

# Charge Transport through a Spatially Periodic Porous Medium: Electrokinetic and Convective Dispersion Phenomena

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# Charge transport through a spatially periodic porous medium: electrokinetic and convective dispersion phenomena

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A general theory is outlined for the transport of charge and the convective dispersion of charged species through a spatially periodic porous medium under the influence of a homogeneous, Darcy-scale electric field  $\bar{\mathbf{E}}$ , as well as a homogeneous applied pressure-gradient field  $\bar{\nabla}p$ . The particulate surfaces of the porous medium are characterized as possessing a non-uniform surface charge, with thin, Helmholtz double layers bordering the charged surfaces in the interstitial fluid phase. The theory uses a straightforward application of macrotransport theory, as well as standard methods of analysis of transport phenomena in spatially periodic systems, to derive, first, general expressions for the following four Darcy-scale, electromechanical-transduction property dyadics: (i) the effective electrical conductivity  $\bar{\sigma}$ ; (ii) the hydraulic permeability  $\bar{\mathbf{K}}$ ; (iii) the 'streaming potential' coupling dyadic  $\bar{\mathbf{K}}_P^c$ ; and (iv) the 'electroosmotic' coupling dyadic  $\bar{\mathbf{K}}_E^c$ . General formulas for these gross-scale, phenomenological coefficients are provided in terms of four spatially periodic, microscale dyadic fields ( $\nabla\mathbf{g}$ ,  $\nabla\mathbf{h}$ ,  $\mathbf{V}$ ,  $\mathbf{V}^E$ ). Unit-cell, boundary-value problems are derived for determining these latter dyadics as functions of the microscale geometrical and physicochemical nature of the porous material. In addition, formulas for computing the mean velocity  $\bar{\mathbf{U}}^*$  and dispersivity  $\bar{\mathbf{D}}^*$  of a charged, convecting and diffusing Brownian particle (or cluster of particles) are presented. Two explicit examples are offered to illustrate the implementation of the theory. In the first example, a charged, pointsize, Brownian particle is imagined as convecting and diffusing within a porous medium composed of parallel, charged, rectilinear plates between which a Newtonian fluid flows and an electric field is applied. In the second example, leading-order expressions are derived for the electrokinetic transductive properties ( $\bar{\sigma}$ ,  $\bar{\mathbf{K}}$ ,  $\bar{\mathbf{K}}_P^c$ ,  $\bar{\mathbf{K}}_E^c$ ) of a highly porous two-dimensional array of charged circular cylinders through which a Newtonian fluid flows. These leading-order results are found to be in agreement with results appearing in the literature.

## Notation

### *Latin letters*

$a$	spherical solute radius	equation (5.7b)
$\mathbf{B}$	vector field related to effective diffusivity	(5.15)
$\bar{\mathbf{B}}$	periodic $\mathbf{B}$ -field vector	(5.22)

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$C$	solute concentration field	(5.6)
$C_0$	initial solute concentration	(5.6)
$\bar{C}$	mean solute concentration	(2.9)
$D$	Brownian diffusivity dyadic	(5.2)
$d\bar{p}/dx$	scalar pressure gradient	(6.2)
$ds$	outwardly directed surface area element	(3.18c)
$dV$	differential volume element	(3.18b)
$\bar{D}^*$	effective solute dispersivity dyadic	(5.15)
$E$	local electric field vector	(3.4)
$\bar{E}$	Darcy-scale electric field	(3.18)
$g$	vector field related to electric potential	(3.38)
$\tilde{g}$	periodic $g$ -field	(3.38)
$h$	vector field related to electric potential	(3.38)
$H$	local magnetic field intensity vector	(3.6a)
$\bar{H}$	Darcy-scale magnetic field intensity vector	(3.29)
$I_s$	surface idemfactor	(3.13)
$J$	solute flux vector	(5.2)
$J_u$	current flux vector	(3.6b)
$J_u^s$	surface current flux vector	(3.2)
$J_u^{sE}$	surface current flux vector (electric-field-driven)	(3.2)
$J_u^{sp}$	surface current flux vector (pressure-gradient-driven)	(3.3c)
$J_0^\infty$	flux of cellular probability	(5.16)
$\bar{J}_u$	Darcy-scale current flux vector	(3.39b)
$k$	Boltzmann constant	(5.7b)
$\bar{K}$	Darcy-scale hydraulic permeability dyadic	(4.20)
$\bar{K}_E^c$	Darcy-scale electroosmotic permeability dyadic	(4.21)
$\bar{K}_p$	Darcy-scale streaming-potential conductivity dyadic	(3.40b)
$\{l_i\}$	set of basic lattice vectors	(2.5)
$M$	hydrodynamic mobility dyadic	(5.8b)
$M_E$	electrophoretic mobility dyadic	(5.2)
$n$	outwardly directed surface normal vector	(3.3d)
$\{n\}$	$n$ th lattice point	(2.4)
$P$	conditional probability density	(5.1)
$p$	local fluid pressure	(4.1)
$\tilde{p}$	periodic pressure field	(4.6)
$P_0^\infty$	cellular probability	(5.15)
$\bar{P}$	mean conditional probability density	(5.10)
$R$	position vector	(2.3)
$r$	local cellular position vector	(2.3)
$R_n$	discrete lattice-point position vector	(2.5)
$\bar{R}$	Darcy-scale position vector	(3.21b)
$R_u^s$	vector field related to surface charge	(3.43)
$\bar{R}'$	initial, Darcy-scale position vector	(2.10)
$s_p$	particle-phase surface	(3.2)
$T$	temperature	(5.7b)
$t$	time	(3.6a)
$\bar{U}^*$	mean solute velocity vector	(5.16)
$V$	dyadic field related to fluid velocity vector	(4.11)
$v$	local fluid velocity vector	(4.1)
$V^E$	dyadic field related to fluid velocity vector	(4.11)
$V_f$	total volume of interstitial fluid	(2.1)
$V_o$	total volume of medium	(2.1)
$V_p$	total volume of particulate phase	(2.1)
$V_s$	surface dyadic field	(3.3d)
$v_s$	surface velocity vector	(3.3b)
$\bar{v}$	Darcy-scale seepage velocity	(4.4)

## Greek letters

$\delta$	Dirac delta function	(5.1)
$\epsilon$	porosity	(2.2)
$\varepsilon$	permittivity	(3.6a)
$\epsilon$	alternator triadic	(3.31)
$\varepsilon_f, \varepsilon_p$	permittivity constants of fluid and particulate phases	(3.6a)
$1/\kappa$	Debye screening length	(3.1b, c)
$\mu_f$	fluid-phase viscosity	(2.13)
$\rho_u^s$	surface-excess charge density	(3.1a)
$\rho_p^s$	surface excess charge of particulate surface	(3.1b)
$\rho_p^d$	surface excess double-layer charge	(3.1c)
$\phi$	solid volume fraction	(7.2)
	(also used to designate solid angle in (7.4))	
$\zeta$	zeta potential of charged particulate surface	(3.3b)
$\tau_o$	total cellular volume	(2.6)
$\tau_p$	particulate-phase cellular volume	(2.6)
$\tau_f$	fluid-phase cellular volume	(2.6)
$\partial\tau_o$	bounding cell surface	(3.45d)
$\bar{\sigma}$	effective electrical conductivity dyadic	(3.40a)
$\Phi$	voltage potential	(3.7)
$\tilde{\Phi}$	periodic voltage potential	(3.17)
$\Pi$	vector field related to pressure	(4.12)
$\Pi^E$	vector field related to pressure	(4.12)
$\bar{\nabla}$	Darcy scale gradient operator	(3.21a)
$\bar{\nabla}\bar{p}$	Darcy scale pressure gradient	(4.7)
$\nabla_s$	surface gradient operator	(3.13)

## 1. Introduction

Electrokinetic transductive and charge-mediated convective–dispersion phenomena potentially arise in biological and synthetic membranes, underground soils, and other porous materials when exposed to external stimuli such as contact stresses, concentration gradients, electrical and/or magnetic fields. The microscale origin of coarse- (i.e. Darcy-) scale electrokinetic phenomena in charged, or sometimes non-charged, porous materials is typically associated with electromechanical forces acting within an interstitial fluid phase. These forces engender motion of unpaired charges (gathered in the form of diffuse double layers about charged surfaces within the porous material) or of charged, suspended colloidal particles, resulting in transport fluxes of an electroosmotic, electrophoretic, streaming current, and/or fluid mass nature.

