35) into (4.33) therefore gives

$$\int_{\partial r_0} ds \cdot \mathbf{J}_0^\infty \mathbf{r} = \int_{r_0} \mathbf{J}_0^\infty d\mathbf{r} + \int_s \mathbf{j}_0^\infty ds, \quad (4.36)$$

whereupon (4.32) becomes

$$\frac{d\mathbf{M}_1}{dt} \simeq \int_{r_0} \mathbf{J}_0^\infty d\mathbf{r} + \int_s \mathbf{j}_0^\infty ds + \text{Exp}. \quad (4.37)$$

Define the constant vector

$$\bar{\mathbf{U}} = \int_{\partial r_0} ds \cdot \mathbf{J}_0^\infty \mathbf{r}, \quad (4.38)$$

or, equivalently, from (4.36),

$$\bar{\mathbf{U}} = \int_{r_0} \mathbf{J}_0^\infty d\mathbf{r} + \int_s \mathbf{j}_0^\infty ds. \quad (4.39)$$

It follows from these definitions and either (4.32) or (4.37) that

$$d\mathbf{M}_1/dt \simeq \bar{\mathbf{U}} + \text{Exp}. \quad (4.40)$$

Integration gives

$$\mathbf{M}_1 \simeq \bar{\mathbf{U}}t + \bar{\mathbf{B}} + \text{Exp}, \quad (4.41)$$

with $\bar{\mathbf{B}}$ a position- and time-independent constant to be determined. Note that since \mathbf{J}_0^∞ and \mathbf{j}_0^∞ are assumed known *a priori* from the prior solution of equations (4.9)–(4.15), the constant $\bar{\mathbf{U}}$ is assumed to be known at this stage of the analysis.

From its definition (3.13), the first total moment is

$$\mathbf{M}_1 = \int_{r_0} \mathbf{P}_1 d\mathbf{r} + \int_s \mathbf{p}_1 ds. \quad (4.42)$$

Considered in conjunction with the asymptotic expansion (4.41), this suggests the pair of asymptotic trial solutions

$$\mathbf{P}_1 \simeq P_0^\infty(\mathbf{r}) [\bar{\mathbf{U}}t + \mathbf{B}(\mathbf{r})] + \text{Exp} \quad (4.43a)$$

and

$$\mathbf{p}_1 \simeq p_0^\infty(\mathbf{r}) [\bar{\mathbf{U}}t + \mathbf{b}(\mathbf{r})] + \text{Exp}, \quad (4.43b)$$

in which $\mathbf{B}(\mathbf{r})$ and $\mathbf{b}(\mathbf{r})$ are time-independent vector fields to be determined. The forms of these expansions will be confirmed *a posteriori*.

Before the determination of the \mathbf{B} and \mathbf{b} fields, observe that substitution of (4.43) and (4.44) into (4.42) yields

$$\mathbf{M}_1 \simeq \bar{\mathbf{U}}t \left(\int_{r_0} P_0^\infty d\mathbf{r} + \int_s p_0^\infty ds \right) + \left(\int_{r_0} P_0^\infty \mathbf{B} d\mathbf{r} + \int_s p_0^\infty \mathbf{b} ds \right) + \text{Exp}.$$

From (4.15) the coefficients of the $\bar{\mathbf{U}}t$ -term is unity. Comparison of the resulting expression for \mathbf{M}_1 with (4.41) gives

$$\bar{\mathbf{B}} = \int_{r_0} P_0^\infty \mathbf{B} d\mathbf{r} + \int_s p_0^\infty \mathbf{b} ds \quad (4.44)$$

for the value of the constant vector $\bar{\mathbf{B}}$.

It remains yet to determine the differential equations and boundary conditions satisfied by the \mathbf{B} and \mathbf{b} fields. The boundary conditions will be considered first.

Substitute (4.43 *a*) and (4.16 *a*) into (4.26) and use (4.13 *a*) to derive the jump condition

$$[[\mathbf{B}]] = -[[\mathbf{r}]]. \quad (4.45)$$

Similarly, substitute (4.43 *a*) and (4.16 *a*) into (4.27) and use (4.13 *a, b*) and (4.45) to obtain

$$[[\nabla \mathbf{B}]] = 0. \quad (4.46)$$

This pair of conditions represents the boundary conditions imposed upon \mathbf{B} at each point \mathbf{r} lying on the cell surfaces $\partial \mathbf{r}_\sigma$.

To obtain the boundary conditions at the phase boundaries, observe from (4.43 *a*) that, at each point \mathbf{r} lying upon s ,

$$\mathbf{P}_1^{(d)} = P_0^{(d)}(\bar{\mathbf{U}}t + \mathbf{B}^{(d)}) + \text{Exp} \quad (4.47a)$$

and

$$\mathbf{P}_1^{(e)} = P_0^{(e)}(\bar{\mathbf{U}}t + \mathbf{B}^{(e)}) + \text{Exp}. \quad (4.47b)$$

Equation (4.24 *b*) in conjunction with (4.14 *b*) therefore requires that

$$\mathbf{B}^{(d)} = \mathbf{B}^{(e)} \quad \text{on } s. \quad (4.48)$$

This is equivalent to the condition

$$\mathbf{B} \text{ is continuous across } s, \quad (4.49)$$

or equivalently $\Delta \mathbf{B} = 0$, so that no distinction need be drawn between $\mathbf{B}^{(d)}$ and $\mathbf{B}^{(e)}$ on s . Equation (4.47 *b*) may therefore be written without ambiguity as

$$\mathbf{P}_1^{(e)} = P_0^{(e)}(\bar{\mathbf{U}}t + \mathbf{B}) + \text{Exp} \quad \text{on } s.$$

Substitute this equation and (4.43 *b*) into (4.24 *a*) and use (4.14 *a*) to obtain

$$\mathbf{b} = \mathbf{B} \quad \text{on } s. \quad (4.50)$$

(In this connection it should be noted that \mathbf{b} is *not* a surface vector, defined only in the tangent plane at an interface. Rather, it is a complete three-dimensional vector. This follows from (4.43 *b*) in conjunction with the fact that \mathbf{P}_1 , defined by (3.1 *b*) for $m = 1$, is a complete three-dimensional vector as a consequence of the comparable property of the vector $\mathbf{R}_n - \mathbf{R}'_n$. Hence, the equality (4.50) is one involving complete vectors.)

Having established all the relevant boundary conditions imposed upon the \mathbf{B} and \mathbf{b} fields, we proceed to derive the differential equation satisfied by the \mathbf{B} field. Substitution of (4.43 *a*) into (4.20) gives

$$\mathbf{J}_1 \simeq J_0^\infty(\bar{\mathbf{U}}t + \mathbf{B}) - P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B} + \text{Exp}, \quad (4.51)$$

in which (4.10) has been used. Form the divergence of this expression and use (4.9) to obtain

$$\nabla \cdot \mathbf{J}_1 \simeq \nabla \cdot (J_0^\infty \mathbf{B} - P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B}) + \text{Exp}. \quad (4.52)$$

In addition, time differentiation of (4.43 *a*) gives

$$\partial \mathbf{P}_1 / \partial t \simeq P_0^\infty \bar{\mathbf{U}} + \text{Exp}. \quad (4.53)$$

Introduction of the last two expressions into (4.19) yields

$$\nabla \cdot (P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B} - J_0^\infty \mathbf{B}) = P_0^\infty \bar{\mathbf{U}}. \quad (4.54)$$

Since P_0^∞ , J_0^∞ and $\bar{\mathbf{U}}$ are assumed known at this stage, equation (4.54) constitutes the differential equation governing the \mathbf{B} field. This inhomogeneous second-order partial differential

equation is physically equivalent to a steady-state convection–diffusion–reaction equation, the ‘reaction’ term being represented by the inhomogeneous ‘source’ term on the right-hand side. In consequence of (4.9) this differential equation can be expressed in the alternative form

$$\nabla \cdot (P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B}) - \mathbf{J}_0^\infty \cdot \nabla \mathbf{B} = P_0^\infty \bar{\mathbf{U}}. \quad (4.55)$$

Observe that only the function $\nabla \mathbf{B}$, rather than \mathbf{B} itself, appears explicitly in this equation.

The differential equation satisfied by the \mathbf{b} field can be established by a similar procedure. Substitution of (4.43 *b*) into (4.22) yields the dyadic field

$$\mathbf{j}_1 \simeq \mathbf{j}_0^\infty (\bar{\mathbf{U}}t + \mathbf{b}) - \rho_0^\infty \mathbf{d} \cdot \nabla_s \mathbf{b} + \text{Exp}. \quad (4.56)$$

Form the surface divergence of this expression, differentiate (4.43 *b*) with respect to time, and introduce each of the resulting expressions into (4.21) along with the asymptotic relation (4.51) to obtain

$$\nabla_s \cdot (\rho_0^\infty \mathbf{d} \cdot \nabla_s \mathbf{b} - \mathbf{j}_0^\infty \mathbf{b}) = \rho_0^\infty \bar{\mathbf{U}} + \Delta[v \cdot (P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B} - \mathbf{J}_0^\infty \mathbf{B})]. \quad (4.57)$$

This equation has been simplified by use of (4.11) to eliminate the $\bar{\mathbf{U}}t$ terms that would otherwise have appeared.

The preceding equation governing the \mathbf{b} field can be written in a variety of different forms. By identity,

$$\nabla_s \cdot (\mathbf{j}_0^\infty \mathbf{b}) = (\nabla_s \cdot \mathbf{j}_0^\infty) \mathbf{b} + \mathbf{j}_0^\infty \cdot \nabla_s \mathbf{b}.$$

With use of (4.11), (4.50) and (4.49) the first term on the right-hand side of this identity becomes

$$(\nabla_s \cdot \mathbf{j}_0^\infty) \mathbf{b} = \Delta(v \cdot \mathbf{J}_0^\infty \mathbf{B}).$$

Consequently, (4.57) may be written alternatively as

$$\nabla_s \cdot (\rho_0^\infty \mathbf{d} \cdot \nabla_s \mathbf{b}) - \mathbf{j}_0^\infty \cdot \nabla_s \mathbf{b} = \rho_0^\infty \bar{\mathbf{U}} + \Delta(P_0^\infty v \cdot \mathbf{D} \cdot \nabla \mathbf{B}). \quad (4.58)$$

This form shows explicitly that the differential equation for \mathbf{b} involves only $\nabla_s \mathbf{b}$, rather than \mathbf{b} itself. In conjunction with the similar remark pertaining to $\nabla \mathbf{B}$ in (4.55), and the boundary conditions imposed upon \mathbf{B} and \mathbf{b} , it follows that the \mathbf{B} and \mathbf{b} fields are each determinate only to within an arbitrary additive constant vector. In consequence of (4.50) this arbitrary constant is necessarily the same for both fields.

Second-order moments

Set $m = 2$ in (3.24) and introduce (3.11 *a*, *b*) into the resulting expression. Upon using (3.9 *a*) to simplify this result, one obtains

$$\frac{d\mathbf{M}_2}{dt} = \sum_{k=1}^3 \int_{s_{+k}} ds \cdot (\mathbf{D} \cdot [\nabla(P_0 \mathbf{W})] - P_0 \mathbf{U}[\mathbf{W}]), \quad (4.59)$$

with \mathbf{W} the dyadic field

$$\mathbf{W} = \mathbf{P}_1 \mathbf{P}_1 / P_0^2. \quad (4.60)$$

By using (3.9 *a*, *b*) and (4.2) this expression can be rewritten as

$$\frac{d\mathbf{M}_2}{dt} = \sum_{k=1}^3 \int_{s_{+k}} ds \cdot (P_0 \mathbf{D} \cdot [\nabla \mathbf{W}] - \mathbf{J}_0[\mathbf{W}]). \quad (4.61)$$

In conjunction with (4.16 *a*) and (4.18 *a*) the preceding equation adopts the asymptotic form

$$\frac{d\mathbf{M}_2}{dt} \simeq \sum_{k=1}^3 \int_{s_{+k}} ds \cdot (P_0 \mathbf{D} \cdot [\nabla \mathbf{W}^\infty] - \mathbf{J}_0^\infty[\mathbf{W}^\infty]) + \text{Exp}, \quad (4.62)$$

in which

$$\mathbf{W}^\infty = \mathbf{P}_1^\infty \mathbf{P}_1^\infty / (P_0^\infty)^2.$$

Here, \mathbf{P}_1^∞ is given by those terms explicitly displayed on the right-hand side of (4.43a).

Explicitly,

$$\mathbf{W}^\infty = (\bar{\mathbf{U}}t + \mathbf{B})(\bar{\mathbf{U}}t + \mathbf{B}) \equiv \bar{\mathbf{U}}\bar{\mathbf{U}}t^2 + 2 \text{sym } \mathbf{B}\bar{\mathbf{U}}t + \mathbf{B}\mathbf{B}, \quad (4.63)$$

where the operator sym denotes the symmetric part of the dyadic; that is, generically,

$$\text{sym } \mathbf{A} = \frac{1}{2}(\mathbf{A} + \mathbf{A}^\dagger) \quad (4.64)$$

for any dyadic \mathbf{A} .

Apply the jump operator to (4.63) and use (4.45) to obtain

$$\llbracket \mathbf{W}^\infty \rrbracket = -2 \text{sym } \llbracket \mathbf{r} \rrbracket \bar{\mathbf{U}}t + \llbracket \mathbf{B}\mathbf{B} \rrbracket. \quad (4.65)$$

Similarly, upon forming the gradient of (4.63), applying the jump operator, and using (4.46), it follows that

$$\llbracket \nabla \mathbf{W}^\infty \rrbracket = \llbracket \nabla(\mathbf{B}\mathbf{B}) \rrbracket. \quad (4.66)$$

Substitute (4.65) and (4.66) into (4.62) and use theorem (3.20) in its converse sense to obtain

$$\frac{d\mathbf{M}_2}{dt} \simeq \int_{\partial r_0} d\mathbf{s} \cdot P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) + 2 \text{sym} \left(\int_{\partial r_0} d\mathbf{s} \cdot J_0^\infty \mathbf{r} \right) \bar{\mathbf{U}}t - \int_{\partial r_0} d\mathbf{s} \cdot J_0^\infty \mathbf{B}\mathbf{B} + \text{Exp.}$$

From (4.38) the second integral is $\bar{\mathbf{U}}$. Consequently,

$$\frac{d\mathbf{M}_2}{dt} \simeq 2\bar{\mathbf{U}}\bar{\mathbf{U}}t + \int_{\partial r_0} d\mathbf{s} \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] + \text{Exp.} \quad (4.67)$$

5. PHENOMENOLOGICAL DARCY-SCALE COEFFICIENTS

Mean tracer velocity and dispersivity

It is demonstrated in the Appendix that the mean velocity vector $\bar{\mathbf{U}}^*$ of the tracer particle and its dispersivity dyadic $\bar{\mathbf{D}}^*$ can be calculated from the pair of formulas

$$\bar{\mathbf{U}}^* = \lim_{t \rightarrow \infty} d\mathbf{M}_1/dt, \quad (5.1)$$

and

$$\bar{\mathbf{D}}^* = \frac{1}{2} \lim_{t \rightarrow \infty} d(\mathbf{M}_2 - \mathbf{M}_1 \mathbf{M}_1)/dt, \quad (5.2)$$

each deriving from Brownian motion theory. From the first of these in conjunction with (4.40) there follows

$$\bar{\mathbf{U}}^* \equiv \bar{\mathbf{U}}, \quad (5.3)$$

with $\bar{\mathbf{U}}$ given by either (4.38) or (4.39). Likewise, (5.2) in conjunction with (4.67) and (4.41) gives

$$\bar{\mathbf{D}}^* = \frac{1}{2} \int_{\partial r_0} d\mathbf{s} \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] - \text{sym } \bar{\mathbf{U}}\bar{\mathbf{B}}. \quad (5.4)$$

The final term in this expression is not very significant physically since the \mathbf{B} and \mathbf{b} fields are uniquely determined only to within an additive constant vector. Thus, one could arbitrarily choose this constant such that $\bar{\mathbf{B}} = 0$ (cf. (4.44) and (4.15)). However, we shall refrain from making this obvious choice in the interests of generality.