A prime example of this microscale→macroscale, electromechanical transduction exchange concerns the function (Gross & Williams 1982; Grodzinsky 1983; Salzstein *et al.* 1987) and characterization (Hoch *et al.* 1983; Frank *et al.* 1987) of connective living tissues. Tendons, cartilage, epithelial membranes – along with numerous other types of connective tissues – are comprised of one of a few basic types of cells enclosed within an extracellular matrix (ECM) typically constructed of collagen and elastin fibrils, as well as of proteoglycans and their constituent, ionized, glycosaminoglycans (GAGs) (Hay 1981). The charged ECM is itself bathed within an aqueous, ion-containing fluid that occupies 70–80% (by weight) of the connective tissue. Electrostatic and electrokinetic phenomena are commonplace in connective tissues. For example, convective/diffusive transport of macromolecules across the kidney's glomerular basement membrane, is understood (Chang *et al.* 1975) to be mediated by charge groups in the membrane; likewise, bacteria are known (Ham

1974) to be prevented from their transport through connective tissues before the secretion of an enzyme capable of depolymerizing GAG protein molecules. The stress-strain behaviour of articular cartilage, on the other hand, which functions within synovial joints as a bearing material, is significantly influenced by electromechanical transduction phenomena (Grodzinsky 1983).

Electrokinetic phenomena in porous media also arise in the removal of contaminants from soils by the application of a direct-current electric field (Probstein & Hicks 1993; Shapiro & Probstein 1993). Owing to the intrinsic surface charge of soil particles, fluid motion within the interstices of the soil may be established and controlled by application of an electric field via electroosmosis. Contaminants may be carried to cathode wells for removal by electroosmotic motion of the interstitial fluid, as well as by electromigration or electrophoretic mechanisms.

Other examples of applied electrokinetic transduction and charge-mediated convective-dispersion phenomena in porous media include electrophoretic separations (Saville & Palusinski 1986), iontophoretic transport of drugs across mammalian skin (Edwards & Langer 1994), and geological exploration (Frankel 1944).

Whereas microscale theories of electrokinetic phenomena in porous media have been the subject of recent articles (e.g. Eisenberg & Grodzinsky 1988; Shapiro *et al.* 1989), a rigorous, microscale→macroscale theoretical understanding of electromechanical transduction and convective-dispersion processes of the type described above has yet to be achieved. It is the purpose of the present article to establish the groundwork for such a theory†.

At the same time, a large amount of theoretical research concerned with spatially periodic porous media has focused in the past on the calculation of *hydraulic permeability* (Hasimoto 1959; Snyder & Stewart 1974; Whitaker 1969; Sorensen & Stewart 1974; Dullien 1975; Neira & Payatakes 1979; Sangani & Acrivos 1982; Zick & Homsy 1982; Adler & Brenner 1984; Drummond & Tahir 1984; Lahbabi & Chang 1985; Larson & Higdon 1986; Edwards *et al.* 1990), electrical conductivity (or diffusivity) (Meredith & Tobias 1960; Keller 1963; Jackson & Coriell 1968; Zuzovsky & Brenner 1977; McKenzie *et al.* 1978; McPhedran & McKenzie 1978; Bergman 1979; Perrins *et al.* 1979; Vogelius & Papanicolaou 1982; Chang 1983; Sangani & Acrivos 1983; Zick 1983; Zwanzig 1983; Carbonell & Whitaker 1983; Weaver 1984; Lehner 1986; Smith 1986; Gautesen 1988; Edwards & Davis 1995), and convective-dispersive properties (Lee 1979; Brenner 1980; Auriault & Strzelecki 1981; Ryan *et al.* 1981; Ene & Sanchez-Palencia 1982; Brenner & Adler 1982; Carbonell & Whitaker 1983; Dill & Brenner 1983; Eidsath *et al.* 1983; Hoagland & Prud'homme 1985; Rubinstein & Mauri 1986; Koch *et al.* 1989; Shapiro & Brenner 1988; Edwards *et al.* 1991*b*, 1993). In the limiting circumstance of a non-charged porous medium through which convects and diffuses a non-charged Brownian particle, the theoretical results of this

† Theories of spatial averaging in non-periodic systems, such as those that entail ensemble averaging (Koch & Brady 1985) or volume averaging (Whitaker 1966), provide an alternative approach to that which is pursued herein for periodic media. The principle advantage of the periodic hypothesis (which hypothesis may, of course, be virtually removed upon identifying the contents of a unit cell with a large degree of randomness (Adler 1992)), lies in affording rigorous averaging principles that may be used to ensure that derived, dynamic macroscale coefficients possess both an Eulerian and Lagrangian interpretation. Ensuring this physical duality is crucial in complex heterogeneous systems, such as those involving microscale reaction, as confusion may arise in regards to the precise definition of macroscale variables (see Edwards *et al.* 1993). (See ch. 9 of Rosensweig (1985) for a volume averaging approach to magnetized, fluid-solid media.)

paper coincide with the past works of Hasimoto (1959), Sangani & Acrivos (1982), Zick & Homsy (1982), Adler & Brenner (1984) and Edwards *et al.* (1990) in regards to hydraulic permeability; of Zuzovsky & Brenner (1977), Sangani & Acrivos (1983), Edwards & Davis (1995) in regards to electrical conductivity; and of Brenner (1980), Brenner & Adler (1982) and Edwards *et al.* (1991*b*) in regards to convective dispersive properties.

Our focus herein is on a model porous medium comprised of a spatially periodic (though arbitrarily complex, potentially disordered at a local scale), space-fixed porous matrix exhibiting a generally inhomogeneous surface charge. In the interstitial space there is presumed to flow a Newtonian liquid which contains various ionic constituents. Whereas electroneutrality is assumed throughout the bulk of the interstitial fluid, very near to the charged surfaces of the medium diffuse electrochemical double layers exist wherein significant, highly inhomogeneous charge distributions prevail. (The assumption of thin Helmholtz double layers greatly simplifies the analysis by allowing the incorporation of (nonlinear) Maxwell stress effects into particle-surface boundary conditions that are of a mathematically linear nature. This simplification, however, somewhat limits the applicability of the theory (e.g. charge groups within the extracellular matrix of cartilage are separated by approximately 1 nm, effectively the thickness of electrical double layers). As discussed at the conclusion of this paper, it is hoped in future contributions to extend the theory to double layers of finite thickness.) Additional details of the system characterization are provided in §2. This is followed by a statement of the overall objectives of the paper. In §3 a scheme is outlined for calculating the microscale electric field given knowledge of the applied macroscale electric and pressure-gradient fields as well as of the microlevel nature of the system. General formulas are developed for the effective conductivity dyadic and streaming-potential coupling dyadic of the medium. In §4, a scheme for calculating the microscale velocity field is proposed. From this we obtain formulas for determining the hydraulic permeability of the medium, as well as the medium's electroosmotic permeability. The micro- and macroscale level convective dispersion descriptions are outlined in §5. Explicit examples of the theory are provided in §§6 and 7, and we conclude with a recapitulation and discussion of the principal theoretical conclusions of the paper in §8.

## 2. Geometry and basic physical description

A charged Brownian entity<sup>†</sup>, potentially comprised of a flexible cluster of hydrodynamically interacting, separately rigid, charged, non-conducting Brownian particles, each generally of non-spherical shape and joined together by internal potentials (figure 1), is introduced into the interstices of a spatially periodic porous medium (figure 2). The characteristic linear dimension  $a$  of the Brownian cluster is presumed to be far smaller than that ( $l$ ) characterizing the porous medium microstructure. The porous medium is composed of a discontinuous solid (or particulate) phase of total volume  $V_p$ , and a continuous fluid phase of total volume  $V_f$ . The overall volume of the medium is

$$V_o = V_f + V_p, \quad (2.1)$$

<sup>†</sup> Whereas explicit attention is given in this article to the transport of charged colloidal particles, the general paradigms developed herein are equally applicable to the transport of ionic species. This application follows upon interpreting the electrophoretic mobility dyadic  $\mathbf{M}_E$  as the ionic mobility dyadic (see Edwards & Langer (1994), where this latter interpretation is made).

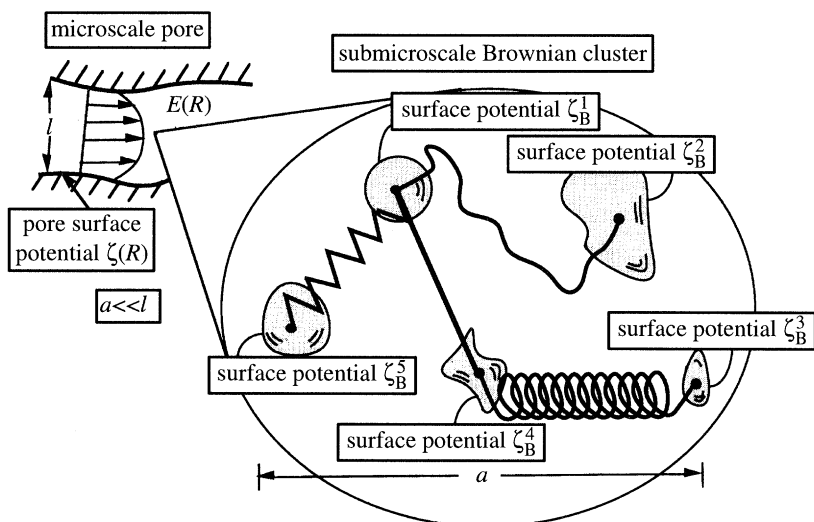


Figure 1. A flexible Brownian cluster, comprised of separately rigid, charged, Brownian particles joined together by conservative potentials, convects and diffuses through the interstices of a porous medium. The characteristic size  $a$  of the cluster is much smaller than the characteristic pore size  $l$ , with the consequence that the cluster effectively convects with the velocity  $\mathbf{v}(\mathbf{R})$  at the interstitial pore-space point  $\mathbf{R}$ , with cluster diffusion arising from a combination of thermal Brownian motion and electrophoretic motion owing to the action of the  $\mathbf{E}(\mathbf{R})$  field.

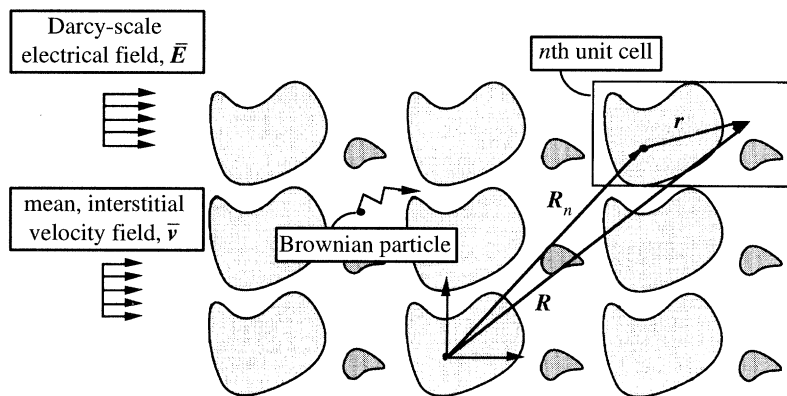


Figure 2. A Brownian particle (or cluster of particles) moves within the interstices of a spatially periodic porous medium. The medium contains space-fixed particles surrounded by a Newtonian liquid which flows with constant, mean interstitial velocity  $\bar{\mathbf{v}}$ . Throughout the medium, in both the particulate and interstitial fluid domains, an electric field acts, with Darcy-scale mean  $\bar{\mathbf{E}}$ .

exhibiting the porosity

$$\epsilon \stackrel{\text{def}}{=} V_f/V_o. \quad (2.2)$$

The Brownian cluster is taken to be wholly confined to the interstitial space of the medium, through which a Newtonian fluid flows with mean, homogeneous interstitial velocity  $\bar{\mathbf{v}}$ . Given the cluster's small scale relative to the tortuous pore-space scale (i.e.  $a/l \ll 1$ ), it will essentially convect together with the local fluid velocity  $\mathbf{v}(\mathbf{R})$  at the point  $\mathbf{R}$  about which it is situated at time  $t$ . In addition to its convective motion, two possible sources of particle diffusion can be identified. The first pertains

to the existence of an externally imposed electric field  $\mathbf{E}(\mathbf{R})$ , possessing Darcy-scale mean  $\bar{\mathbf{E}}$  (cf. (3.18) and the discussion thereof). Owing to the net charge of the Brownian particle, in the presence of the electric field  $\mathbf{E}(\mathbf{R})$  it will undergo a ‘forced diffusive’ motion  $\mathbf{M}_E \cdot \mathbf{E}$ , where  $\mathbf{M}_E$  is the cluster’s mean electrophoretic mobility dyadic, obtained by a suitable coarse-graining of the instantaneous, configuration-specific electrophoretic mobility of the Brownian entity over all of its possible internal configurations (as discussed in §5). The second diffusive mechanism, characterized by the pointwise, ‘diffusion’ (literally, ‘convective–dispersion’) dyadic  $\mathbf{D}(\mathbf{R})$ , generally combines a Brownian diffusion contribution with a position-dependent convective contribution arising as a consequence of our assumption that the Brownian cluster moves with a forced-diffusive motion  $\mathbf{M}_E \cdot \mathbf{E}$  in the presence of the  $\mathbf{E}$ -field, when its configuration-specific forced-diffusive motion generally differs from its mean value  $\mathbf{M}_E \cdot \mathbf{E}$ .