The generalized divergence theorem (3.17) may be applied to the integral in (5.4) to obtain

$$\int_{\partial r_0} d\mathbf{s} \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] = \int_{r_0} \nabla \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] d\mathbf{r} - \int_s d\mathbf{s} \Delta \{v \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}]\}. \quad (5.5)$$

To evaluate the volume integral on the right, pre- and post-multiply (4.54) by the field \mathbf{B} , add the resulting two expressions, and use some elementary vector and dyadic identities to obtain

$$\nabla \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] = 2P_0^\infty [(\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} + \text{sym } \mathbf{B} \bar{\mathbf{U}}] + \mathbf{B}\mathbf{B} \nabla \cdot J_0^\infty, \quad (5.6)$$

in which $\mathbf{D}^s = \text{sym } \mathbf{D}$. From (4.9) the last term on the right-hand side is zero. In addition, use the general identity

$$\mathbf{v} \cdot \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) = 2 \text{sym } \mathbf{v} \cdot \mathbf{D} \cdot (\nabla \mathbf{B}) \mathbf{B} \quad (5.7)$$

in the surface integral in (5.5). In this manner one obtains

$$\int_{\partial r_0} d\mathbf{s} \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] = 2 \int_{r_0} P_0^\infty (\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} d\mathbf{r} + 2 \text{sym} \left(\int_s P_0^\infty \mathbf{B} d\mathbf{r} \right) \bar{\mathbf{U}} - \text{sym} \int_s d\mathbf{s} \Delta [\mathbf{v} \cdot (2P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B} - J_0^\infty \mathbf{B})] \mathbf{B}. \quad (5.8)$$

In the surface integral we have used the continuity condition (4.49) to write

$$\Delta [\mathbf{v} \cdot (\mathbf{A}\mathbf{B})] = [\Delta (\mathbf{v} \cdot \mathbf{A})] \mathbf{B}. \quad (5.9)$$

Pre- and post-multiply (4.57) by the vector field \mathbf{b} , add the resulting expressions, and use some elementary vector and dyadic identities to obtain

$$\nabla_s \cdot [p_0^\infty \mathbf{d} \cdot \nabla_s(\mathbf{b}\mathbf{b}) - j_0^\infty \mathbf{b}\mathbf{b}] = 2p_0^\infty [(\nabla_s \mathbf{b})^\dagger \cdot \mathbf{d}^s \cdot \nabla_s \mathbf{b} + \text{sym } \mathbf{b} \bar{\mathbf{U}}] + \mathbf{H}, \quad (5.10)$$

in which

$$\mathbf{H} = \mathbf{b}\mathbf{b}(\nabla_s \cdot j_0^\infty) + 2 \text{sym} \Delta [\mathbf{v} \cdot (P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B} - J_0^\infty \mathbf{B})] \mathbf{b}. \quad (5.11)$$

Here, $\mathbf{d}^s = \text{sym } \mathbf{d}$. (Except for the Δ -term in \mathbf{H} , the surface identity (5.10) is completely analogous to the volumetric identity (5.6).) However, from (4.50), $\mathbf{b} = \mathbf{B}$ on s . If, in addition, (4.11) is used in the first term on the right-hand side of (5.11), there results

$$\mathbf{H} = \text{sym} \Delta [\mathbf{v} \cdot (2P_0^\infty \mathbf{D} \cdot \nabla \mathbf{B} - J_0^\infty \mathbf{B})] \mathbf{B} \quad (5.12)$$

upon using (5.9). Note that \mathbf{H} is precisely the integrand appearing in the last term in (5.8).

Form the surface integral of (5.10) over s . Owing to the single-valued nature of the integrand on the left-hand side of (5.10), the value of that integral is zero over any closed surface, in particular over s . Thus one obtains from (5.10)

$$\int_s d\mathbf{s} \mathbf{H} = -2 \int_s p_0^\infty (\nabla_s \mathbf{b})^\dagger \cdot \mathbf{d}^s \cdot \nabla_s \mathbf{b} d\mathbf{s} - 2 \text{sym} \left(\int_s p_0^\infty \mathbf{b} d\mathbf{s} \right) \bar{\mathbf{U}}. \quad (5.13)$$

Substitute this integral for the last term appearing on the right-hand side of (5.8) and obtain

$$\int_{\partial r_0} d\mathbf{s} \cdot [P_0^\infty \mathbf{D} \cdot \nabla(\mathbf{B}\mathbf{B}) - J_0^\infty \mathbf{B}\mathbf{B}] = 2 \int_{r_0} P_0^\infty (\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} d\mathbf{r} + 2 \int_s p_0^\infty (\nabla_s \mathbf{b})^\dagger \cdot \mathbf{d}^s \cdot \nabla_s \mathbf{b} d\mathbf{s} + 2 \text{sym} \left(\int_{r_0} P_0^\infty \mathbf{B} d\mathbf{r} + \int_s p_0^\infty \mathbf{b} d\mathbf{s} \right) \bar{\mathbf{U}}. \quad (5.14)$$

Observe from (4.44) that the last term in parentheses is $\bar{\mathbf{B}}$. Finally, substitute (5.14) into (5.4). This yields

$$\bar{\mathbf{D}}^* = \int_{r_0} P_0^\infty (\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} d\mathbf{r} + \int_s p_0^\infty (\nabla_s \mathbf{b})^\dagger \cdot \mathbf{d}^s \cdot \nabla_s \mathbf{b} d\mathbf{s}. \quad (5.15)$$

Equation (5.15) constitutes one of the main results of our analysis. It represents the generalization of a comparable formula for $\bar{\mathbf{D}}^*$ obtained in I. It also represents the counterpart of a comparable relation arising in the general theory of Taylor dispersion (Brenner 1980*b*, 1982)

when the global variable is continuous, rather than discrete. In principle, this formula permits the calculation of the dispersion dyadic from knowledge of the \mathbf{B} and \mathbf{b} fields.

The fact that the \mathbf{B} and \mathbf{b} fields are each uniquely determined only to within an arbitrary additive constant is clearly without physical relevance as far as (5.15) is concerned, since only the gradients of these functions appear in the integrands, rather than the functions themselves.

Symmetry and positive-definiteness of $\bar{\mathbf{D}}^$*

The bulk and surface diffusion dyadics \mathbf{D}^s and \mathbf{d}^s appearing in (5.15) are each symmetric and positive definite. Accordingly, by following the general methods outlined in I, it is easily demonstrated that $\bar{\mathbf{D}}^*$ is both symmetric and positive definite. The proof so nearly parallels that outlined in I and in the general theory of Taylor dispersion (Brenner 1980*b*) that we shall omit the detailed demonstration.

It is proved in §6 that the value of $\bar{\mathbf{D}}^*$ is independent of which of the infinitely many consistent choices is made for the shape ∂r_0 of the unit cell r_0 over which the integration in (5.15) is to be performed. Similar remarks apply to the formula (4.39) for $\bar{\mathbf{U}}^*$ as a consequence of the spatial periodicity (see §6) of the integrands \mathbf{J}_0^∞ and \mathbf{j}_0^∞ appearing therein.

6. SPATIALLY PERIODIC \mathbf{B} AND \mathbf{b} FIELDS

Equations (4.9)–(4.15) uniquely determine the zero-order asymptotic fields (P_0^∞, J_0^∞) and (p_0^∞, j_0^∞). Given that in this system of equations the phenomenological coefficients

$$U, \mathbf{D}, \mathbf{u}, \mathbf{d}, K, k \quad \text{are spatially periodic,} \quad (6.1)$$

one is led to the conclusion that

$$P_0^\infty, J_0^\infty, p_0^\infty, j_0^\infty \quad \text{are spatially periodic.} \quad (6.2)$$

This conclusion derives in part from the fact that the unit cell boundary conditions (4.13) apply to *all* of the infinitely many possible choices (see I) for the unit cell shapes.

The spatial periodicity of the functions in (6.2) may be demonstrated formally as follows. In the system of equations (4.9)–(4.15), *excluding* (4.13), replace the functions ($P_0^\infty, J_0^\infty, p_0^\infty, j_0^\infty$) by other functions ($\check{P}_0^\infty, \check{J}_0^\infty, \check{p}_0^\infty, \check{j}_0^\infty$), which are now assumed to depend upon \mathbf{R} rather than \mathbf{r} . (In making the transition, note that the \mathbf{r} -space gradient operator (2.21) must be replaced by the \mathbf{R} -space gradient operator $\nabla \equiv \partial/\partial\mathbf{R}$.) The resulting system of \cup equations clearly possesses periodic solutions as a consequence of the spatial periodicity of the phenomenological coefficients appearing therein. Moreover, these spatially periodic functions are uniquely defined (see I) by (4.9)–(4.15), excluding (4.13). Furthermore, the periodic counterparts,

$$\llbracket \check{P}_0^\infty \rrbracket = 0, \quad \llbracket \nabla \check{P}_0^\infty \rrbracket = 0,$$

of (4.13) are *automatically* satisfied in consequence of the spatial periodicity of the \cup functions. Since the previous \mathbf{r} -space system of equations (4.9)–(4.15) also possesses a unique solution (see I) at each point \mathbf{r} , this leads to the conclusion that at any point \mathbf{r} within a unit cell, $P_0^\infty(\mathbf{r}) = \check{P}_0^\infty(\mathbf{R}), \dots, j_0^\infty(\mathbf{r}) = \check{j}_0^\infty(\mathbf{R})$, with \mathbf{R} given by (2.4). Thus, the spatial periodicity of the four functions $P_0^\infty, \dots, j_0^\infty$ satisfying (4.9)–(4.15) – in the extended \mathbf{R} sense – is confirmed.

In effect we have extended the domain of definition of $P_0^\infty, J_0^\infty, p_0^\infty, j_0^\infty$ from the bounded region $\mathbf{r} \in r_0$ contained within a single unit cell to all points $\mathbf{R} \in V_{0\infty}$ within the entire infinite system. Therefore, instead of solving (4.9)–(4.15) within a single unit cell (for any one specific,

but arbitrary, choice of the infinitely many compatible cell shapes (see I)), one may elect to solve the same system of equations, excluding the now superfluous conditions (4.13), for the spatially periodic functions (6.2). This can be done by conventional methods with the use of Bloch functions (Brillouin 1953; Sachs 1963).

As in I, in place of the \mathbf{B} and \mathbf{b} fields, define the closely related vector fields

$$\check{\mathbf{B}} = \mathbf{B} + \mathbf{r}, \quad \check{\mathbf{b}} = \mathbf{b} + \mathbf{r}. \quad (6.3a, b)$$

As an immediate consequence of (4.45), from the first of these we obtain

$$[[\check{\mathbf{B}}]] = 0. \quad (6.4)$$

Moreover, since $\nabla \check{\mathbf{B}} = \nabla \mathbf{B} + \mathbf{I}$, it follows from (4.46) that

$$[[\nabla \check{\mathbf{B}}]] = 0. \quad (6.5)$$

From (4.49), (4.50), (4.55) and (4.58) one finds that the $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ fields satisfy the respective differential equations

$$\nabla \cdot (P_0^\infty \mathbf{D} \cdot \nabla \check{\mathbf{B}}) - \mathbf{J}_0^\infty \cdot \nabla \check{\mathbf{B}} = P_0^\infty (\bar{\mathbf{U}} - \mathbf{U} + \nabla \cdot \mathbf{D}) + 2\mathbf{D}^s \cdot \nabla P_0^\infty, \quad (6.6)$$

$$\nabla_s \cdot (p_0^\infty \mathbf{d} \cdot \nabla_s \check{\mathbf{b}}) - \mathbf{j}_0^\infty \cdot \nabla_s \check{\mathbf{b}} = p_0^\infty (\bar{\mathbf{U}} - \mathbf{u} + \nabla_s \cdot \mathbf{d}) + 2\mathbf{d}^s \cdot \nabla_s p_0^\infty + \Delta [P_0^\infty \mathbf{v} \cdot (\mathbf{D} \cdot \nabla \check{\mathbf{B}} - \mathbf{D})] \quad (6.7)$$

(in which (4.10) and (4.12) have been used), and interphase continuity conditions

$$\check{\mathbf{B}} \text{ is continuous across } s, \quad (6.8)$$

$$\check{\mathbf{b}} = \check{\mathbf{B}} \text{ on } s. \quad (6.9)$$

The $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ fields, defined on the unit cell $\mathbf{r} \in \mathbf{r}_0 \oplus s$, represent the solutions of the system of equations (6.4)–(6.9). They are each unique to within the same arbitrary additive constant vector. Using the same line of reasoning as that used in connection with the proof of (6.2), we are led to the conclusion that

$$\check{\mathbf{B}} \text{ and } \check{\mathbf{b}} \text{ are spatially periodic;} \quad (6.10)$$

that is the solutions of (6.6)–(6.9) possess the property (6.10). Conditions (6.4) and (6.5) are automatically satisfied in consequence of (6.10).

It is convenient to recast the expression for $\bar{\mathbf{D}}^*$ in terms of $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ rather than \mathbf{B} and \mathbf{b} . While this can be done trivially by substituting (6.3) into (5.15), the integration of the resulting expression is no less complex than that of (6.3) itself, since it involves the fields $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ *non-linearly*. Owing to the expected algebraic complexity of $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$, effecting the quadrature of (6.3) is likely to prove very difficult analytically. Accordingly, one can return to the original expression (5.4) for $\bar{\mathbf{D}}^*$ as the starting point for the calculation. The algebraic details entering into the calculation are tedious and will be omitted for brevity. Note only that we make extensive use of the fact that integrals of spatially periodic functions over $\partial \mathbf{r}_0$ are identically zero (see I). The result obtained is

$$\bar{\mathbf{D}}^* = \bar{\mathbf{D}}_M^* + \bar{\mathbf{D}}_C^*, \quad (6.11)$$

in which

$$\bar{\mathbf{D}}_M^* = \int_{\mathbf{r}_0} P_0^\infty \mathbf{D}^s d\mathbf{r} + \int_s p_0^\infty \mathbf{d}^s ds \quad (6.12)$$

and

$$\bar{\mathbf{D}}_C^* = \text{sym} \int_{\mathbf{r}_0} [P_0^\infty (\mathbf{U} - \bar{\mathbf{U}}) \check{\mathbf{B}} - \mathbf{D} \cdot \nabla (P_0^\infty \check{\mathbf{B}})] d\mathbf{r} + \text{sym} \int_s [p_0^\infty (\mathbf{u} - \bar{\mathbf{U}}) \check{\mathbf{b}} - \mathbf{d} \cdot \nabla_s (p_0^\infty \check{\mathbf{b}})] ds. \quad (6.13)$$

This symmetrical expression involves $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ linearly.

All of the functions entering into the calculation of $\bar{\mathbf{D}}^*$ via (6.11) are spatially periodic. It is proved in I that volume integrals of spatially periodic functions over a unit cell \mathbf{r}_0 are invariant to the particular choice made for the shape $\partial\mathbf{r}_0$ of the unit cell. It follows that $\bar{\mathbf{D}}^*$ is an *invariant*, independent of cell shape; that is $\bar{\mathbf{D}}^*$ is a property of the lattice alone, and not of its mode of subdivision into unit cells. This conclusion is physically gratifying since it is only the particle arrangement (i.e. the lattice) that possesses physical reality, not the unit cells themselves.

7. NOTATIONAL CHANGES AND RECAPITULATION

The elaborate system of subscripts and superscripts that has stealthily accumulated during the natural development of the theory is unnecessary in applications, and can be eliminated. At the same time, introduction of the new notation that follows serves to summarize the main working equations of the theory for the benefit of those readers interested only in applications. It is convenient to introduce the following notational equivalences:

$$P_0^\infty \leftrightarrow P, \quad p_0^\infty \leftrightarrow p, \quad \mathbf{J}_0^\infty \leftrightarrow \mathbf{J}, \quad \mathbf{j}_0^\infty \leftrightarrow \mathbf{j}. \quad (7.1)$$

While use of the 'new' symbols $P, p, \mathbf{J}, \mathbf{j}$ may appear confusing in view of their prior use in a slightly different sense, the proposed notation possesses the important advantage that the 'new' equations look precisely like the 'old' equations of §2, at least in the steady-state context of the final working equations whose solution is a prerequisite for the calculation of $\bar{\mathbf{U}}^*$ and $\bar{\mathbf{D}}^*$. Where necessary a clear distinction will be drawn between the old and new $P, p, \mathbf{J}, \mathbf{j}$ in the text.

In terms of the altered notation the asymptotic zero-order equations (4.9)–(4.15) (except (4.13)) governing the fields $P, p, \mathbf{J}, \mathbf{j}$ are

$$\nabla \cdot \mathbf{J} = 0, \quad (7.2)$$

$$\mathbf{J} = \mathbf{U}P - \mathbf{D} \cdot \nabla P, \quad (7.3)$$

$$\nabla_s \cdot \mathbf{j} = \Delta(\mathbf{v} \cdot \mathbf{J}) \quad \text{on } s, \quad (7.4)$$

$$\mathbf{j} = \mathbf{u}p - \mathbf{d} \cdot \nabla_s p \quad \text{on } s, \quad (7.5)$$

$$p = kP_c \quad \text{on } s, \quad (7.6)$$

$$p_d = KP_c \quad \text{on } s \quad (7.7)$$

and

$$\int_{\mathbf{r}_0} P d\mathbf{r} + \int_s p ds = 1. \quad (7.8)$$

If the functions $P, p, \mathbf{J}, \mathbf{j}$ are regarded as defined at all points \mathbf{R} within the infinite domain $V_{0\infty}$, the equations serve to define these four quantities uniquely, provided that they are supplemented by the additional requirements that

$$P, p, \mathbf{J}, \mathbf{j} \text{ are spatially periodic.} \quad (7.9)$$

Alternatively, if these four dependent variables are regarded as defined only at points $\mathbf{r} \in \mathbf{r}_0$ within the interior of a unit cell, equations (7.2)–(7.8) must then be supplemented by the additional cell-face boundary conditions

$$[[P]] = 0, \quad [[\nabla P]] = 0 \quad \text{on } \partial\mathbf{r}_0, \quad (7.10)$$

which now serve to render the four variables unique within a unit cell.

Solution of the foregoing equations permits calculation of the mean velocity of the tracer particle, from either the symmetric formula

$$\bar{U}^* = \int_{r_o} J d\mathbf{r} + \int_s \mathbf{j} ds, \quad (7.11)$$

or the asymmetric formula

$$\bar{U}^* = \int_{\partial r_o} d\mathbf{s} \cdot \mathbf{J} \mathbf{r} \equiv \int_{\partial r_o} d\mathbf{s} \cdot \mathbf{J} \mathbf{R}. \quad (7.12)$$

In terms of the new notation the \mathbf{B} and \mathbf{b} equations are

$$\nabla \cdot (P\mathbf{D} \cdot \nabla \mathbf{B}) - \mathbf{J} \cdot \nabla \mathbf{B} = P\bar{U}^*, \quad (7.13)$$

$$\nabla_s \cdot (\rho \mathbf{d} \cdot \nabla_s \mathbf{b}) - \mathbf{j} \cdot \nabla_s \mathbf{b} = \rho \bar{U}^* + \Delta(P\mathbf{v} \cdot \mathbf{D} \cdot \nabla \mathbf{B}) \quad \text{on } s, \quad (7.14)$$

$$\mathbf{B} \text{ is continuous across } s, \quad (7.15)$$

$$\mathbf{b} = \mathbf{B} \quad \text{on } s, \quad (7.16)$$

and
$$[\mathbf{B}] = -[\mathbf{r}], \quad [\nabla \mathbf{B}] = 0 \quad \text{on } \partial r_o. \quad (7.17 a, b)$$

The \mathbf{B} and \mathbf{b} fields are defined only within the interior $\mathbf{r} \in r_o$ of a unit cell, and are unique only to within an arbitrary additive constant. The dispersion dyadic can be calculated from knowledge of these fields by the formula

$$\bar{\mathbf{D}}^* = \int_{r_o} P(\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} d\mathbf{r} + \int_s \rho(\nabla_s \mathbf{b})^\dagger \cdot \mathbf{d}^s \cdot \nabla_s \mathbf{b} ds, \quad (7.18)$$

or any of its numerous variants given in §§5 and 6.

Alternatively, the dispersivity can be calculated by solving instead for fields $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ defined for all points $\mathbf{R} \in V_{o\infty}$ in the entire composite medium by the following system of equations:

$$\check{\mathbf{B}}, \check{\mathbf{b}} \quad \text{are spatially periodic,} \quad (7.19)$$

$$\nabla \cdot (P\mathbf{D} \cdot \nabla \check{\mathbf{B}}) - \mathbf{J} \cdot \nabla \check{\mathbf{B}} = (\bar{U}^* - U + \nabla \cdot \mathbf{D})P + 2\mathbf{D}^s \cdot \nabla P, \quad (7.20)$$

$$\nabla_s \cdot (\rho \mathbf{d} \cdot \nabla_s \check{\mathbf{b}}) - \mathbf{j} \cdot \nabla_s \check{\mathbf{b}} = (\bar{U}^* - \mathbf{u} + \nabla_s \cdot \mathbf{d})\rho + 2\mathbf{d}^s \cdot \nabla_s \rho + \Delta[P\mathbf{v} \cdot (\mathbf{D} \cdot \nabla \check{\mathbf{B}} - \mathbf{D})] \quad \text{on } s, \quad (7.21)$$

$$\check{\mathbf{B}} \text{ is continuous across } s, \quad (7.22)$$

$$\check{\mathbf{b}} = \check{\mathbf{B}} \quad \text{on } s. \quad (7.23)$$

These fields are unique only to within an arbitrary additive constant. The dispersivity can again be calculated from (7.18) via the relations

$$\nabla \mathbf{B} = \nabla \check{\mathbf{B}} - \mathbf{I} \quad \text{and} \quad \nabla_s \mathbf{b} = \nabla_s \check{\mathbf{b}} - \mathbf{I} \quad (7.24 a, b)$$

connecting the pairs of fields (\mathbf{B}, \mathbf{b}) and $(\check{\mathbf{B}}, \check{\mathbf{b}})$ (cf. equations (6.3)).

It will prove convenient in later discussions to introduce the decomposition

$$\mathbf{r}_o \equiv \mathbf{r}_o^{(c)} \oplus \mathbf{r}_o^{(d)}, \quad (7.25)$$

where $\mathbf{r}_o^{(c)}$ and $\mathbf{r}_o^{(d)}$ represent the domains of the continuous and discontinuous phases, respectively, within the unit cell \mathbf{r}_o . In the same context, one may write

$$\tau_o = \tau_c + \tau_d, \quad (7.26)$$

where
$$\tau_o = \int_{r_o} d\mathbf{r}, \quad \tau_c = \int_{r_o^{(c)}} d\mathbf{r}, \quad \tau_d = \int_{r_o^{(d)}} d\mathbf{r} \quad (7.27)$$

represent the superficial volume of a unit cell, and the volumes occupied by the continuous and discontinuous phases within the cell respectively. The quantity

$$\epsilon = \tau_c / \tau_o \quad (7.28)$$

is the 'porosity' of a unit cell, which is obviously also the porosity of the entire spatially periodic porous medium.

The quantity

$$S = \int_s ds \quad (7.29)$$

represents the total interfacial surface area of the discontinuous phase within a unit cell, while

$$\alpha = S / \tau_o \quad (7.30)$$

is the 'specific surface area' of the interfacial phase within a unit cell, and hence the specific surface area of the spatially periodic porous medium as a whole.

*Eulerian interpretation of \bar{U}^**

As in the general theory of Taylor dispersion (Brenner 1982*b*, 1982) the tracer velocity vector \bar{U}^* , defined by (5.1), is interpreted as representing the average Lagrangian velocity of the tracer after sufficient time has been allowed for it to sample all accessible local positions \mathbf{r} many times (not necessarily, however, within the same unit cell \mathbf{R}_n). Equivalently, it is the number-average Lagrangian velocity of a collection of identical tracer particles for any arbitrary distribution of initial local positions \mathbf{r}' .

One may also place a Eulerian interpretation (see also §14) on \bar{U}^* , analogous to that advanced in I for the special case where the local tracer velocity $U(\mathbf{r})$ appearing in (2.13) is identical to the local *fluid* velocity vector $\mathbf{v}(\mathbf{r})$, a fact that has *not* been assumed in the present analysis. As a consequence of the spatial periodicity of \mathbf{J} in equations (7.2)–(7.9), we have, as in I, that

$$\mathbf{s}_k \cdot \int_{\partial r_o} (d\mathbf{s} \cdot \mathbf{J}\mathbf{r}) = \tau_o \int_{s_k} d\mathbf{s} \cdot \mathbf{J} \quad (7.31)$$

valid for \mathbf{J} any spatially periodic function. Here, the vector

$$\mathbf{s}_k = \int_{s_k} d\mathbf{s} \quad (k = \pm 1, \pm 2, \pm 3) \quad (7.32)$$

is the directed surface area of any curvilinear face s_k of a unit cell ∂r_o . As a consequence of (7.12), this makes

$$\mathbf{s}_k \cdot \bar{U}^* = \int_{s_k} d\mathbf{s} \cdot \mathbf{J}. \quad (7.33)$$

From the definition of \mathbf{J} given earlier in this section, the vector field \mathbf{J} represents the tracer flux density for a *steady-state* tracer distribution within a unit cell. Hence, the integral appearing on the right-hand side of (7.33) represents the Eulerian time rate of flow of tracer across face s_k of the cell in the steady state. Accordingly, since (7.33) holds for each of the infinitely many (cf. I) directed areal vectors \mathbf{s}_k , it follows that the orientation-independent vector \bar{U}^* , defined by (7.12), or equivalently (7.11), represents the steady-state Eulerian tracer velocity on the 'Darcy-length scale' (cf. I), on which scale \mathbf{s}_k plays the role of a *differential* directed element of superficial area $d\bar{s}_v$; that is if

$$Q_k = \int_{s_k} d\mathbf{s} \cdot \mathbf{J} \quad (7.34)$$

denotes the time rate of tracer flow across the 'arbitrarily oriented' surface $d\bar{s}_v \equiv s_{vk}$, equation (7.33) is equivalent to the Darcy-scale relation

$$d\bar{Q}_v = d\bar{s}_v \cdot \bar{U}^*, \quad (7.35)$$

where $d\bar{Q}_v \equiv Q_k$ is the flux across $d\bar{s}_v$. Since this relation holds for 'arbitrary' orientations v of the Darcy-scale surface element $d\bar{s}_v$, and since \bar{U}^* is independent of the orientation v , equation (7.35) is consistent with the classical Eulerian definition of the tracer velocity vector \bar{U}^* on the Darcy scale.

8. SPECIAL LIMITING CASES

There exist a number of limiting cases, which require special considerations to bring them within the purview of the preceding theory. These are discussed in this section.

No surface-excess adsorption or transport

When the phase boundary s (if indeed one exists) is inert, we have that

$$p = 0 \quad \text{and} \quad j = 0. \quad (8.1)$$

Equation (7.4) thereby adopts the form

$$\Delta(v \cdot J) = 0 \quad \text{on} \quad s, \quad (8.2)$$

which now plays the role of a boundary condition imposed upon J ; in particular, it requires that the normal component of the bulk flux J be continuous across s . In addition, the interfacial adsorption boundary condition (7.6) no longer obtains; equivalently, $k = 0$.

The relevant formulas for computing \bar{U}^* and \bar{D}^* in the present case are given by (7.11) and (7.18), respectively, with the surface contributions suppressed. Their calculation thus requires knowledge only of the fields (P, J) and B (or \check{B}) within the continuous and discontinuous phases. As regards the B field, equation (7.16) is now eliminated whereas (7.14) is replaced by the requirement that

$$\Delta(Pv \cdot D \cdot \nabla B) = 0 \quad \text{on} \quad s. \quad (8.3)$$

That is the function in parentheses is continuous across the phase boundaries. This constitutes a boundary condition imposed upon ∇B across s . (The equivalent $\nabla \check{B}$ continuity condition is easily worked out from the first of equations (7.24).)

No transport in the interior of the discontinuous phase

In terms of the notation of (7.25) we have in this limiting case that

$$P = 0 \quad \text{and} \quad J = 0 \quad \text{in} \quad r_0^{(d)}. \quad (8.4)$$

In this manner the right-hand side of (7.4) becomes

$$\Delta(v \cdot J) = -v \cdot J_c \equiv -v \cdot J \quad \text{on} \quad s, \quad (8.5)$$

where J denotes the flux in the continuous phase. In addition, the boundary condition (7.7) on s no longer obtains.

The corresponding consequences for the B and \check{B} fields are easily established, and are not further discussed here.

Continuous-phase transport only

This case represents the simplest physical situation, and perhaps the most important one in conventional applications. The conditions discussed in the previous two limiting cases are simultaneously applicable. The relevant equations are thus

$$\nabla \cdot \mathbf{J} = 0, \quad \mathbf{J} = \mathbf{U}P - \mathbf{D} \cdot \nabla P, \quad (8.6a, b)$$

$$\mathbf{v} \cdot \mathbf{J} = 0 \quad \text{on } s \quad (8.7)$$

and

$$\int_{\mathbf{r}_0^{(c)}} P d\mathbf{r} = 1. \quad (8.8)$$

These are to be solved in the region $\mathbf{r} \in \mathbf{r}_0^{(c)}$ subject to one of the two auxiliary conditions (7.9) and (7.10), whichever is appropriate. The corresponding \mathbf{B} equations (to be solved in this same domain) now consist of (7.13), (7.17), and the condition

$$\mathbf{v} \cdot \mathbf{D} \cdot \nabla \mathbf{B} = 0 \quad \text{on } s, \quad (8.9)$$

derived from (7.14). The solution of these equations permits the calculation of $\bar{\mathbf{U}}^*$ and $\bar{\mathbf{D}}^*$ from the formulas

$$\bar{\mathbf{U}}^* = \int_{\mathbf{r}_0^{(c)}} \mathbf{J} d\mathbf{r} \quad (8.10)$$

and

$$\bar{\mathbf{D}}^* = \int_{\mathbf{r}_0^{(c)}} P (\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} d\mathbf{r}. \quad (8.11)$$

In the physically important case where

$$\nabla \cdot \mathbf{U} = 0 \quad \text{in } \mathbf{r}_0^{(c)} \quad (8.12)$$

and

$$\mathbf{v} \cdot \mathbf{U} = 0 \quad \text{on } s, \quad (8.13)$$

equations (8.6)–(8.8) and either (7.9) or (7.10) possess the ‘trivial’ solutions

$$P = 1/\tau_c = \text{const.} \quad \text{and} \quad \mathbf{J} = \mathbf{U}/\tau_c. \quad (8.14a, b)$$

In such circumstances (8.10) becomes

$$\bar{\mathbf{U}}^* = \frac{1}{\tau_c} \int_{\mathbf{r}_0^{(c)}} \mathbf{U} d\mathbf{r}, \quad (8.15)$$

whereas (8.11) adopts the form

$$\bar{\mathbf{D}}^* = \frac{1}{\tau_c} \int_{\mathbf{r}_0^{(c)}} (\nabla \mathbf{B})^\dagger \cdot \mathbf{D}^s \cdot \nabla \mathbf{B} d\mathbf{r}. \quad (8.16)$$

From (7.13), \mathbf{B} is now the solution of the differential equation

$$\nabla \cdot (\mathbf{D} \cdot \nabla \mathbf{B}) - \mathbf{U} \cdot \nabla \mathbf{B} = \bar{\mathbf{U}}^*, \quad (8.17)$$

satisfying the boundary conditions (7.17) and (8.9).