The position vector  $\mathbf{R}$ , possessing the useful decomposition,

$$\mathbf{R} = \mathbf{R}_n + \mathbf{r}, \quad (2.3)$$

is drawn relative to a fixed origin O at the lattice point

$$\{\mathbf{n}\} \stackrel{\text{def}}{=} \{n_1, n_2, n_3\} = \{0, 0, 0\} \equiv \{\mathbf{0}\}, \quad (2.4)$$

contained within the ‘zeroth’ cell  $\tau_o\{\mathbf{0}\}$ . The location of all other lattice points  $\{\mathbf{n}\}$  of the spatially periodic array are specified relative to the zeroth lattice point  $\{\mathbf{0}\}$  by the discrete position vector  $\mathbf{R}_n$ . In particular,

$$\mathbf{R}_n = n_1 \mathbf{l}_1 + n_2 \mathbf{l}_2 + n_3 \mathbf{l}_3, \quad (2.5)$$

where  $(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$  are a set of basic lattice vectors, from which the volume  $\tau_o$  of a unit cell may be deduced

$$\tau_o = \mathbf{l}_1 \cdot (\mathbf{l}_2 \times \mathbf{l}_3). \quad (2.6)$$

The spatially periodic medium may thus be regarded as a space-filling assemblage of unit cells, each of volume  $\tau_o$  and peripheral surface  $\partial\tau_o$  and containing an identical configuration of fluid and solid phases as every other unit cell. Let

$$\tau_o = \tau_f + \tau_p, \quad (2.7)$$

where  $\tau_f$  is the cellular fluid domain and  $\tau_p$  the cellular particulate domain. Then,

$$V_f = \sum_{\mathbf{n}} \tau_f\{\mathbf{n}\}, \quad (2.8a)$$

$$V_p = \sum_{\mathbf{n}} \tau_p\{\mathbf{n}\} \quad (2.8b)$$

and

$$V_o = \sum_{\mathbf{n}} \tau_o\{\mathbf{n}\}. \quad (2.8c)$$

Here,

$$\sum_{\mathbf{n}} \equiv \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty}. \quad (2.8d)$$

Beginning with knowledge of the uniform Darcy-scale fields,  $\bar{\nabla} \bar{p}$  (corresponding to a uniform applied pressure gradient) and  $\bar{\mathbf{E}}$ , as well as the detailed geometrical microstructure of the porous medium and all pertinent physicochemical attributes of the cluster-medium system, the final aim of the subsequent analysis is to derive



the following Darcy-scale convective–dispersive description for a swarm of identical, charged (non-interacting) solute particles (i.e. clusters) in terms of the mean Darcy-scale concentration  $\overline{C}(\mathbf{R}, t)$ :

$$\frac{\partial \overline{C}}{\partial t} + \overline{\mathbf{U}}^* \cdot \nabla \overline{C} = \overline{\mathbf{D}}^* : \nabla \nabla \overline{C}, \quad (2.9)$$

$$\overline{C} = \begin{cases} \overline{C}_0(\overline{\mathbf{R}}) & (t = 0) \\ 0 & (t < 0) \end{cases}, \quad (2.10)$$

$$(\overline{C}, \nabla \overline{C}) \rightarrow (0, \mathbf{0}) \quad \text{as} \quad |\overline{\mathbf{R}} - \overline{\mathbf{R}}'| \rightarrow \infty. \quad (2.11)$$

Here,  $\overline{\mathbf{R}}$  denotes a (suitably coarse-grained) Darcy-scale position vector and  $(\overline{\mathbf{U}}^*, \overline{\mathbf{D}}^*)$  are a pair of ( $\overline{\mathbf{E}}$ - and  $\nabla \overline{p}$ -dependent) phenomenological coefficients to be derived in the course of the analysis as functions of the exact, microscale physicochemical transport system.

The derivation of (2.9)–(2.11), with explicit formulas for  $(\overline{\mathbf{U}}^*, \overline{\mathbf{D}}^*)$ , is to be accomplished in the following by way of three stages. In the first, undertaken in §3, the exact, non-uniform microscale  $\mathbf{E}(\mathbf{R})$  field is derived starting with knowledge of the mean Darcy-scale field  $\overline{\mathbf{E}}$  and relevant details of the particular porous medium concerned. As a byproduct of the analysis, we derive the Darcy-scale Maxwell equation

$$\nabla \times \overline{\mathbf{H}} = \overline{\mathbf{J}}_u \quad (2.12a)$$

(this form of Ampere’s law being valid for steady-state circumstances; cf. (3.39a) for the more general, time-dependent form of the equation) with the Darcy-scale current flux vector (Katchalsky & Curran 1967; DeGroot & Mazur 1969)

$$\overline{\mathbf{J}}_u = \overline{\boldsymbol{\sigma}} \cdot \overline{\mathbf{E}} + \frac{1}{\mu_f} \overline{\mathbf{K}}_p^c \cdot \nabla \overline{p}. \quad (2.12b)$$

Here,  $\overline{\mathbf{H}}$  is the Darcy-scale magnetic field intensity ( $\text{A m}^{-1}$ ),  $\overline{\boldsymbol{\sigma}}$  the effective electrical conductivity dyadic ( $\Omega^{-1} \text{m}^{-1}$ ) of the medium, and  $\overline{\mathbf{K}}_p^c$  a Darcy-scale cross-coupling (streaming potential) transduction dyadic ( $\text{C m}^{-1}$ ). An explicit scheme is formulated for calculating  $\overline{\boldsymbol{\sigma}}$  and  $\overline{\mathbf{K}}_p^c$  given pertinent details of the porous medium’s physicochemical constitution. Both dyadics are demonstrated to be independent of the external applied fields  $(\overline{\mathbf{E}}, \nabla \overline{p})$ , depending only upon the geometrical and physicochemical nature of the porous-medium/diffusing-species system. The effective electrical conductivity  $\overline{\boldsymbol{\sigma}}$  is shown to be symmetric and positive-definite.

With  $\mathbf{E}(\mathbf{R})$  known and the Darcy-scale pressure-gradient field  $\nabla \overline{p}$  specified, the microscale  $\mathbf{v}(\mathbf{R})$  field is next obtained. The consequence of this analysis is deduction of the generalized Darcy’s law (Katchalsky & Curran 1967; DeGroot & Mazur 1969)

$$\overline{\mathbf{v}} = -\frac{1}{\mu_f} \overline{\mathbf{K}} \cdot \nabla \overline{p} - \frac{1}{\mu_f} \overline{\mathbf{K}}_E^c \cdot \overline{\mathbf{E}}, \quad (2.13)$$

with  $\overline{\mathbf{K}}$  the hydraulic permeability dyadic ( $\text{m}^2$ ),  $\overline{\mathbf{K}}_E^c$  a cross-coupling (electro-osmotic) permeability dyadic ( $\text{C m}^{-1}$ ), and  $\mu_f$  the interstitial fluid viscosity. As with  $(\overline{\boldsymbol{\sigma}}, \overline{\mathbf{K}}_p^c)$ , an explicit scheme is formulated for calculating  $\overline{\mathbf{K}}$  and  $\overline{\mathbf{K}}_E^c$  from the porous medium’s microscale description. The permeability dyadic  $\overline{\mathbf{K}}$  is shown to be symmetric and positive-definite.

Finally, with the  $\mathbf{E}(\mathbf{R})$  and  $\mathbf{v}(\mathbf{R})$  fields, it is possible to determine  $(\bar{\mathbf{U}}^*, \bar{\mathbf{D}}^*)$  through a direct application of macrotransport theory as applied to spatially periodic media.

### 3. Determination of the microscale electric field

The fluid ( $V_f$ ) and particulate ( $V_p$ ) phases of the porous medium are characterized by their respective permittivities ( $\varepsilon_f, \varepsilon_p$ ) and electrical conductivities ( $\sigma_f, \sigma_p$ ), each property pair taken to be uniformly constant in its respective phase. The ionic constituents comprising the interstitial fluid are assumed uniformly distributed in  $V_f$ , satisfying the condition of electroneutrality at all interstitial points  $\mathbf{R}$  – barring positions very near to the fixed particulate surfaces  $s_p$ , whose surface-excess charge density is denoted by  $\rho_p^s(\mathbf{R})$ . The diffuse ionic double layers existing near to the charged particulate boundaries are assumed to be characterized by a screening thickness ( $1/\kappa$ ) that is much smaller than either the characteristic length scale ( $\tau_f^{1/3}$ ) of the cellular fluid domain, or that ( $\tau_p^{1/3}$ ) of the cellular particulate domain. Since, then, the mobile double layers are indistinguishable at the cell-level (micro-) scale from the particulate surfaces  $s_p$ , the ionic non-uniformities and concomitant charge accumulation in these very thin regions are to be assigned to the (total) surface-excess charge density distribution  $\rho_u^s(\mathbf{R})$  (cf. Edwards *et al.* 1991a). It proves worthwhile, nonetheless, to maintain the distinction between the mobile double layer charge and the immobile surface charge by denoting the former as  $\rho_d^s(\mathbf{R})$ . In the absence of an external  $\mathbf{E}$ -field, we assume satisfaction of the electroneutrality condition

$$\rho_u^s(\mathbf{R}) = \rho_d^s(\mathbf{R}) + \rho_p^s(\mathbf{R}) = 0. \quad (3.1a)$$

In the remainder of this article we will assume the fixed  $\rho_p^s(\mathbf{R})$  and mobile  $\rho_d^s(\mathbf{R})$  surface-excess charge densities to be expressible in terms of the potential difference  $\zeta(\mathbf{R})$  existing across the mobile double layer thickness ( $1/\kappa$ ). In particular, using the Helmholtz model of electrochemical double layers (see Dukhin & Derjaguin 1974), we have

$$\rho_p^s(\mathbf{R}) = \varepsilon_f \zeta(\mathbf{R}) / \kappa^{-1}, \quad (3.1b)$$

whence from (3.1a),

$$\rho_d^s(\mathbf{R}) = -\varepsilon_f \zeta(\mathbf{R}) / \kappa^{-1}. \quad (3.1c)$$

Deviations from the expressions provided by (3.1b, c), as may arise in conditions of non-equilibrium (i.e.  $\rho_u^s(\mathbf{R}) \neq 0$ ), will be assumed sufficiently small so as to consider the expressions (3.1b, c) valid for both equilibrium and non-equilibrium circumstances. We thus constrain our attention to the limiting scenario of very thin, equilibrium, Helmholtz double layers.

We now imagine the existence of an externally imposed  $\mathbf{E}(\mathbf{R})$  field combined with the flow field  $\mathbf{v}(\mathbf{R})$ . These two microfields are characterized at the macro- or Darcy-scale by the uniform constant vectors  $\bar{\mathbf{E}}$  and  $\bar{\mathbf{v}}$  (whose definitions are respectively provided in (3.18) and (4.4)). One consequence of the  $\mathbf{v}(\mathbf{R})$  field is to produce a surface current  $\mathbf{J}_u^s(\mathbf{R})$  at the particulate surfaces  $s_p$  via convection of the mobile double-layer ions. In particular,

$$\mathbf{J}_u^s(\mathbf{R}) = \mathbf{J}_u^{sE}(\mathbf{R}) + \mathbf{J}_u^{sP}(\mathbf{R}) \quad (\mathbf{R} \in s_p), \quad (3.2)$$

where the  $\mathbf{E}$ -field-induced surface current flux vector  $\mathbf{J}_u^{sE}$  is given by

$$\mathbf{J}_u^{sE}(\mathbf{R}) = \rho_d^s(\mathbf{R}) \mathbf{v}_s(\mathbf{R}) \quad (\mathbf{R} \in s_p), \quad (3.3a)$$

with

$$\mathbf{v}_s(\mathbf{R}) = -\frac{\varepsilon_f}{\mu_f} \zeta(\mathbf{R}) \mathbf{E}_s(\mathbf{R}) \quad (\mathbf{R} \in s_p) \quad (3.3b)$$

the apparent slip velocity (Keh & Anderson 1985) at the solid surface  $s_p$  as derives from the convection of double-layer ions. Here,  $\mathbf{E}_s(\mathbf{R})$  is the tangentially directed electric field at the point  $\mathbf{R}$  on the particulate surface  $s_p$ .

The second contribution  $\mathbf{J}_u^{\text{SP}}$  shown in (3.2) also derives from convection of the mobile double-layer ions, yet as a consequence of the applied pressure gradient  $\bar{\nabla} \bar{p}$ , rather than of the applied electric field  $\bar{\mathbf{E}}$ . The small pressure-gradient-induced velocities in the double-layer zone result in a finite surface current of the constitutive form

$$\mathbf{J}_u^{\text{SP}}(\mathbf{R}) = -\frac{\varepsilon_f}{\mu_f} \zeta(\mathbf{R}) \mathbf{V}_s \cdot \bar{\nabla} \bar{p} \quad (\mathbf{R} \in s_p), \quad (3.3c)$$

with

$$\mathbf{V}_s(\mathbf{R}) \stackrel{\text{def}}{=} \frac{1}{\kappa^{-1}} \mathbf{V}(\mathbf{R} + \mathbf{n} \kappa^{-1}) \quad (\mathbf{R} \in s_p). \quad (3.3d)$$

The spatially periodic dyadic field  $\mathbf{V}(\mathbf{R})$  (units of  $\text{m}^2$ ), from which the ‘surface’ dyadic  $\mathbf{V}_s(\mathbf{R})$  (units of  $\text{m}$ ) derives, is related to the microscale velocity field  $\mathbf{v}(\mathbf{R})$  by way of (4.11). As will be discussed in the next section, the configuration-specific dyadic  $\mathbf{V}(\mathbf{R})$  is to be obtained by solution of the boundary-value problem (4.13) to (4.15). Here,  $\mathbf{n}$  designates the unit normal of the particulate surfaces  $s_p$ .