It should be clearly noted that we have not assumed the local tracer velocity field $\mathbf{U}(\mathbf{r})$ to be identical to the local fluid velocity field $\mathbf{v}(\mathbf{r})$, a fact that is not generally true (see §11). Suppose, however, that $\mathbf{U} = \mathbf{v}$ (in which case (8.12) and (8.13) are consistent with the properties of the incompressible fluid), and suppose simultaneously that for such point-size, force-free, Brownian particles, \mathbf{D} is isotropic and constant at each point $\mathbf{r} \in \mathbf{r}_0^{(c)}$, i.e.

$$\mathbf{D} = ID, \quad D = \text{const.} \quad (8.18a, b)$$

Then equations (8.15)–(8.17) reduce to those already considered in I. The case $\mathbf{U} = \mathbf{v}$ will not be further considered here since it is pursued in a broader context (including surface and discontinuous-phase transport) in §10.

Pure molecular conduction: composite materials

As a final limiting case consider the situation where $\mathbf{U} = \mathbf{u} = 0$, corresponding to purely diffusive transport. As is readily confirmed, the solution of equations (7.2)–(7.9) or (7.10) for this case corresponds to $\mathbf{J} = \mathbf{j} = 0$ and

$$P_c = C/\tau_o, \quad P_d = KC/\tau_o, \quad p = kC/\tau_o, \quad (8.19)$$

where, in the notation of equations (7.28) and (7.30), C is the constant

$$1/C = \epsilon + (1 - \epsilon)K + k\alpha. \quad (8.20)$$

For simplicity we have supposed that K and k are constants, independent of position. Furthermore, from (7.11), $\bar{\mathbf{U}}^* = 0$. In this case (7.13) and (7.14) reduce to

$$\nabla \cdot (\mathbf{D}'_c \cdot \nabla \mathbf{B}_c) = 0, \quad \nabla \cdot (\mathbf{D}'_d \cdot \nabla \mathbf{B}_d) = 0 \quad (8.21)$$

and
$$\nabla_s \cdot (\mathbf{d}' \cdot \nabla_s \mathbf{b}) = \mathbf{v} \cdot [\mathbf{D}'_d \cdot \nabla \mathbf{B}_d - \mathbf{D}'_c \cdot \nabla \mathbf{B}_c] \quad \text{on } s, \quad (8.22)$$

in which
$$\mathbf{D}'_c = \mathbf{D}_c, \quad \mathbf{D}'_d = K\mathbf{D}_d, \quad \mathbf{d}' = k\mathbf{d}. \quad (8.23)$$

Because of the large number of phenomenological parameters entering into the theory, even the simplest calculation quickly becomes algebraically tedious. For illustration it will therefore prove convenient to consider the closely related *heat conduction* problem (see §13), with P taken to be the temperature T , and \mathbf{D} the thermal conductivity. Suppose further, again for simplicity, that surface adsorption and diffusion are absent, so that $k = 0$ and $\mathbf{d} = 0$. Continuity of temperature across the phase boundary requires that $K = 1$, whence P adopts the simple form

$$P = 1/\tau_o \quad \text{for all } \mathbf{r}_o. \quad (8.24)$$

This constant value is the same for both the continuous and the discontinuous phases. Moreover,

$$p = 0. \quad (8.25)$$

As a simple example of conductive transport in spatially periodic structures, consider heat transfer through the ‘one-dimensional’ laminated composite shown in figure 1. This periodic composite consists of an infinite sequence of alternate layers (of thicknesses l_c and l_d) of two separately homogeneous substances of uniform isotropic conductivities D_c and D_d stacked in the z -direction. Figure 1 shows a typical lamina of thickness

$$l_z = l_c + l_d. \quad (8.26)$$

In defining the local \mathbf{r} -space it is convenient to imagine an infinite sequence of equidistant parallel planes $x = \text{const.}$ and $y = \text{const.}$, spaced l_x and l_y units apart, as in figure 1. This artifice effectively divides the space into rectangular parallelepipeds of dimensions $l_x \times l_y \times l_z$, and permits one to regard the infinite space as being composed of such parallelepipeds, regularly stacked. These may be taken to be the unit cells of which the spatially periodic medium is composed. Since l_x and l_y may be arbitrarily chosen, the (physical) results ultimately obtained must show themselves to be independent of the explicit choices made for these two lengths.

With $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ unit vectors along the rectangular coordinate axes (x, y, z) in figure 1, the position vector \mathbf{R} at any point in the array may be expressed in the form (2.4), in which

$$\mathbf{R}_n = \mathbf{i}n_x l_x + \mathbf{j}n_y l_y + \mathbf{k}n_z l_z \quad (8.27)$$

and

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z. \quad (8.28)$$

Here, each of the $\{n_x, n_y, n_z\}$ are positive or negative integers, including zero. The cartesian coordinates (x, y, z) span the bounded regions

$$0 < x < l_x, \quad 0 < y < l_y, \quad 0 < z < l_z. \quad (8.29)$$

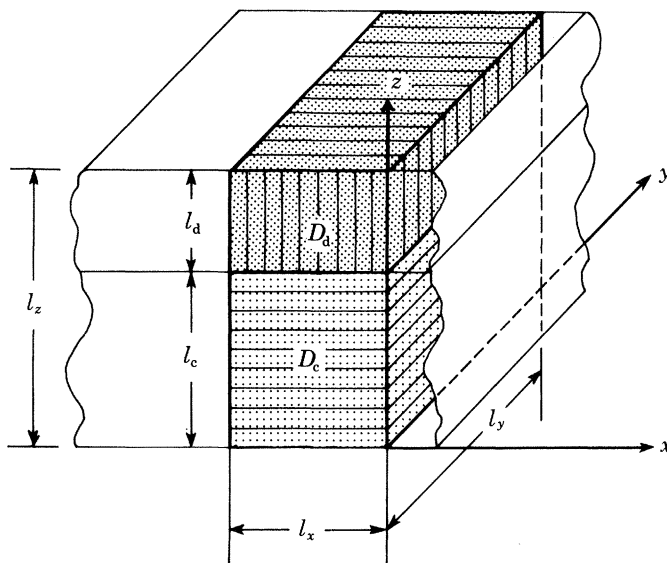


FIGURE 1. Unit cell for heat conduction in a spatially periodic layered composite.

In the present example, \mathbf{D} is the isotropic dyadic

$$\mathbf{D} = \mathbf{I}D(z), \quad (8.30)$$

with

$$\mathbf{I} = \mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j} + \mathbf{k}\mathbf{k} \quad (8.31)$$

the dyadic idemfactor, and $D(z)$ the discontinuous scalar

$$D(z) = \begin{cases} D_c & (0 < z < l_c), \\ D_d & (l_c < z < l_c + l_d), \end{cases} \quad (8.32)$$

in which D_c and D_d are constants. In view of the constancy (8.24) of P in both the 'continuous' and the 'discontinuous' phases, equation (7.13) reduces in present circumstances to

$$\nabla \cdot [D(z) \cdot \nabla \mathbf{B}] = 0 \quad \text{in} \quad \mathbf{r}_0^{(c)} \oplus \mathbf{r}_0^{(d)}. \quad (8.33)$$

Likewise since $\mathbf{v} = \pm \mathbf{k}$ in (7.14), (8.33) requires that

$$D(z) \partial \mathbf{B} / \partial z \quad \text{is continuous at} \quad z = l_c. \quad (8.34)$$

Subject to *a posteriori* verification, assume the trial solution

$$\mathbf{B} = \mathbf{k}B(z) - (\mathbf{i}x + \mathbf{j}y), \quad (8.35)$$

with $B(z)$ an x - and y -independent scalar field to be determined. Differentiation of (8.35) gives

$$\nabla \mathbf{B} = \mathbf{k} \mathbf{k} dB/dz - (\mathbf{ii} + \mathbf{jj}), \quad (8.36)$$

whence from (8.33) the differential equation satisfied by $B(z)$ becomes

$$\frac{d}{dz} \left[D(z) \frac{dB}{dz} \right] = 0 \quad (0 < z < l_c + l_d). \quad (8.37)$$

The continuity condition (7.15) requires that

$$B(z) \text{ is continuous at } z = l_c, \quad (8.38)$$

whereas (8.34) requires that

$$D(z) dB/dz \text{ is continuous at } z = l_c. \quad (8.39)$$

The last two conditions in conjunction with the fact that the same continuity conditions necessarily prevail at all points in the separately homogeneous 'continuous' and 'discontinuous' phases lead to the conclusion that the left-hand sides of (8.38) and (8.39) are continuous for all z . Thus, in integrating (8.37) one need not explicitly distinguish between the two phases.

Integration of (8.37) gives

$$dB/dz = -C/D(z), \quad (8.40)$$

where, from (8.39), the constant C has the same value in both phases. A second integration with the use of (8.38) gives

$$B(z) - B(0) = -C \int_0^z dz'/D(z'), \quad (8.41)$$

in which the constant $B(0)$ has the same value in both phases. Since as \mathbf{B} and, hence, $B(z)$ are uniquely determined only to within an arbitrary additive constant, the numerical value of $B(0)$ is irrelevant.

As a consequence of the assumed form (8.35), the requisite cell-face boundary conditions (7.17) are automatically satisfied for all pairs of points on the lateral unit cell faces, $x = (0, l_x)$ and $y = (0, l_y)$, whereas the boundary conditions on the remaining cell faces, $z = (0, l_z)$, require that

$$B(l_z) - B(0) = -l_z \quad (8.42)$$

and

$$dB/dz|_{l_z} - dB/dz|_0 = 0. \quad (8.43)$$

It follows from the fact that $D(z)$ is spatially periodic, and thus possesses the same values at $z = 0$ and $z = l_z$,† that equation (8.43) is automatically satisfied as a consequence of (8.40). Hence, it remains only to satisfy (8.42). From (8.41) it therefore follows that the constant C is given explicitly by the formula

$$C = l_z / \int_0^{l_z} \frac{dz}{D(z)}. \quad (8.44)$$

That we have succeeded in satisfying all of the conditions imposed upon the \mathbf{B} -field, coupled with the uniqueness of this field (to within an arbitrary additive constant), thereby provides *a posteriori* confirmation of the assumed form of the trial solution (8.35).

† The possible ambiguity in interpretation here illustrates one of the potential difficulties associated with allowing the unit cell faces to coincide with the phase boundary s , as we have inadvertently done in this example. To remove the ambiguity one needs to note that $D(0+) = D(l_z+)$, since $z = 0$ and $z = l_z$ each lie on a phase boundary.

Since $\tau_0 = l_x l_y l_z$, introduction of (8.24), (8.25), (8.30) and (8.36) into (7.18) yields

$$\bar{\mathbf{D}}^* = \frac{1}{l_x l_y l_z} \int_0^{l_x} \int_0^{l_y} \int_0^{l_z} D(z) \left[\mathbf{k}\mathbf{k} \left(\frac{dB}{dz} \right)^2 + (\mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j}) \right] dx dy dz.$$

Upon performing the x and y integrations, and using (8.40) and (8.31), this becomes

$$\bar{\mathbf{D}}^* = \mathbf{k}\mathbf{k}\bar{D}_{\parallel}^* + (\mathbf{I} - \mathbf{k}\mathbf{k})\bar{D}_{\perp}^*, \quad (8.45)$$

in which

$$\bar{D}_{\parallel}^* = \frac{C^2}{l_z} \int_0^{l_z} \frac{dz}{D(z)} \equiv l_z \int_0^{l_z} \frac{dz}{D(z)} \quad (8.46)$$

and

$$\bar{D}_{\perp}^* = \frac{1}{l_z} \int_0^{l_z} D(z) dz. \quad (8.47)$$

In accordance with intuition, equation (8.45) shows the composite medium to be transversely isotropic (with respect to an axis parallel to the direction of periodicity) as regards its 'effective conductivity' $\bar{\mathbf{D}}^*$. The axial scalar component \bar{D}_{\parallel}^* , along the z -axis, corresponds to the effective conductivity for resistances in *series*, whereas the transverse scalar component \bar{D}_{\perp}^* corresponds to that for resistances in *parallel*.

Equations (8.45)–(8.47) apply for *any* one-dimensional spatially periodic conductivity field $D(z)$, continuous or discontinuous. In the particular case of the discontinuous laminated structure described by (8.32), equations (8.46) and (8.47) reduce to the forms

$$l_z/\bar{D}_{\parallel}^* = l_c/D_c + l_d/D_d \quad (8.48)$$

and

$$l_z\bar{D}_{\perp}^* = l_c D_c + l_d D_d. \quad (8.49)$$

These are the usual formulas for effective series and parallel conductivities, respectively, for layered media.

For illustration it is useful to confirm in the present simple example that the function $\check{\mathbf{B}}$ defined by (6.3a) is indeed spatially periodic. With use of (8.28) and (8.35) this function possesses the form $\check{\mathbf{B}} = \mathbf{k}\check{B}(z)$, in which $\check{B}(z) = B(z) + z$. Explicitly, from (8.41),

$$\check{B}(z) = B(0) + z - C \int_0^z dz'/D(z'), \quad (8.50)$$

where z now spans the infinite range $-\infty < z < \infty$, rather than the unit cell range indicated in (8.29). Hence, by definition, from (8.50),

$$\check{B}(z + n_z l_z) = B(0) + z + n_z l_z - C \int_0^{z+n_z l_z} dz'/D(z'). \quad (8.51)$$

However, from the definition of a definite integral,

$$\int_z^{z+n_z l_z} dz'/D(z') = \int_0^z dz'/D(z') + \int_z^{z+n_z l_z} dz'/D(z').$$

Since the integrand of the last term in this expression is spatially periodic (with period l_z), and since n_z is an integer, we have successively that

$$\int_z^{z+n_z l_z} \frac{dz'}{D(z')} = \int_0^{n_z l_z} \frac{dz''}{D(z'')} = n_z \int_0^{l_z} \frac{dz''}{D(z'')} = \frac{n_z l_z}{C},$$

where C is the constant defined in (8.44). Equation (8.51) therefore becomes

$$\check{B}(z + n_z l_z) = B(0) + z - C \int_0^z dz'/D(z'). \quad (8.52)$$

Comparison with (8.50) thereby yields

$$\check{B}(z + n_z l_z) = \check{B}(z).$$

This equality confirms that \check{B} and, hence, the vector field $\check{\mathbf{B}}$ are indeed spatially periodic functions.

9. MEAN FLUID VELOCITY

Eulerian and Lagrangian interpretations

Emphasis thus far has been exclusively upon transport of the Brownian tracer particle through the porous medium. To analyse fully transport processes in such media, one must also consider the motion of the fluid in which the tracer is suspended, that is the 'undisturbed' vector velocity field \mathbf{v} , which prevails in the absence of the tracer. Of course, if the tracer is of point dimensions and experiences no external force, the fluid motion will be the same in the presence of the tracer as it is in its absence, i.e. \mathbf{v} . However, a tracer of non-zero size or one that is subjected to external forces, such as gravity, will perturb the undisturbed flow \mathbf{v} .

As in I, consider a steady, incompressible, *macroscopically* homogeneous, uniform flow at constant superficial (seepage) velocity $\bar{\mathbf{v}}$ through the porous medium, occurring in the absence of the tracer. This constant mean flow may be regarded as generated by the application of a steady, macroscopically homogeneous, uniform pressure gradient maintained throughout the porous medium, as in a one-dimensional Darcy flow.