In the absence of a finite charge density (consistent with very thin electrical double layers), the  $\mathbf{E}(\mathbf{R})$  field satisfies the trio of Maxwell equations

$$\nabla \times \mathbf{E} = \mathbf{0} \quad (\mathbf{R} \in V_o), \quad (3.4)$$

$$\nabla \cdot \mathbf{E} = \mathbf{0} \quad (\mathbf{R} \in V_o), \quad (3.5)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_u + \frac{\partial}{\partial t} (\varepsilon \mathbf{E}) \quad (\mathbf{R} \in V_o), \quad (3.6a)$$

where the current flux vector of unpaired charges is taken to satisfy the ohmic conduction law

$$\mathbf{J}_u = \sigma \mathbf{E} \quad (\mathbf{R} \in V_o). \quad (3.6b)$$

In the above,  $\varepsilon$  and  $\sigma$  are the respective permittivity and electrical conductivity scalars, possessing the explicit values  $(\varepsilon_f, \varepsilon_p)$  and  $(\sigma_f, \sigma_p)$  depending upon whether the position vector  $\mathbf{R}$  identifies either the fluid or solid particle phase. Equation (3.4) is solved identically by

$$\mathbf{E} = -\nabla \Phi \quad (\mathbf{R} \in V_o), \quad (3.7)$$

whence (3.5) gives

$$\nabla^2 \Phi = 0 \quad (\mathbf{R} \in V_o), \quad (3.8)$$

being subject to the boundary conditions

$$\mathbf{n} \times \|\mathbf{E}\| = \mathbf{0} \quad (\mathbf{R} \in s_p), \quad (3.9)$$

$$\mathbf{n} \cdot \|\varepsilon \mathbf{E}\| = \rho_u^s \quad (\mathbf{R} \in s_p) \quad (3.10)$$

and

$$-\mathbf{n} \cdot \|\sigma \mathbf{E}\| = \nabla_s \cdot \mathbf{J}_u^s + \frac{\partial \rho_u^s}{\partial t} \quad (\mathbf{R} \in s_p). \quad (3.11)$$

Here, we have used the notation

$$\mathbf{n} \cdot \|\mathbf{f}\| \equiv \mathbf{f}_f(\mathbf{R}) - \mathbf{f}_p(\mathbf{R}) \quad (\mathbf{R} \in s_p) \quad (3.12)$$

for the ‘jump’ in the generic (scalar, vector or tensor) field  $\mathbf{f}$  across the singular surface  $s_p$  whose fluid-directed unit normal is  $\mathbf{n}$ . Also,

$$\nabla_s \stackrel{\text{def}}{=} \mathbf{I}_s \cdot \nabla \quad (3.13)$$

is the surface-gradient operator, with  $\mathbf{I}_s$  the surface idemfactor.

Thus far we have made no explicit use of the spatially periodic character of the dependent-field quantities ( $\mathbf{E}$ ,  $\mathbf{J}_u^s$ ,  $\rho_u^s$ ) appearing in the boundary-value problem statement (3.7)–(3.11). This character follows as a consequence of the spatially periodic nature of the medium and the *a priori* postulate that a uniform, Darcy-scale field  $\bar{\mathbf{E}}$  is, for such a medium, manifested at the microscale level by a spatially periodic  $\mathbf{E}(\mathbf{R})$  field. This latter postulate, confirmed *a posteriori* below, may be expressed mathematically as

$$\mathbf{E}(\mathbf{R} + \mathbf{R}_n) = \mathbf{E}(\mathbf{R}), \quad (3.14)$$

or, simply,

$$\mathbf{E} \equiv \mathbf{E}(\mathbf{r}). \quad (3.15)$$

That is, the electric field  $\mathbf{E}$  possesses an identical magnitude and direction in all cells of the periodic medium at a given cellular position  $\mathbf{r}$ . The explicit appearance of the cellular vector  $\mathbf{r}$  in the argument of spatially dependent variables will, as in (3.15), be used in the subsequent analysis to indicate the spatially periodic character of microscale field quantities. This gives, from (3.4),

$$\nabla \Phi = \text{spatially periodic}. \quad (3.16)$$

A fundamental decomposition theorem for spatially periodic gradients (Brenner & Edwards 1993), permits, on the basis of (3.16)†,

$$\Phi(\mathbf{R}) \equiv \tilde{\Phi}(\mathbf{r}) - \mathbf{R} \cdot \bar{\mathbf{E}}, \quad (3.17)$$

where

$$\bar{\mathbf{E}} \stackrel{\text{def}}{=} -\frac{1}{\tau_0} \oint_{\partial\tau_0} d\mathbf{s} \Phi. \quad (3.18a)$$

The definition (3.18a) is equivalent to a volume-average definition of the Darcy-scale electric field, as may be seen upon application of the divergence theorem (Brand 1947) to the surface integral, and use of the fact (cf. (3.9)) that the voltage potential  $\Phi$  is continuous across  $s_p$ , to rewrite (3.18a) as

$$\bar{\mathbf{E}} = \frac{1}{\tau_0} \int_{\tau_0} \mathbf{E} dV. \quad (3.18b)$$

The Darcy-scale quantity  $\bar{\mathbf{E}}$  defined by (3.18a) may be shown (Brenner & Edwards

† Equations (3.17) and (3.18) are easily seen to be self-consistent upon multiplication of both sides of (3.17) by the directed surface-area element  $d\mathbf{s}$  and integration of the result over the surface  $\partial\tau_0$  of a single unit cell. Use the fact that the surface integral of any spatially periodic function is necessarily zero, and that

$$\mathbf{I} = \frac{1}{\tau_0} \oint_{\partial\tau_0} d\mathbf{s} \mathbf{R}$$

(with  $\mathbf{I}$  the unit dyadic) to obtain from (3.17) the result displayed in (3.18).

1993) to be a lattice constant. This terminology is taken to mean that the value of  $\overline{\mathbf{E}}$  is independent of either the manner of apportioning the periodic medium into repetitive domains  $\tau_o$ , or of the (arbitrary) shape  $\partial\tau_o$  of the cellular boundaries. In addition to these physically expected attributes, at a length scale  $L$  much larger than the scale  $l$  of the microstructure of the porous medium, the field  $\overline{\mathbf{E}}$  defined by (3.18a) may ultimately be expressed as (Brenner & Edwards 1993)

$$\overline{\mathbf{E}} \equiv -\nabla\overline{\Phi}, \quad (3.19)$$

where

$$\overline{\Phi}(\mathbf{R}) \stackrel{\text{def}}{=} \frac{1}{\tau_o} \int_{\partial\tau_o} \Phi \, dV \quad (3.20)$$

is the mean (macroscopically inhomogeneous) electrical potential and the vectors

$$\overline{\nabla} \equiv \frac{\partial}{\partial \mathbf{R}} \quad \overline{\mathbf{R}} \equiv \mathbf{R}_n \quad (3.21a, b)$$

possess, at the course scale  $L$ , physically and mathematically meaningful interpretations as the Darcy-scale gradient operator and position vector, respectively.

Finally, upon substitution of (3.17) into (3.7)–(3.11), we arrive at a unit-cell boundary-value problem for determination of the spatially periodic field  $\tilde{\Phi}$ , given knowledge of the applied field  $\overline{\mathbf{E}}$ :

$$\nabla^2 \tilde{\Phi} = 0 \quad (\mathbf{r} \in \tau_o), \quad (3.22)$$

subject to

$$\mathbf{n} \times \left\| \nabla \tilde{\Phi} \right\| = 0 \quad (\mathbf{r} \in s_p), \quad (3.23)$$

$$-\mathbf{n} \cdot \left\| \varepsilon \nabla \tilde{\Phi} \right\| = \rho_u^s(\mathbf{r}) - \mathbf{n} \cdot \overline{\mathbf{E}} \|\varepsilon\| \quad (\mathbf{r} \in s_p) \quad (3.24)$$

and

$$\begin{aligned} \mathbf{n} \cdot \left\| \sigma \nabla \tilde{\Phi} \right\| &= \frac{\rho_d^s \varepsilon_f}{\mu_f} \nabla_s \cdot [\zeta(\nabla_s \tilde{\Phi})] - \frac{\rho_d^s \varepsilon_f}{\mu_f} \overline{\mathbf{E}} \cdot \nabla_s \zeta \\ &\quad - \frac{\varepsilon_f}{\mu_f} \nabla_s \cdot (\zeta \mathbf{V}_s) \cdot \overline{\nabla} \bar{p} + \mathbf{n} \cdot \overline{\mathbf{E}} \|\sigma\| + \frac{\partial \rho_u^s}{\partial t} \quad (\mathbf{r} \in s_p). \end{aligned} \quad (3.25)$$

In the above we have made use of the fact that  $\rho_d^s(\mathbf{r})$ ,  $\rho_u^s(\mathbf{r})$  and  $\zeta(\mathbf{R})$  are necessarily spatially periodic functions owing to the spatial periodicity of the medium and of the  $\mathbf{E}(\mathbf{R})$  field. The boundary-value problem (3.22) to (3.25) is uniquely defined for  $\tilde{\Phi}$  to within an arbitrary constant.