In contrast with the comparable situation analysed in I, the possibility is now allowed of a non-zero fluid motion occurring within the interior $\mathbf{r}_0^{(d)}$ of the discontinuous phase (as well as on the particle surfaces s). This would arise, for example, if the discrete phase were composed of non-neutrally buoyant emulsion droplets (held in place by gravity) allowing internal circulation. As in I, it will be assumed to be a consequence of the constancy of $\bar{\mathbf{v}}$ throughout the porous medium, considered in conjunction with the incompressibility condition,

$$\nabla \cdot \mathbf{v} = 0, \quad (9.1)$$

that

$$\mathbf{v} \text{ is spatially periodic} \quad (9.2)$$

at all points $\mathbf{r}_0^{(e)} \oplus \mathbf{r}_0^{(d)} \oplus s$ in \mathbf{r}_0 .

The mean velocity of the fluid may be defined in either of two ways (cf. I):

(i) *Eulerian view.* The mean velocity is defined by the relation

$$\mathbf{s}_k \cdot \bar{\mathbf{v}} = q_k, \quad (9.3)$$

where as in (7.32) \mathbf{s}_k is the directed area of face s_k of a unit cell, and

$$q_k = \int_{s_k} d\mathbf{s} \cdot \mathbf{v} \quad (9.4)$$

is the volumetric flow rate through this face;

(ii) *Lagrangian view.* The mean velocity is defined as

$$\bar{\mathbf{v}} = d\bar{\mathbf{R}}/dt \quad (9.5)$$

where

$$\bar{\mathbf{R}} = \frac{1}{\tau_0} \int_{\mathbf{r}_0(t)} \mathbf{R} d\mathbf{r} \quad (9.6)$$

is the instantaneous position vector of the centre of volume of the moving unit cell $\mathbf{r}_0(t)$ at time t . This volume consists of both the continuous and the discontinuous phases, though the surface s bounding the latter remains stationary in space.

It is demonstrated in I that both of these definitions lead independently to the same expression, namely

$$\bar{\mathbf{v}} = \frac{1}{\tau_0} \int_{\partial \mathbf{r}_0} d\mathbf{s} \cdot \mathbf{v} \mathbf{r}. \quad (9.7)$$

This formula relates the mean fluid velocity $\bar{\mathbf{v}}$ to the local fluid velocity \mathbf{v} at points \mathbf{r} lying on the surface $\partial \mathbf{r}_0$ of a unit cell. The proof of (9.7) given in I holds equally well here since the surface integral in (9.7) lies wholly within the continuous phase, and thus does not depend upon the absence or presence of flow within the discontinuous phase. As in I, as a consequence of (9.2), the integral on the right-hand side of (9.7) can be shown to be an invariant vector, possessing the same constant value for each of the infinitely many choices for the (generally curvilinear) unit cell shape $\partial \mathbf{r}_0$ consistent with the specified lattice.

In I the bed particles were assumed to be solid, and hence characterized by $\mathbf{v} = 0$ in $\mathbf{r}_0^{(d)}$. This is no longer assumed. Application of the generalized divergence theorem, (3.17) and (2.12), to (9.7) gives

$$\tau_0 \bar{\mathbf{v}} = \int_{\mathbf{r}_0} \nabla \cdot (\mathbf{v} \mathbf{r}) d\mathbf{r} - \int_s d\mathbf{s} \mathbf{r} \Delta(\mathbf{v} \cdot \mathbf{v}). \quad (9.8)$$

In view of (9.1), an elementary vector identity shows that

$$\nabla \cdot (\mathbf{v} \mathbf{r}) = \mathbf{v}. \quad (9.9)$$

Furthermore, physical considerations require that

$$\mathbf{v} \cdot \mathbf{v} \text{ is continuous across } s. \quad (9.10)$$

Consequently,

$$\bar{\mathbf{v}} = \frac{1}{\tau_0} \int_{\mathbf{r}_0} \mathbf{v} d\mathbf{r}. \quad (9.11)$$

Thus the mean velocity is identical to the volume-average local velocity taken over both the continuous and the discontinuous phases. Of course when the bed particles are solid they make no contribution to the integrand, and the formula reduces to that given in I.

When the interphase continuity condition (9.10) is replaced by the stronger condition

$$\mathbf{v} \cdot \mathbf{v} = 0 \quad \text{on } s, \quad (9.12)$$

as, for example, for emulsion droplets, equation (9.11) simplifies to the form

$$\bar{\mathbf{v}} = \frac{1}{\tau_0} \int_{\mathbf{r}_0^{(c)}} \mathbf{v} d\mathbf{r}, \quad (9.13)$$

since

$$\int_{\mathbf{r}_0^{(d)}} \mathbf{v} d\mathbf{r} = 0. \quad (9.14)$$

To prove (9.14) use (9.9) in $\mathbf{r}_0^{(d)}$ in conjunction with the divergence theorem to derive

$$\int_{\mathbf{r}_0^{(d)}} \mathbf{v} d\mathbf{r} = \int_s d\mathbf{s} \mathbf{r} (\mathbf{v} \cdot \mathbf{v}).$$

Equation (9.12) shows the right-hand integral to be zero, thereby confirming (9.14). Consequently, when (9.12) obtains, only the continuous phase contributes directly to the mean velocity, as in (9.13). In this connection we note that if (cf. I)

$$\bar{\mathbf{v}}^* = \frac{1}{\tau_0} \int_{\mathbf{r}_0^{(c)}} \mathbf{v} d\mathbf{r} \quad (9.15)$$

is *defined* as the mean velocity of the fluid through the continuous phase, (i.e. the mean interstitial fluid velocity vector), then, when condition (9.12) prevails,

$$\bar{\mathbf{v}}^* = \mathbf{v}/\epsilon, \quad (9.16)$$

where ϵ is the porosity, as in (7.28).

'Statistical' interpretation of the mean fluid velocity

Finally, we note that equation (9.11) can also be derived 'statistically', via Taylor dispersion theory, by the expedient of choosing the Brownian tracer particle in the preceding theory to be a *fluid* molecule. Thus, if in (7.2)–(7.10) we disallow the possibility of surface adsorption and transport for such a fluid molecule at the phase boundary, and put the partition coefficient K equal to unity, it follows that the asymptotic solutions of the zero-order local moment equations are $P = 1/\tau_0 = \text{const.}$ and $\mathbf{J} = \mathbf{v}/\tau_0$ at *all* points in \mathbf{r}_0 . Substitution into (7.11) (with the surface contribution suppressed) thereby yields

$$\bar{\mathbf{U}}^* = \frac{1}{\tau_0} \int_{\mathbf{r}_0} \mathbf{v} d\mathbf{r} \equiv \bar{\mathbf{v}}$$

for the mean Lagrangian velocity of the fluid molecule. This agrees with (9.11). (This statistical interpretation of the mean fluid velocity appears to be internally consistent. In particular, for *solid* bed particles, whose interiors cannot be penetrated by a fluid molecule, the solution of (7.2)–(7.10) is $P = 1/\tau_c$ in $\mathbf{r}_0^{(c)}$ and $P = 0$ in $\mathbf{r}_0^{(d)}$. This yields $\mathbf{J} = \mathbf{v}/\tau_c$ in $\mathbf{r}_0^{(c)}$ and $\mathbf{J} = 0$ in $\mathbf{r}_0^{(d)}$, in which case equation (7.11) gives

$$\bar{\mathbf{U}}^{*'} = \frac{1}{\tau_c} \int_{\mathbf{r}_0^{(c)}} \mathbf{v} d\mathbf{r} \equiv \bar{\mathbf{v}}^*.$$

The prime has been added to \mathbf{U}^* to avoid confusion with the comparable quantity in (9.16). This result agrees with that obtained in I for solid particles.)

10. APPLICATIONS TO CONVENTIONAL FLOW AND DISPERSION PROBLEMS IN PACKED BEDS

In this section the bed particles will be assumed solid so that the suspending fluid is confined exclusively to the continuous phase. The tracer, however, is not assumed to be similarly restricted but is, rather, free to move along the surfaces s of the bed particles by surface diffusion, or through the particle interiors $\mathbf{r}_0^{(d)}$ by molecular diffusion.

In most situations of practical interest the tracer is effectively of point or molecular dimensions (relative to the interstitial pore dimensions) and is not subjected to any external forces, except perhaps those ultra-short-range forces already implicitly accounted for in the assumed adsorption and surface diffusion phenomena (Brenner & Leal 1982). As regards the continuous phase transport of such point-size, force-free tracers, the tracer will simply move quasistatically and passively with the local velocity $\mathbf{v}(\mathbf{r})$ of the fluid at the point \mathbf{r} in the interstitial region $\mathbf{r}_0^{(c)}$ that it instantaneously occupies. Hence

$$\mathbf{U} = \mathbf{v} \quad \text{in} \quad \mathbf{r}_0^{(c)}. \quad (10.1)$$

As in §9, for the macroscopically homogeneous uniform fluid motions $\bar{\mathbf{v}}$ to which the current analysis pertains, \mathbf{v} is spatially periodic. Thus, this same property attaches to \mathbf{U} . Moreover, since the bed particles are solid and no external forces act upon the tracer,

$$\mathbf{U} = 0 \quad \text{in} \quad \mathbf{r}_0^{(d)} \quad (10.2)$$

and
$$\mathbf{u} = 0 \quad \text{on } s. \quad (10.3)$$

The latter is a consequence of the no-slip condition satisfied by the fluid on the surfaces of the bed particles, considered in conjunction with the absence of external forces on the adsorbed tracer.

In view of conditions (9.1) and (9.12), \mathbf{U} satisfies equations (8.12) and (8.13). As a consequence of these, the system of equations (7.2)–(7.10) simplifies considerably. In particular, P and \mathbf{j} are each constant within their respective bulk domains $\mathbf{r}_0^{(e)} \oplus \mathbf{r}_0^{(d)}$ and surface domain s , and in fact possess the values cited in (8.19). Hence, in (7.3) and (7.5),

$$\mathbf{J} = \begin{cases} \mathbf{v}P_c & \text{in } \mathbf{r}_0^{(e)}, \\ 0 & \text{in } \mathbf{r}_0^{(d)} \end{cases} \quad (10.4)$$

and
$$\mathbf{j} = 0. \quad (10.5)$$

Accordingly, from (7.11), the mean tracer velocity is

$$\bar{\mathbf{U}}^* = P_c \int_{\mathbf{r}_0^{(e)}} \mathbf{v} d\mathbf{r}. \quad (10.6)$$

However, from (9.11) the superficial Darcy-scale seepage velocity vector $\bar{\mathbf{v}}$ through the porous medium is given by (9.13) in the present case. In this manner the mean tracer velocity is found to be

$$\bar{\mathbf{U}}^* = C\bar{\mathbf{v}}, \quad (10.7)$$

where C is the constant given in (8.20), namely†

$$C^{-1} = \epsilon + (1 - \epsilon)K + k\alpha. \quad (10.8)$$

Equation (10.7) shows that while the superficial tracer and fluid velocities are parallel, they are not generally equal in magnitude. (It is only in the combined equipartition ($K = 1$) and non-adsorbing ($k = 0$) case that the mean tracer and fluid velocities are equal, for these require that $C = 1$.) This non-equivalence of mean velocities is similar to that obtained for flow and Taylor dispersion of wall-adsorbed species in a circular capillary tube (Golay 1958). Thus, equation (10.7) offers a simple rationale for the functional mechanism of partition chromatographic separation phenomena (Lee *et al.* 1977; Yau *et al.* 1979; Provder 1980). If in a mixture the different chemical species ($i = 1, 2, \dots, N$) possess different adsorption coefficients K_i or adsorption coefficients k_i , their C_i -values will differ. As a consequence, each species will move at a different average velocity $\bar{\mathbf{U}}_i^*$ through the packed column, which will result in a chromatographic separation.

The general equations governing the \mathbf{B} and \mathbf{b} fields also simplify considerably in the present case. Because of the assumed point-size dimensions of the tracer, it will experience no ‘wall effects’ near the bed particles. (See §11 for a discussion of such ‘wall effects’ for finite-size tracers.) In consequence of the Stokes–Einstein equation, the tracer diffusivity \mathbf{D} in the fluid phase will be a scalar rather than a tensor, and will be everywhere constant, independent of position \mathbf{r} ; that is

$$\mathbf{D} = ID_e, \quad D_e = \text{const. in } \mathbf{r}_0^{(e)}. \quad (10.9)$$

† Observe that in the impermeable ($K = 0$) non-adsorbing ($k = 0$) case, equation (10.7) becomes

$$\bar{\mathbf{U}}^* = \bar{\mathbf{v}}^*,$$

where, as in (9.16), $\bar{\mathbf{v}}^*$ is the mean *interstitial* velocity of the field. Therefore, in such circumstances, the tracer moves on average through the interstices with the same mean velocity as the fluid, an unsurprising conclusion.

If, further, the solid phase is locally amorphous (isotropic and homogeneous), it will also be true that

$$\mathbf{D} = lD_d, \quad D_d = \text{const. in } \mathbf{r}_0^{(d)}. \quad (10.10)$$

Similar assumptions regarding the adsorbed surface phase make

$$\mathbf{d} = l_s d, \quad d = \text{const. on } s. \quad (10.11)$$

In such circumstances the relevant $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ equations, (7.20) and (7.21), become

$$D_c \nabla^2 \check{\mathbf{B}}_c - \mathbf{v} \cdot \nabla \check{\mathbf{B}}_c = \bar{U}^* - \mathbf{v} \quad \text{in } \mathbf{r}_0^{(c)}, \quad (10.12)$$

$$D_d \nabla^2 \check{\mathbf{B}}_d = \bar{U}^* \quad \text{in } \mathbf{r}_0^{(d)} \quad (10.13)$$

and
$$kd \nabla_s^2 \check{\mathbf{b}} + (D_c \partial \check{\mathbf{B}}_c / \partial v - KD_d \partial \check{\mathbf{B}}_d / \partial v) = k \bar{U}^* + v(D_c - KD_d) \quad \text{on } s. \quad (10.14)$$

In (10.14), $\partial/\partial v \equiv \mathbf{v} \cdot \nabla$ denotes the derivative normal to the phase boundary s . Equations (10.12)–(10.14) are to be solved for the periodic fields $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ subject to the boundary conditions

$$\check{\mathbf{B}}_c = \check{\mathbf{B}}_d = \mathbf{b} \quad \text{on } s. \quad (10.15)$$

Solution of these equations allows the calculation of the dispersivity dyadic from the formula

$$\bar{\mathbf{D}}^* = \frac{C}{\tau_0} \left[D_c \int_{\mathbf{r}_0^{(c)}} (\nabla \mathbf{B}_c)^{\dagger} \cdot (\nabla \mathbf{B}_c) d\mathbf{r} + KD_d \int_{\mathbf{r}_0^{(d)}} (\nabla \mathbf{B}_d)^{\dagger} \cdot (\nabla \mathbf{B}_d) d\mathbf{r} + kd \int_s (\nabla_s \mathbf{b})^{\dagger} \cdot \nabla_s \mathbf{b} ds \right], \quad (10.16)$$

derived from (7.18) and (8.19). As usual, equations (6.3) relate the \mathbf{B} and \mathbf{b} , and $\check{\mathbf{B}}$ and $\check{\mathbf{b}}$ field pairs.

Various limiting cases of the foregoing may be obtained as outlined in §8. In particular, the results for the impermeable, non-adsorbing, bed particle (§8(c)) then reduce to those already obtained in I. As in the footnote pertaining to equation (10.7), note that $\bar{U}^* = \bar{v}^*$ in this situation, and that $C = 1/\epsilon$.

Finally, we note that in chromatographic separation devices, the dispersion dyadic $\bar{\mathbf{D}}_i^*$ will generally be different for the different chemical species i , as was also true of their mean velocities \bar{U}_i^* . Calculation of these dispersivities by the methods outlined permits the sharpness of the chromatographic peaks to be ascertained.

11. TRANSPORT OF FINITE-SIZE BROWNIAN PARTICLES CONFINED TO THE INTERSTITIAL FLUID REGION

Introduction

Potential applications of the present theory exist in such fields as hydrodynamic chromatography (Small 1974; Brenner & Gaydos 1977; Prieve & Hoysan 1978; Silebi & McHugh 1978, 1979; Giddings 1978) and deep-bed filtration (Ives 1975, 1978). These phenomena share the common property that the local tracer velocity $\mathbf{U}(\mathbf{r})$ differs from the (undisturbed) local fluid velocity $\mathbf{v}(\mathbf{r})$ at points \mathbf{r} in the interstitial region $\mathbf{r}_0^{(c)}$. This velocity disparity may arise as a consequence of the non-zero size a of the Brownian tracer (relative to the interstitial pore size l of the bed), or the action of external forces upon the tracer, even if it is of point size. Such forces often tend to deposit the tracer onto the surfaces s of the bed particles. Inertial or Basset 'forces' constitute yet another mechanism causing \mathbf{U} and \mathbf{v} to differ within the interstices.

As previously discussed, attention is confined to spherical Brownian particles. This simplifies the analysis considerably since the tracer-particle orientation is then eliminated as an independent variable (Brenner 1979, 1981), thereby allowing attention to be focused exclusively on the motion of the centre-point of the Brownian particle.† In dealing with such finite-size particles it is the instantaneous location \mathbf{R} of this centre-point to which the original probability density $P(\mathbf{R}, t | \mathbf{R}')$ refers. Thus, despite the finite size of the particle, the preceding theoretical development of ‘point’ transport phenomena may still be applied (Brenner & Gaydos 1977).

It will be assumed in the subsequent development of this section that the (centre of the) Brownian particle is permanently confined to the continuous fluid phase. Hence, surface adsorption and surface-excess transport are assumed absent, as also is transport through the bed-particle interiors. The working equations are then equations (8.6)–(8.11).

Tracer flux

The general constitutive flux expression in this case is

$$\mathbf{J} = \mathbf{U}'(\mathbf{r})P + \mathbf{M}(\mathbf{r}) \cdot \mathbf{F}(\mathbf{r})P - \mathbf{D}(\mathbf{r}) \cdot \nabla P \quad (11.1)$$

in $\mathbf{r}_0^{(c)}$. These three contributions to the flux density \mathbf{J} represent convective transport arising from the fluid motion, external force-driven transport, and diffusive transport, respectively. The individual contributions are separately discussed subsequently. Each of the phenomenological coefficients \mathbf{U}' , \mathbf{M} , \mathbf{F} and \mathbf{D} will be shown to be spatially periodic. The main point we wish to make, however, is that the flux expressions (11.1) can be trivially brought within the context of the previous flux expression (2.13) or (7.3) merely by defining

$$\mathbf{U} = \mathbf{U}' + \mathbf{M} \cdot \mathbf{F}, \quad (11.2)$$

and then proceeding as before. Even for point-size tracers, where $\mathbf{U}' = \mathbf{v}$, it still will not be generally true that $\mathbf{U} = \mathbf{v}$, unless $\mathbf{F} = 0$.

Velocity of a neutrally buoyant tracer

The vector field \mathbf{U}' represents the velocity of the centre of the freely rotating, torque-free sphere as it is carried along by the flowing fluid in the absence of external forces \mathbf{F} . In other words, \mathbf{U}' is the velocity of the neutrally buoyant sphere when suspended in the otherwise undisturbed spatially periodic flow \mathbf{v} . Clearly, \mathbf{U}' will itself be spatially periodic since it necessarily possesses the same values at geometrically equivalent points \mathbf{r} in every cell \mathbf{R}_n , since the different configurations are physically indistinguishable as \mathbf{R}_n is varied while \mathbf{r} is kept fixed.

In general, owing to ‘wall effects’ arising from the proximity of the bed particles to the sphere, its velocity $\mathbf{U}'(\mathbf{r})$ will differ from the comparable fluid velocity $\mathbf{v}(\mathbf{r})$ that would prevail at \mathbf{r} in its absence. At least for quasistatic Stokes flows, the magnitude of the slip-velocity can be expected to be of the functional form

$$|\mathbf{v} - \mathbf{U}'| = \bar{v}^* f(\mathbf{r}/l, a/l), \quad (11.3)$$

† However, the general theory of Taylor dispersion (Brenner 1980*b*) allows a relatively straightforward extension of the analysis to non-spherical Brownian particles, by the explicit introduction of particle orientation as yet another independent *local* variable (in addition to the local position \mathbf{r} of the locator point of the tracer particle within a unit cell). With the introduction of this additional orientational variable, the ensuing asymptotic dispersion analysis is then concerned with situations in which *translational* Brownian motion permits the particle locator point to sample all accessible positions \mathbf{r} within a unit cell, while *rotational* Brownian motion permits the particle to sample all accessible orientations (Brenner 1979, 1981).

where \bar{v}^* is the magnitude $|\bar{\mathbf{v}}^*|$ of the mean interstitial fluid velocity (9.15). Only when $a \rightarrow 0$, or more precisely $a/l \rightarrow 0$, will \mathbf{U}' be identical to \mathbf{v} .

Since the fluid streamlines characterizing \mathbf{v} will generally be curvilinear, rather than rectilinear, local pressure gradients arising from the undisturbed flow \mathbf{v} will exist at each point \mathbf{r} . Such pressure gradients will tend to cause the sphere centre to deviate from the streamline upon which it instantaneously finds itself.† Hence, not only will \mathbf{U}' differ in magnitude from \mathbf{v} , but also it will generally not even lie parallel to \mathbf{v} . Such cross-streamline particle motions \mathbf{U}' thereby provide a possible ‘impaction’ mechanism for deposition of the Brownian tracer onto the bed particles. This viscous pressure-gradient mechanism for deposition is in addition to the so-called ‘inertial’ impaction mechanism, which arises from particle inertia.

External forces

The vector field \mathbf{F} in (11.1) denotes the external force exerted upon the tracer by its surroundings. It may be written generally in the form

$$\mathbf{F} = \mathbf{F}^e + \mathbf{F}^i. \quad (11.4)$$

Here, \mathbf{F}^e denotes those forces exerted on the tracer by an agency lying entirely outside the porous medium, and thus ‘external’ to it. The most common example is a gravitational force arising from a density difference between the particle and fluid. In general, \mathbf{F}^e is assumed to be independent of \mathbf{R}_n , dependent at most upon \mathbf{r} ; that is \mathbf{F}^e is assumed to be spatially periodic. In the gravitational case \mathbf{F}^e is everywhere a constant, and hence independent of \mathbf{r} too.

The force \mathbf{F}^i represents an ‘internal’ force exerted by the bed particles upon the tracer. Typically, these will arise as a result of London–van der Waals forces, Debye double-layer forces, etc. (Ruckenstein & Prieve 1980; Lightfoot *et al.* 1981). All other things being equal, these internal forces depend only upon the immediate physical environment in which the tracer particle instantaneously finds itself. Because of the spatial periodicity of this environment, the forces \mathbf{F}^i will themselves also be periodic. Often, this force may be derived from a periodic potential energy function $V(\mathbf{r})$ in the form

$$\mathbf{F}^i = -\nabla V. \quad (11.5)$$

The necessity for classifying the total force \mathbf{F} into separate external and internal contributions is imposed upon us by our *a priori* rejection of the possibility of surface adsorption and surface-excess transport in analysing the Brownian tracer particle of non-zero size. Thus, whereas ultra-short-range internal forces may previously have been *implicitly* incorporated into the concept of surface adsorption and transport along the phase boundary (Brenner & Leal 1982), this possibility does not exist for tracers of finite size. Rather, any such short-range, spatially periodic, internal forces \mathbf{F}^i (London–van der Waals, etc.) acting upon the tracer must now be *explicitly* accounted for by incorporation into the force \mathbf{F} contributing to the total tracer velocity \mathbf{U} . On the other hand, the distant forces \mathbf{F}^e play the same role for finite-size tracers as they do for ‘molecular’-size tracers. Thus, the subdivisions of \mathbf{F} into external and internal components is very natural.

† Indeed, to first order in a/l , Faxen’s law (Happel & Brenner 1973),

$$\mathbf{U}'(\mathbf{r}) = \mathbf{v}(\mathbf{r}) + (a^2/6\mu)\nabla p,$$

may be used to calculate \mathbf{U}' . Here μ is the fluid viscosity and ∇p the local undisturbed pressure gradient at \mathbf{r} due to the field \mathbf{v} .

Tracer mobility and diffusivity dyadics

The mobility dyadic \mathbf{M} appearing in (11.1) can, in principle, be computed from the hydrodynamic solution of a Stokes flow problem involving motion of the torque-free sphere under the action of an external force \mathbf{F} when moving through the interstices of the porous medium filled with an otherwise *quiescent* fluid. Owing to 'wall effects' arising from the finite size of the sphere, \mathbf{M} is generally a (symmetric) dyadic rather than a scalar. Moreover, since such 'wall effects' depend upon the position \mathbf{r} of the sphere centre relative to the bed particles, \mathbf{M} will generally be a function of position, in particular a spatially periodic function.

Computation of \mathbf{M} provides the key to the corresponding calculation of the tracer diffusivity \mathbf{D} appearing in the last term of (11.1). For these two dyadics are related through the Stokes-Einstein equation (Brenner & Gaydos 1977)

$$\mathbf{D} = \mathbf{M}/kT, \quad (11.6)$$

with k the Boltzmann constant and T the absolute temperature. Thus, the reasons that render \mathbf{M} spatially periodic are equally applicable to \mathbf{D} .

Applications to hydrodynamic chromatography

As opposed to partition or adsorption chromatography (see §10), hydrodynamic chromatography (Small 1974; Brenner & Gaydos 1977; Prieve & Hoysan 1978; Silebi & McHugh 1978, 1979; Giddings 1978) arises as a consequence of the finite size of the tracer particle. This fact is easily put in evidence by our theory. Suppose for simplicity that $\mathbf{F} = 0$ in (11.1). From Faxen's law (cf. the second footnote in this section) it follows that

$$\mathbf{U}' = \mathbf{v} + O[(a/l)^2]. \quad (11.7)$$

Thus, though the finite-size, neutrally buoyant particle and the fluid do not generally move together, they do in fact do so to terms of zero- and first-order in a/l . This makes possible the development of a simple theory of hydrodynamic chromatography in packed columns, which takes account of first-order particle-size effects, and thus illustrates the general principles. In a sense the analysis is similar to that of Brenner & Gaydos (1977) for the comparable capillary tube problem. (Among other things their analysis shows that, despite the inapplicability of (11.7) at points \mathbf{r} very near to the bed particle surfaces s , the error thereby introduced manifests itself only in terms of $O[(a/l)^2]$. These are supposed negligible compared with the first-order terms.)

Because the sphere centre cannot approach more closely than its radius a to any point on s , it is confined to some region $\mathbf{r}_0^{(e)} - \Delta$, say, lying wholly within the continuous phase. Here, Δ is some positive volume whose base is s and whose thickness is at least a . Whereas the points \mathbf{r} within the volume Δ are accessible to a fluid molecule, they are inaccessible to the sphere centre. From (11.7), (11.2) (with $\mathbf{F} = 0$) and (8.6*b*) we have that

$$\mathbf{J} = \mathbf{v}P - \mathbf{D} \cdot \nabla P + O[(a/l)^2] \quad (11.8)$$

for $\mathbf{r} \in \mathbf{r}_0^{(e)} - \Delta$. Further, $\mathbf{J} = 0$ for all other points, $\mathbf{r} \in \mathbf{r}_0^{(d)} + \Delta$, in \mathbf{r}_0 . Since $\nabla \cdot \mathbf{v} = 0$, the solution of the zero-order interstitial equations (8.6)–(8.8) in the region $\mathbf{r}_0^{(e)}$ is therefore

$$P = \begin{cases} 1/(\tau_e - \Delta) & \text{in } \mathbf{r}_0^{(e)} - \Delta, \\ 0 & \text{in } \Delta. \end{cases} \quad (11.9)$$

Hence, equation (8.10) gives for the mean tracer velocity,

$$\begin{aligned}\bar{\mathbf{U}}^* &= \frac{1}{\tau_c - \Delta} \int_{r_0^{(c)} - \Delta} \mathbf{v} \, d\mathbf{r} + O[(a/l)^2] \\ &\equiv \frac{1}{\tau_c - \Delta} \left[\int_{r_0^{(c)}} \mathbf{v} \, d\mathbf{r} - \int_{\Delta} \mathbf{v} \, d\mathbf{r} \right] + O[(a/l)^2].\end{aligned}\quad (11.10)$$

With the constant mean interstitial fluid velocity $\bar{\mathbf{v}}^*$ defined as in (9.15), $\bar{\mathbf{U}}^*$ may be written alternatively as

$$\bar{\mathbf{U}}^* = \bar{\mathbf{v}}^* + \frac{1}{\tau_c - \Delta} \int_{\Delta} (\bar{\mathbf{v}}^* - \mathbf{v}) \, d\mathbf{r} + O[(a/l)^2].\quad (11.11)$$

However, for sufficiently small a/l , $\Delta = O(Sa)$, with S defined in (7.29). Hence it is easily shown that

$$\frac{1}{\tau_c - \Delta} = \frac{1}{\tau_c} [1 + O(a/l)].$$

Since the integral in (11.11) is already of $O(a/l)$, to the order of the approximation, equation (11.11) can be replaced by

$$\bar{\mathbf{U}}^* = \bar{\mathbf{v}}^* + \frac{1}{\tau_c} \int_{\Delta} (\bar{\mathbf{v}}^* - \mathbf{v}) \, d\mathbf{r} + O[(a/l)^2].\quad (11.12)$$

In a mixture of non-interacting spheres of different radii a_i the excluded volumes Δ_i will differ for each species i . Since $\bar{\mathbf{v}}^*$, \mathbf{v} and τ_c are each independent of i , the preceding relation shows that each species will generally move with a different mean velocity $\bar{\mathbf{U}}_i^*$. This is the basis of hydrodynamic chromatography. Furthermore, since $\mathbf{v} = 0$ on s owing to the no-slip condition, the largest contributions to $\bar{\mathbf{v}}^*$ will generally come from those points in the fluid farthest from s ; hence equation (11.12) suggests that $|\bar{\mathbf{U}}^*| \geq |\bar{\mathbf{v}}^*|$ as in the comparable capillary tube problem (Brenner & Gaydos 1977), though we have not found a general proof of this. By this same reasoning, the larger the sphere radius a_i , the larger is $|\bar{\mathbf{U}}_i^*|$. These conclusions are consistent with experimental observations (Small 1974; Silebi & McHugh 1978, 1979), which show that all of the suspended colloidal particles move through the bed faster on average than does the fluid, and that the larger the particle the greater its mean speed, at least up to some fixed size, beyond which retarding 'wall effects' arising from the neglected $O[(a_i/l)^2]$ -terms ultimately begin to manifest themselves (Brenner & Gaydos 1977).

12. CHEMICAL REACTIONS IN THE CONTINUOUS PHASE

When the solute is confined exclusively to the continuous, interstitial fluid phase, and there decays by a first-order, irreversible, homogeneous, chemical reaction (e.g. radioactive decay), the fundamental equations (2.8) and (2.13) are replaced by

$$\partial P_r / \partial t + \nabla \cdot \mathbf{J}_r - \kappa P_r = \delta(\mathbf{R} - \mathbf{R}') \delta(t) \quad (12.1)$$

and

$$\mathbf{J}_r = \mathbf{U} P_r - \mathbf{D} \cdot \nabla P_r, \quad (12.2)$$

respectively. In these expressions P_r refers to, say, the number density of solute molecules, and \mathbf{J}_r to the corresponding solute flux. (The subscript r is used to refer to the 'reactive' cases; no subscript will be used for the non-reactive cases.) Moreover, $\kappa \geq 0$ is the reaction-velocity rate coefficient, assumed to be a constant, independent of \mathbf{R} and t .