It is instructive to calculate the magnetic field  $\mathbf{H}(\mathbf{R})$  given knowledge of  $\mathbf{E}(\mathbf{R})$ , via (3.6a, b). In combination, these relations give

$$\nabla \times \mathbf{H} = \sigma \mathbf{E} + \frac{\partial}{\partial t} (\varepsilon \mathbf{E}) \quad (\mathbf{R} \in V_o). \quad (3.26)$$

Since  $\mathbf{E}$ ,  $\varepsilon$  and  $\sigma$  are each spatially periodic functions, the product of any combination of these quantities is also spatially periodic, whence

$$\nabla \mathbf{H} = \text{spatially periodic}. \quad (3.27)$$

As in (3.17), we may now decompose  $\mathbf{H}(\mathbf{R})$  as

$$\mathbf{H}(\mathbf{R}) = \widetilde{\mathbf{H}}(\mathbf{r}) + \mathbf{R} \cdot \overline{\nabla} \mathbf{H}, \quad (3.28)$$

where

$$\overline{\nabla \mathbf{H}} \stackrel{\text{def}}{=} \frac{1}{\tau_o} \int_{\partial\tau_o} d\mathbf{s} \mathbf{H} \quad (3.29)$$

possesses an interpretation as the Darcy-scale magnetic field intensity gradient.

Now, form the gradient of (3.28),

$$\nabla \mathbf{H}(\mathbf{R}) = \nabla \widetilde{\mathbf{H}}(\mathbf{r}) + \overline{\nabla \mathbf{H}}, \quad (3.30)$$

and use the vector identity (Brand 1947)

$$\nabla \times \mathbf{f} \equiv -\boldsymbol{\varepsilon} : \nabla \mathbf{f}, \quad (3.31)$$

where  $\boldsymbol{\varepsilon}$  is the unit alternator triadic, to obtain

$$\nabla \times \mathbf{H}(\mathbf{R}) = \nabla \times \widetilde{\mathbf{H}}(\mathbf{r}) + \overline{\nabla} \times \overline{\mathbf{H}}, \quad (3.32)$$

with

$$\overline{\nabla} \times \overline{\mathbf{H}} = \frac{1}{\tau_o} \int_{\partial\tau_o} d\mathbf{s} \times \mathbf{H}. \quad (3.33)$$

Integrate (3.32) over the volume  $\tau_o$  of a unit cell to find

$$\frac{1}{\tau_o} \int_{\tau_o} \nabla \times \mathbf{H} dV = \overline{\nabla} \times \overline{\mathbf{H}} + \frac{1}{\tau_o} \int_{\tau_o} \nabla \times \widetilde{\mathbf{H}} dV. \quad (3.34)$$

Application of Green's theorem (Brand 1947) to the last integral of the above and use of the boundary condition

$$\mathbf{n} \times \|\mathbf{H}\| = \mathbf{J}_u^s \quad (\mathbf{R} \in s_p), \quad (3.35)$$

shows that

$$\frac{1}{\tau_o} \int_{\tau_o} \nabla \times \mathbf{H} dV = \overline{\nabla} \times \overline{\mathbf{H}} - \frac{1}{\tau_o} \int_{s_p} \mathbf{J}_u^s d\mathbf{s}. \quad (3.36)$$

Substitute (3.36) into the left-hand side of (3.37) to find

$$\overline{\nabla} \times \overline{\mathbf{H}} = \frac{1}{\tau_o} \int_{\tau_o} \sigma \mathbf{E} dV + \frac{\partial}{\partial t} \left[ \frac{1}{\tau_o} \int_{\tau_o} \varepsilon \mathbf{E} dV \right] + \frac{1}{\tau_o} \int_{s_p} \mathbf{J}_u^s d\mathbf{s}. \quad (3.37)$$

Now, we note from (3.17) and (3.22)–(3.25) that, owing to the linearity of the problem,

$$\Phi(\mathbf{R}) \equiv g(\mathbf{R}) \cdot \overline{\mathbf{E}} + \frac{1}{\sigma_f} \mathbf{h}(\mathbf{R}) \cdot \overline{\nabla} \bar{p}, \quad (3.38)$$

where  $g(\mathbf{R})$  and  $\mathbf{h}(\mathbf{R})$ † are vector fields independent of  $\overline{\mathbf{E}}$  and  $\overline{\nabla} \bar{p}$ , dependent only upon the geometry and physical chemistry of the medium (cf. (3.41)–(3.45) for a verification of this statement). Substitution of (3.38) into (3.37) (via (3.7)), with (3.2) and (3.3a–c) furnishes the Darcy-scale Maxwell equation

$$\overline{\nabla} \times \overline{\mathbf{H}} = \overline{\mathbf{J}}_u + \frac{\partial}{\partial t} (\overline{\varepsilon \mathbf{E}}), \quad (3.39 a)$$

where we have defined the Darcy-scale current flux vector

$$\overline{\mathbf{J}}_u = \overline{\boldsymbol{\sigma}} \cdot \overline{\mathbf{E}} + \frac{1}{\mu_f} \overline{\mathbf{K}}_p^c \cdot \overline{\nabla} \bar{p}, \quad (3.39 b)$$

† Observe upon comparison of (3.17) and (3.38) that  $\mathbf{h}(\mathbf{R})$  must necessarily be a spatially periodic vector field. Explicitly,  $\mathbf{h}(\mathbf{R}) \equiv \mathbf{h}(\mathbf{r})$ .

and with (cf. (3.18b))

$$\overline{(\varepsilon \mathbf{E})} \stackrel{\text{def}}{=} \frac{1}{\tau_o} \int_{\tau_o} \varepsilon \mathbf{E} dV. \quad (3.39 c)$$

In the relation (3.39b) we have defined

$$\overline{\sigma} \stackrel{\text{def}}{=} -\frac{1}{\tau_o} \int_{\tau_o} \sigma \nabla \mathbf{g} dV + \frac{1}{\tau_o} \int_{s_p} \left( \frac{\rho_d^s \varepsilon_f}{\mu_f} \zeta \right) \nabla_s \mathbf{g} ds \quad (3.40 a)$$

as the effective electrical conductivity of the medium, and

$$\overline{\mathbf{K}}_P^c \stackrel{\text{def}}{=} -\frac{\mu_f}{\tau_o} \int_{\tau_o} \nabla \mathbf{h} dV - \frac{1}{\tau_o} \int_{s_p} \varepsilon_f \zeta \mathbf{V}_s ds \quad (3.40 b)$$

as a mean (streaming potential) electromechanical coupling dyadic. The nature of this pair of dyadics is further elaborated upon in §8, following the example calculations of §§6 and 7.