The impenetrability of the discontinuous phase to the solute, coupled with the assumed absence of surface adsorption and transport at the fluid–particle interface, requires imposition of the no-flux boundary condition

$$\mathbf{v} \cdot \mathbf{J}_r = 0 \quad \text{on } s. \quad (12.3)$$

Upon introducing the dual transformations

$$(P_r, J_r) = e^{-\kappa t} (P, J) \quad (12.4)$$

into (12.1)–(12.3), it is easily demonstrated that (P, J) satisfy precisely the same equations (2.8) and (2.13) as in the non-reactive case, and that

$$\mathbf{v} \cdot \mathbf{J} = 0 \quad \text{on } s. \quad (12.5)$$

Define the mean values

$$(\bar{P}_r, \bar{J}_r) = \frac{1}{\tau_0} \int_{r_0^{(e)}} (P_r, J_r) dr \quad (12.6)$$

for the reactive case, and

$$(\bar{P}, \bar{J}) = \frac{1}{\tau_0} \int_{r_0^{(e)}} (P, J) dr \quad (12.7)$$

for the non-reactive case. It is demonstrated in §14 that for the non-reactive case \bar{P} and \bar{J} asymptotically satisfy the Darcy–scale equations

$$\partial \bar{P} / \partial t + \bar{\nabla} \cdot \bar{J} = \delta(\bar{\mathbf{R}} - \bar{\mathbf{R}}') \delta(t) \quad (12.8)$$

and

$$\bar{J} = \bar{\mathbf{U}}^* P - \bar{\mathbf{D}}^* \cdot \bar{\nabla} \bar{P}, \quad (12.9)$$

wherein $\bar{\nabla} \equiv \partial / \partial \bar{\mathbf{R}}$, with $\bar{\mathbf{R}}$ the continuum counterpart of the discrete variable \mathbf{R}_n . Since from (12.4), (12.6) and (12.7)

$$(\bar{P}, \bar{J}) = e^{\kappa t} (\bar{P}_r, \bar{J}_r), \quad (12.10)$$

it follows, upon substituting this equation in (12.8) and (12.9), that

$$\partial \bar{P}_r / \partial t + \bar{\nabla} \cdot \bar{J}_r - \kappa \bar{P}_r = \delta(\bar{\mathbf{R}} - \bar{\mathbf{R}}') \delta(t) \quad (12.11)$$

and

$$\bar{J}_r = \bar{\mathbf{U}}^* \bar{P}_r - \bar{\mathbf{D}}^* \cdot \bar{\nabla} \bar{P}_r. \quad (12.12)$$

It can be concluded, at least in the asymptotic sense of Taylor dispersion theory, that the reaction velocity constant κ has the same value on the Darcy scale as it has on the local scale, and that the Darcy-scale velocity $\bar{\mathbf{U}}^*$ and dispersivity $\bar{\mathbf{D}}^*$ are unaffected by the chemical reaction. This lack of coupling between transport and chemical reaction would not obtain if, for example, κ varied with position \mathbf{r} , or if transport and reaction occurred either on the bed particle surfaces s or in the particle interiors $r_0^{(d)}$, or if the chemical reaction was either reversible or a nonlinear function of P .

That, in present circumstances, the mean tracer velocity and dispersivity are unaffected by the chemical reaction is concordant with the comparable Taylor dispersion analysis for capillary tubes of Subramanian *et al.* (1974), who properly criticized the earlier incorrect conclusions of Gupta & Gupta (1972) on this score. The type of proof offered by Subramanian *et al.* is, however, considerably less transparent than that offered here, which simply transforms the reactive problem to a non-reactive one.

13. HEAT-TRANSFER PROCESSES IN PACKED BEDS

The prior development requires several minor modifications to be directly applied to heat-transfer problems. For, with $P \equiv T$ (temperature), the basic differential equation governing P is now (Bird *et al.* 1960)[†]

$$C \partial P / \partial t + \nabla \cdot \mathbf{J} = \delta(\mathbf{R} - \mathbf{R}') \delta(t), \quad (13.1)$$

rather than (2.8). Here \mathbf{J} is given by (2.13) with

$$\mathbf{U} = C\mathbf{v}. \quad (13.2)$$

In these expressions, $C(\mathbf{r})$, $\mathbf{D}(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$ are, respectively, the heat capacity per unit volume, thermal conductivity dyadic, and local fluid velocity, each of which is assumed to be spatially periodic.

As in §9, the fluid velocity \mathbf{v} is assumed to satisfy the incompressibility condition (9.1). It will also be assumed here for simplicity that the particles making up the porous medium are solid. This requires that

$$\mathbf{v} = 0 \quad \text{in} \quad \mathbf{r}_0^{(d)}, \quad (13.3)$$

as well as satisfaction of the boundary condition (9.12).

Surface-excess concepts do not normally arise in heat transfer problems, and it will be supposed that this is so here. Accordingly, the surface-excess probability density p and flux density \mathbf{j} on s may be put equal to zero. The continuity conditions across s will be assumed to be the usual thermal ones, namely – with Δ defined as in (2.12) –

$$\Delta P = 0 \quad (13.4)$$

and

$$\Delta(\mathbf{v} \cdot \mathbf{J}) = 0. \quad (13.5)$$

In view of (9.12) the latter requires that

$$\Delta(\mathbf{v} \cdot \mathbf{D} \cdot \nabla P) = 0. \quad (13.6)$$

In place of (2.15) the normalization condition is now

$$\int_{V_{\infty}} CP d\mathbf{R} = 1, \quad (13.7)$$

corresponding to overall conservation of the internal energy. This relation is consistent with (13.1), which corresponds to the introduction of an instantaneous unit source of heat (internal energy) into the system at the point \mathbf{R}' at $t = 0$. This energy is then transported by convection and conduction throughout the entire infinite system, but otherwise conserved in total amount since there is no heat flow across the ‘boundary’ ∂V_{∞} at infinity. (Proof of this consistency is

[†] Actually, the basic energy equation is (Bird *et al.* 1960)

$$\partial E / \partial t + \nabla \cdot (\mathbf{E}\mathbf{v} + \mathbf{q}) = \delta(\mathbf{R} - \mathbf{R}') \delta(t),$$

in which the constitutive equation for the heat flux is $\mathbf{q} = -\mathbf{D} \cdot \nabla P$. The internal energy E per unit volume is

$$E = \int C dP.$$

Strictly, this reduces to (13.1) only when $C = \text{const.}$ (and (9.1) holds). However, since the only specific applications we shall make involve situations in which C is piecewise constant in \mathbf{r}_0 (see (13.22)), equation (13.1) may be regarded as exact. The issue does not arise in the non-convective case $\mathbf{v} = 0$, for which (13.1) applies rigorously, even for non-piecewise constant values of $C(\mathbf{r})$.

readily constructed by using arguments similar to those used for the function Π defined in the paragraph following equation (2.18). That is, if Π is defined as being the left-hand member of (13.7), equation (13.1) then leads to the conclusion that $\Pi = 1$ for all $t > 0$, independently of the value of \mathbf{R}' .)

Define \mathbf{P}_m as in (3.1). In place of (3.2) one now obtains the sequence of local moment equations

$$C \partial \mathbf{P}_m / \partial t + \nabla \cdot \mathbf{J}_m = \delta_{m0} \delta(\mathbf{r} - \mathbf{r}') \delta(t), \quad (13.8)$$

with \mathbf{J}_m given by (3.4). Boundary conditions (3.9)–(3.11) on the cell faces $\partial \mathbf{r}_0$ continue to apply. The local moments satisfy the following interphase boundary conditions on s :

$$\Delta \mathbf{P}_m = 0 \quad \text{and} \quad \Delta(\mathbf{v} \cdot \mathbf{J}_m) = 0. \quad (13.9)$$

As regards the zero-order local moment, note that (3.12) is here replaced by

$$\int_{\mathbf{r}_0} C P_0 d\mathbf{r} = 1. \quad (13.10)$$

The total moments are now defined as

$$\mathbf{M}_m = \int_{\mathbf{r}_0} C \mathbf{P}_m d\mathbf{r}, \quad (13.11)$$

rather than (3.13). From (13.10) it follows immediately that

$$M_0 = 1. \quad (13.12)$$

The procedure from this point on is sufficiently similar to the analysis of §§3–5 for further details to be omitted. Accordingly only the results will be cited.

In the compact notation of §7 ($P_0^\infty \equiv P$, $\mathbf{J}_0^\infty \equiv \mathbf{J}$) the asymptotic zero-order local moment P is the solution of the differential equation

$$\nabla \cdot (\mathbf{D} \cdot \nabla P) - \mathbf{v} \cdot \nabla (CP) = 0, \quad (13.13)$$

satisfying the auxiliary conditions (13.4) and (13.6), the normalization condition

$$\int_{\mathbf{r}_0} CP d\mathbf{r} = 1, \quad (13.14)$$

and either

$$P \quad \text{is spatially periodic,} \quad (13.15)$$

or the jump boundary conditions (7.10) on $\partial \mathbf{r}_0$. Equation (13.13) derives from the differential equation $\nabla \cdot \mathbf{J} = 0$ (cf. (7.2)) in conjunction with (9.1), wherein

$$\mathbf{J} = CP\mathbf{v} - \mathbf{D} \cdot \nabla P. \quad (13.16)$$

The mean velocity $\bar{\mathbf{U}}^*$ ($\equiv \bar{\mathbf{U}}$) at which the internal energy is transported is defined by (5.1), and may be computed via the formula (cf. (7.11))

$$\bar{\mathbf{U}}^* = \int_{\mathbf{r}_0} \mathbf{J} d\mathbf{r}, \quad (13.17)$$

or its variant (7.12).

Assuming the zero-order asymptotic moments (P , \mathbf{J}) as well as $\bar{\mathbf{U}}^*$ to be now known, the dispersivity of the internal energy, defined by (5.2), may be calculated from the formula (cf. (7.18))

$$\bar{\mathbf{D}}^* = \int_{\mathbf{r}_0} P(\nabla B)^\dagger \cdot \mathbf{D}^s \cdot \nabla B d\mathbf{r}. \quad (13.18)$$

Here \mathbf{B} is the solution of the differential equation (cf. (7.13))

$$\nabla \cdot (P\mathbf{D} \cdot \nabla \mathbf{B}) - \mathbf{J} \cdot \nabla \mathbf{B} = CP\bar{\mathbf{U}}^*, \quad (13.19)$$

satisfying the auxiliary conditions on s ,

$$\Delta \mathbf{B} = 0 \quad \text{and} \quad \Delta(\mathbf{v} \cdot \mathbf{D} \cdot \nabla \mathbf{B}) = 0, \quad (13.20a, b)$$

as well as conditions (7.17) on the cell faces. Alternatively, one can solve instead for the spatially periodic field

$$\check{\mathbf{B}} = \mathbf{B} + \mathbf{r}, \quad (13.21)$$

for which field conditions (7.17) are automatically fulfilled.

Calculation of the zero-order asymptotic fields is particularly simple in the physically important case where

$$C = \begin{cases} C_c = \text{const.} & \text{in } \mathbf{r}_0^{(c)}, \\ C_d = \text{const.} & \text{in } \mathbf{r}_0^{(d)}. \end{cases} \quad (13.22)$$

The solution of (13.13) in the region $\mathbf{r}_0^{(c)} \oplus \mathbf{r}_0^{(d)}$ satisfying the cited subsidiary conditions for this case is

$$P = \text{const.} = 1/\bar{C}\tau_0, \quad (13.23)$$

whence

$$\mathbf{J} = C\mathbf{v}/\bar{C}\tau_0, \quad (13.24)$$

with $\mathbf{v} = 0$ in $\mathbf{r}_0^{(d)}$. Here,

$$\bar{C} = \frac{1}{\tau_0} \int_{\mathbf{r}_0} C d\mathbf{r} \quad (13.25)$$

is the mean, Darcy-scale, volumetric heat capacity.

The mean velocity $\bar{\mathbf{U}}^*$ appropriate to this special case can be obtained from (13.17), (13.24), (13.26) and (13.3) as

$$\bar{\mathbf{U}}^* = \{\epsilon C_c / [\epsilon C_c + (1 - \epsilon) C_d]\} \bar{\mathbf{v}}^*, \quad (13.26)$$

with ϵ the porosity, as in (7.28), and $\bar{\mathbf{v}}^*$ the mean interstitial fluid velocity, as in (9.15). Thus, the mean propagation velocity $\bar{\mathbf{U}}^*$ of a thermal disturbance is less than the mean interstitial fluid velocity, except when $C_d = 0$ or, more precisely, when $(1 - \epsilon) C_d / \epsilon C_c \rightarrow 0$. This conclusion accords with intuition as does equation (13.26) itself since, on the Darcy-scale, local thermodynamic equilibrium prevails between the continuous and discontinuous phases as a consequence of the interphase boundary condition (13.4) in conjunction with the fundamental assumption (4.17) underlying Taylor dispersion theory. In the present context, the latter is tantamount to the assumption of local thermal equilibrium on the \mathbf{r}_0 length scale (but not at the \mathbf{R}_n scale).

14. EULERIAN INTERPRETATION OF TAYLOR DISPERSION THEORY IN PERIODIC MEDIA

The coefficients $\bar{\mathbf{U}}^*$ and $\bar{\mathbf{D}}^*$, defined in equations (5.1) and (5.2) via the theory of Brownian movement (cf. the Appendix), possess a clear physical Lagrangian interpretation in terms of the 'history' of conserved quantities such as mass and energy. In this section these coefficients will be given a more traditional Eulerian interpretation (see also §7) as phenomenological coefficients appearing in the expression for the Darcy-scale flux vector $\bar{\mathbf{J}}$ relative to a stationary observer fixed in the porous medium. Attention will be confined to mass-transport phenomena. The results of the closely related heat-transfer analysis will be cited at the end.

Assuming the spatially periodic coefficients \mathbf{U} , \mathbf{D} , \mathbf{K} and \mathbf{u} , \mathbf{d} , \mathbf{k} to be known functions of

\mathbf{r} , one can in principle solve the system of equations (2.8)–(2.18) and (2.23)–(2.24) for the original probability densities, $P(\mathbf{R}, t | \mathbf{R}') \equiv P(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}')$ and $p(\mathbf{R}, t | \mathbf{R}') \equiv p(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}')$, at each and every point $\mathbf{R} \equiv (\mathbf{R}_n, \mathbf{r})$ in the system. In applications, however, one is rarely interested in such detailed information. Rather, interest normally centres on the less detailed mean probability density \bar{P} , defined at a point $\bar{\mathbf{R}}$ on the length scale of the Darcy continuum. This *continuous* Darcy-scale probability density is closely related to the *discrete* quantity \bar{P} defined by the relation

$$\tau_0 \bar{P}(\mathbf{R}_n - \mathbf{R}'_n, t | \mathbf{r}') = \int_{\mathbf{r}_0\{\mathbf{n}\}} P(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}') d\mathbf{r} + \int_{s\{\mathbf{n}\}} p(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}') ds \quad (14.1)$$

on the entire contents of a single unit cell $\mathbf{r}_0\{\mathbf{n}\}$. The remarks made at the beginning of this paragraph show that this \bar{P} is, in principle, calculable. This discrete quantity varies discontinuously from one unit cell to the next. For definiteness, as well as for the purpose of ultimately rationalizing the ‘smoothing’ or ‘homogenization’ process to be described, one can imagine that the discrete \bar{P} value calculated via (14.1) is arbitrarily assigned to the centre, \mathbf{R}_n , say, of the unit cell $\mathbf{r}_0\{\mathbf{n}\}$ over which it is calculated.

By exchanging the order of summation over \mathbf{n} with integration over a unit cell in the definitions (3.13) and (3.1) of the total moments \mathbf{M}_m , one obtains

$$\mathbf{M}_m(t | \mathbf{r}') = \tau_0 \sum_{\mathbf{n}} (\mathbf{R}_n - \mathbf{R}'_n)^m \bar{P}(\mathbf{R}_n - \mathbf{R}'_n, t | \mathbf{r}'). \quad (14.2)$$

For the reasons outlined earlier, these total moments are, in principle, calculable quantities for each m . After a long period of time, defined by (4.17), the Brownian particle will have sampled all local positions $\mathbf{r} \in \mathbf{r}_0$ (not necessarily within the *same* unit cell) many times, and thus will have essentially achieved a steady or equilibrium state with regard to the local \mathbf{r} -space transport. As a consequence, for the large values of t defined by (4.17), the influence of the original local position \mathbf{r}' upon the value of $\mathbf{M}_m(t | \mathbf{r}')$ will monotonically diminish. That is, for each m , and for sufficiently long times, the dominant terms in the asymptotic expansion of \mathbf{M}_m will depend only upon t , but not upon \mathbf{r}' . Denote these dominant terms by $\mathbf{M}_m(t)$. Again, in principle, these quantities are calculable. Indeed, from the analysis of §§3 and 4, the first few of these terms are, explicitly,

$$\mathbf{M}_0(t) = 1, \quad (14.3a)$$

$$\mathbf{M}_1(t) = \bar{\mathbf{U}}^* t \quad (14.3b)$$

and

$$\mathbf{M}_2(t) = \bar{\mathbf{U}}^* \bar{\mathbf{U}}^* t^2 + 2\bar{\mathbf{D}}^* t, \quad (14.3c)$$

in which for simplicity we have set the arbitrary constant $\bar{\mathbf{B}} = 0$ in (14.3c).

The asymptotic-moment sequence $\mathbf{M}_m(t)$ obtained in this way may be used to define a *continuous* probability density function,

$$\bar{P} \equiv \bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t) \quad (14.4)$$

(with $\bar{\mathbf{R}}'$ fixed), such that

$$\mathbf{M}_m(t) = \int_{V_{\infty}} (\bar{\mathbf{R}} - \bar{\mathbf{R}}')^m \bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t) d\bar{\mathbf{R}}, \quad (14.5)$$

in which $\bar{\mathbf{R}}$ is a continuous variable, defined in the range $0 \leq |\bar{\mathbf{R}}| < \infty$. It will be assumed that the integrand of (14.5) vanishes sufficiently rapidly as $|\bar{\mathbf{R}} - \bar{\mathbf{R}}'| \rightarrow \infty$ to insure convergence for each m . In (14.5) we are using a well known uniqueness theorem (Cramér 1951; Kendall

1952; Korn & Korn 1968) that, under appropriately defined circumstances, the moments $M_m(t)$ of a distribution function \bar{P} serve to define uniquely the distribution function itself. It will be assumed on physical grounds that these conditions are met here. Thus, knowledge of all the $M_m(t)$ serves to determine $\bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t)$ uniquely.

It will now be demonstrated that this continuous probability density function satisfies the differential equation

$$\partial \bar{P} / \partial t + \bar{\nabla} \cdot \bar{\mathbf{J}} = \delta(\bar{\mathbf{R}} - \bar{\mathbf{R}}') \delta(t), \quad (14.6)$$

in which $\bar{\nabla} \equiv \partial / \partial \bar{\mathbf{R}}$, and

$$\bar{\mathbf{J}} = \bar{\mathbf{U}}^* \bar{P} - \bar{\mathbf{D}}^* \cdot \bar{\nabla} \bar{P}, \quad (14.7)$$

where $\bar{\mathbf{U}}^*$ and $\bar{\mathbf{D}}^*$ are the constants defined by (5.1) and (5.2), and given explicitly in the analysis of §5 *et seq.* The proof consists of showing that the moments (14.5) of the solution of this differential equation do indeed possess the values indicated in (14.3) *et seq.* This can be done either by time differentiation of (14.5) and subsequent integration by parts, or explicitly by observing that the solution of (14.6), (14.7) satisfying the condition that the integrand of (14.5) vanish sufficiently rapidly as $|\bar{\mathbf{R}} - \bar{\mathbf{R}}'| \rightarrow \infty$ is

$$\bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t) = (4\pi t)^{-\frac{3}{2}} (\det \bar{\mathbf{D}}^*)^{-\frac{1}{2}} \exp [- (\bar{\mathbf{R}} - \bar{\mathbf{R}}' - \bar{\mathbf{U}}^* t) \cdot \bar{\mathbf{D}}^{*-1} \cdot (\bar{\mathbf{R}} - \bar{\mathbf{R}}' - \bar{\mathbf{U}}^* t) / 4t]. \quad (14.8)$$

Here, $\det \bar{\mathbf{D}}^*$ and $\bar{\mathbf{D}}^{*-1}$ are, respectively, the determinant and inverse of the dyadic $\bar{\mathbf{D}}^*$. While either of these two procedures only demonstrates that the moment matching is achieved for $m = 0, 1$ and 2 , it can be shown (Dill 1982) that the moment matching is also achieved for $m > 2$, at least asymptotically for sufficiently large values of t satisfying (4.17).

For times t satisfying (4.17), the continuous Darcy-scale field $\bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t)$ is expected to approximate closely the discrete field $\bar{P}(\mathbf{R}_n - \mathbf{R}'_n, t | \mathbf{r}')$ in circumstances where

$$\bar{\mathbf{R}} - \bar{\mathbf{R}}' = \mathbf{R}_n - \mathbf{R}'_n + O(l), \quad (14.9)$$

with l a characteristic cell size, e.g. the cube root of the superficial volume τ_0 . This asymptotic equivalence is not, however, likely to be uniformly valid in space; rather, it may be expected to apply only when

$$|\mathbf{R}_n - \mathbf{R}'_n| \gg l. \quad (14.10)$$

That is, asymptotic equivalence of the two \bar{P} s is to be expected only when the cell \mathbf{R}_n being examined is far removed from the cell \mathbf{R}'_n into which the Brownian particle was originally placed. For in such circumstances $\bar{P}(\mathbf{R}_n - \mathbf{R}'_n, t | \mathbf{r}')$ is expected to be insensitive to the precise *local* initial position \mathbf{r}' of the particle within cell \mathbf{R}'_n . At the same time, when (14.10) is satisfied, the variation of the discrete function $\bar{P}(\mathbf{R}_n - \mathbf{R}'_n, t | \mathbf{r}')$ from cell \mathbf{R}_n to a neighbouring cell is likely to be sufficiently small to be representable by the *continuous* function $\bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t)$. Thus it is to be expected that the fractional difference between the continuous and discrete distributions,

$$[\bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t) - \bar{P}(\bar{\mathbf{R}}_n - \bar{\mathbf{R}}'_n, t | \mathbf{r}')] / \bar{P}(\bar{\mathbf{R}} - \bar{\mathbf{R}}', t), \quad (14.11)$$

tends to zero when conditions (4.17) and (14.10) are both satisfied, though not uniformly in $\bar{\mathbf{R}} - \bar{\mathbf{R}}'$ and t . We shall not attempt a formal proof of this fact, though several specific examples (Dill 1982; Brenner & Adler 1983) have been constructed that confirm this conclusion.

In the light of the asymptotic equivalence between the continuous and the discrete versions of \bar{P} , equation (14.6) can be given an interesting interpretation. From equations (14.1), (2.8) and (2.9) one obtains *exactly* for the discrete \bar{P} ,

$$\frac{\partial \bar{P}}{\partial t} + \frac{1}{\tau_0} \int_{\partial \mathbf{r}_0\{\mathbf{n}\}} d\mathbf{s} \cdot \mathbf{J} = \frac{1}{\tau_0} \delta_{mm} \delta(t), \quad (14.12)$$

where $\delta_{nn'}$ is the Kronecker- δ defined in (2.22). Comparison with the corresponding continuous differential equation (14.6) for long times ($\delta(t) = 0$) or situations for which (14.10) is satisfied ($\delta_{nn'} = 0$) reveals that, to the extent that the two \bar{P} 's are asymptotically equal,

$$\bar{\nabla} \cdot \bar{\mathbf{J}} \simeq \frac{1}{\tau_0} \int_{\partial r_0\{\mathbf{n}\}} d\mathbf{s} \cdot \mathbf{J}. \quad (14.13)$$

This formula is consistent with the physical nature of the integral on the right-hand side, representing the net efflux of probability through the faces of the unit cell, which constitutes a differential volume element $d\bar{\mathbf{R}} \equiv \tau_0$ at the Darcy scale (Brenner & Adler 1983). For the fundamental definition (Brand 1957; Moon & Spencer 1965)† of the divergence of a continuous vector field at a point $\bar{\mathbf{R}}$ is such that $\bar{\nabla} \cdot \bar{\mathbf{J}}$ represents the net efflux per unit volume at the point.

Finally, we note that in the heat transfer case discussed in §13, equations (14.6) and (14.7) are replaced by

$$\bar{C} \partial \bar{P} / \partial t + \bar{\nabla} \cdot \bar{\mathbf{J}} = \delta(\bar{\mathbf{R}} - \bar{\mathbf{R}}') \delta(t), \quad (14.14)$$

where

$$\bar{\mathbf{J}} = \bar{\mathbf{U}}^* \bar{C} \bar{P} - \bar{\mathbf{D}}^* \cdot \bar{\nabla} \bar{P}, \quad (14.15)$$

in which \bar{P} is the mean temperature on the Darcy scale, whose discrete counterpart is defined as

$$\bar{C} \bar{P} = \frac{1}{\tau_0} \int_{r_0\{\mathbf{n}\}} C P d\mathbf{r}, \quad (14.16)$$

analogous to (14.1). With equations (14.14), (14.15) combined and expressed in the usual form (Bird *et al.* 1960), one obtains the Darcy-scale energy equation,

$$\partial \bar{P} / \partial t + \bar{\mathbf{U}}^* \cdot \bar{\nabla} \bar{P} = \bar{\boldsymbol{\alpha}}^* : \bar{\nabla} \bar{\nabla} \bar{P} + \delta(\bar{\mathbf{R}} - \bar{\mathbf{R}}') \delta(t), \quad (14.17)$$

in which the 'thermal dispersivity' dyadic is found to be

$$\bar{\boldsymbol{\alpha}}^* = \bar{\mathbf{D}}^* / \bar{C}, \quad (14.18)$$

with $\bar{\mathbf{D}}^*$ the thermal conductivity dyadic.

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APPENDIX. DERIVATION OF EQUATIONS (5.1) AND (5.2)

At any instant t the 'centre of probability' is situated at the point whose position vector $\mathbf{R}^* \equiv \mathbf{R}^*(t | \mathbf{R}')$ is defined as

$$\mathbf{R}^* = \int_{V_{\infty}} \mathbf{R} P d\mathbf{R} + \int_{s_{\infty}} \mathbf{R} p d\mathbf{s}. \quad (\text{A } 1)$$

Here, P and p are the volumetric and surface probability densities defined in §2. In an ergodic or ensemble sense \mathbf{R}^* also represents the expected or mean value of the position vector of the tracer at time t , given that it was at \mathbf{R}' at $t = 0$. In view of (2.15), the mean displacement of the particle from its original position is thus

$$\mathbf{R}^* - \mathbf{R}' = \int_{V_{\infty}} (\mathbf{R} - \mathbf{R}') P d\mathbf{R} + \int_{s_{\infty}} (\mathbf{R} - \mathbf{R}') p d\mathbf{s}.$$

† Explicitly,

$$\bar{\nabla} \cdot \bar{\mathbf{J}} \stackrel{\text{def.}}{=} \lim_{\epsilon \rightarrow 0} \frac{1}{\bar{V}_{\epsilon}} \int_{\bar{s}_{\epsilon}} d\bar{\mathbf{s}} \cdot \bar{\mathbf{J}},$$

where \bar{V}_{ϵ} is a small volume surrounding the point $\bar{\mathbf{R}}$, and \bar{s}_{ϵ} is the surface bounding this volume externally.

Equation (2.4), applied to both the unprimed and primed variables, in conjunction with (2.5) and (2.7), thereby yields

$$\mathbf{R}^* - \mathbf{R}' = \int_{r_0} [\sum_n (\mathbf{R}_n - \mathbf{R}'_n) P + (\mathbf{r} - \mathbf{r}') \sum_n P] d\mathbf{r} + \int_s [\sum_n (\mathbf{R}_n - \mathbf{R}'_n) p + (\mathbf{r} - \mathbf{r}') \sum_n p] ds.$$

Equation (3.1) with $m = 0$ or 1 permits this to be rewritten as

$$\mathbf{R}^* - \mathbf{R}' = \int_{r_0} \mathbf{P}_1 d\mathbf{r} + \int_s \mathbf{p}_1 ds + \int_{r_0} (\mathbf{r} - \mathbf{r}') P_0 d\mathbf{r} + \int_s (\mathbf{r} - \mathbf{r}') p_0 ds.$$

From the definitions (3.13) of \mathbf{M}_1 and M_0 , and (3.14), the preceding equation adopts the form

$$\mathbf{R}^* - \mathbf{R}' = \mathbf{M}_1 + \mathbf{r}^* - \mathbf{r}', \quad (\text{A } 2)$$

where $\mathbf{r}^*(t | \mathbf{r}')$ is defined as

$$\mathbf{r}^* = \int_{r_0} \mathbf{r} P_0 d\mathbf{r} + \int_s \mathbf{r} p_0 ds. \quad (\text{A } 3)$$

The fundamental definition of mean velocity as displacement divided by elapsed time leads to the following definition of the mean tracer velocity:

$$\bar{\mathbf{U}}^* = \lim_{t \rightarrow \infty} (\mathbf{R}^* - \mathbf{R}')/t. \quad (\text{A } 4)$$

As will now be shown, this vector tends to a constant, which is independent of \mathbf{R}' .

Introduce the expansions (4.16) into (A 3) to obtain, as $t \rightarrow \infty$,

$$\mathbf{r}^* \simeq \boldsymbol{\gamma} + \text{Exp}, \quad (\text{A } 5)$$

with

$$\boldsymbol{\gamma} = \int_{r_0} \mathbf{r} P_0^\infty(\mathbf{r}) d\mathbf{r} + \int_s \mathbf{r} p_0^\infty(\mathbf{r}) ds$$

a time-independent constant vector. This asymptotic expansion in conjunction with the time-independent nature of the constant \mathbf{r}' appearing in (A 2) shows that

$$\bar{\mathbf{U}}^* = \lim_{t \rightarrow \infty} \mathbf{M}_1/t. \quad (\text{A } 6)$$

Finally, the general asymptotic expansion of \mathbf{M}_1 in (4.41) (with $\bar{\mathbf{U}}$ a time-independent constant, whose value may be zero in some circumstances) shows that an equivalent formulation of (A 6) is that cited in (5.1).

A similar approach may be used to obtain the dispersivity dyadic $\bar{\mathbf{D}}^*$ via Brownian motion theory by generalizing the arguments of I to include surface transport. We omit details, but the counterpart of (A 6) obtained in this manner is

$$\bar{\mathbf{D}}^* = \frac{1}{2} \lim_{t \rightarrow \infty} (\mathbf{M}_2 - \mathbf{M}_1 \mathbf{M}_1)/t.$$

The asymptotic forms of \mathbf{M}_1 and \mathbf{M}_2 in (4.41) and (the integrated form of) (4.67) are such that this equation may be replaced by the equivalent form (5.2).

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