The fields  $\mathbf{g}(\mathbf{R})$  and  $\mathbf{h}(\mathbf{R})$  appearing in (3.40a, b) are to be obtained, each to within an arbitrary (physically irrelevant) constant vector, by solving the following pair of boundary-value problems (cf. (3.7)–(3.11) with (3.38)):

(i)  $\mathbf{g}(\mathbf{R})$  problem

$$\nabla^2 \mathbf{g} = \mathbf{0} \quad (\mathbf{R} \in V_o), \quad (3.41)$$

$$\mathbf{n} \times \|\nabla \mathbf{g}\| = \mathbf{0} \quad (\mathbf{R} \in s_p), \quad (3.42 a)$$

$$-\mathbf{n} \cdot \|\varepsilon \nabla \mathbf{g}\| = \mathbf{R}_u^s \quad (\mathbf{R} \in s_p), \quad (3.42 b)$$

$$\mathbf{n} \cdot \|\sigma \nabla \mathbf{g}\| = \frac{\rho_d^s \varepsilon_f}{\mu_f} \nabla_s \cdot (\zeta \nabla_s \mathbf{g}) + \frac{\partial \mathbf{R}_u^s}{\partial t} \quad (\mathbf{R} \in s_p) \quad (3.42 c)$$

and

$$\nabla \mathbf{g} \text{ spatially periodic} \quad (3.42 d)$$

(see (8.2) for the condition upon  $\mathbf{g}$  at the cell boundaries). Here, we have used the representation

$$\rho_u^s \equiv \mathbf{R}_u^s \cdot \overline{\mathbf{E}}, \quad (3.43)$$

where  $\mathbf{R}_u^s$  is to be obtained simultaneously with  $\mathbf{g}(\mathbf{R})$  from the above problem.

(ii)  $\mathbf{h}(\mathbf{R})$  problem

$$\nabla^2 \mathbf{h} = \mathbf{0} \quad (\mathbf{r} \in \tau_f), \quad (3.44)$$

$$\mathbf{n} \times \|\nabla \mathbf{h}\| = \mathbf{0} \quad (\mathbf{r} \in s_p), \quad (3.45 a)$$

$$-\mathbf{n} \cdot \nabla \mathbf{h} = \frac{\varepsilon_f}{\mu_f} \nabla_s \cdot (\zeta \mathbf{V}_s) \quad (\mathbf{r} \in s_p) \quad (3.45 b)$$

and

$$\mathbf{h}, \nabla \mathbf{h} \text{ spatially periodic.} \quad (3.45 c)$$

One consequence of the spatially periodic character of  $\mathbf{h}$  is the fact that the integral of  $\mathbf{h}$  over the boundary of a unit cell must vanish, i.e.

$$\int_{\partial \tau_o} d\mathbf{s} \mathbf{h} = \mathbf{0}. \quad (3.45 d)$$

This property is of particular utility in the implementation of approximate, dilute-limit schemes, such as used in §7.

It is useful to recast the boundary-value problem (3.41)–(3.42) in terms of a spatially periodic equivalent of the  $\mathbf{g}(\mathbf{R})$  field. This may be done by combining (3.17) and (3.38) to give

$$\tilde{\Phi}(\mathbf{r}) = [\mathbf{R} + \mathbf{g}(\mathbf{R})] \cdot \bar{\mathbf{E}} + \frac{1}{\sigma_f} \mathbf{h}(\mathbf{r}) \cdot \bar{\nabla} \bar{p}. \quad (3.46)$$

This reveals that

$$\tilde{\mathbf{g}}(\mathbf{r}) \stackrel{\text{def}}{=} \mathbf{R} + \mathbf{g}(\mathbf{R}) \quad (3.47)$$

is a spatially periodic vector field. Substituting (3.47) into (3.41)–(3.42) provides the following unit-cell boundary-value problem for determination of the field  $\tilde{\mathbf{g}}(\mathbf{r})$ :

(iii) *Alternative  $\tilde{\mathbf{g}}(\mathbf{r})$  problem*

$$\nabla^2 \tilde{\mathbf{g}} = \mathbf{0} \quad (\mathbf{r} \in \tau_o), \quad (3.48)$$

$$\mathbf{n} \times \|\nabla \tilde{\mathbf{g}}\| = \mathbf{0} \quad (\mathbf{r} \in s_p), \quad (3.49)$$

$$-\mathbf{n} \cdot \|\varepsilon(\nabla \tilde{\mathbf{g}} - \mathbf{I})\| = \mathbf{R}_u^s \quad (\mathbf{r} \in s_p) \quad (3.50)$$

$$\mathbf{n} \cdot \|\sigma(\nabla \tilde{\mathbf{g}} - \mathbf{I})\| = \frac{\rho_d^s \varepsilon_f}{\mu_f} \nabla_s \cdot [\zeta (\nabla_s \tilde{\mathbf{g}} - \mathbf{I}_s)] + \frac{\partial \mathbf{R}_u^s}{\partial t} \quad (\mathbf{r} \in s_p) \quad (3.51 a)$$

and

$$\tilde{\mathbf{g}}, \nabla \tilde{\mathbf{g}} \text{ spatially periodic.} \quad (3.51 b)$$

Owing to the spatial periodicity of  $\tilde{\mathbf{g}}(\mathbf{r})$ , it follows from (3.50) that

$$\mathbf{R}_u^s \equiv \mathbf{R}_u^s(\mathbf{r})$$

is also spatially periodic. Moreover, as in (3.45d), it follows from the spatially periodic nature of  $\tilde{\mathbf{g}}(\mathbf{r})$ , that

$$\int_{\partial \tau_o} d\mathbf{s} \tilde{\mathbf{g}} = \mathbf{0}. \quad (3.52)$$

In performing actual calculations, it may often prove easiest to solve for the spatially periodic  $\tilde{\mathbf{g}}(\mathbf{r})$  field via (3.48) to (3.51), rather than the (non-periodic)  $\mathbf{g}(\mathbf{R})$  field directly. The latter may then be found from (3.47), and this result used to calculate the effective conductivity dyadic  $\tilde{\boldsymbol{\sigma}}$  of the medium. Alternatively, the  $\tilde{\mathbf{g}}(\mathbf{r})$ -field may be used directly in the formulation

$$\tilde{\boldsymbol{\sigma}} = \frac{1}{\tau_o} \int_{\tau_o} \sigma (\mathbf{I} - \nabla \tilde{\mathbf{g}}) dV - \frac{1}{\tau_o} \int_{s_p} \left( \frac{\rho_d^s \varepsilon_f}{\mu_f} \zeta \right) (\mathbf{I}_s - \nabla_s \tilde{\mathbf{g}}) ds, \quad (3.53)$$

which provides an alternative expression to (3.40a) for the effective electrical conductivity.

The scheme outlined above for calculating the effective electrical conductivity dyadic  $\tilde{\boldsymbol{\sigma}}$  of a charged porous medium with fluid flowing through its interstices is highly analogous to the macrotransport scheme for determining the effective diffusivity of a point-size, surface-adsorbing solute through a spatially periodic medium (Brenner & Edwards 1993). Indeed, in the common case of the latter wherein spatial and surface cellular probability distributions are uniform, the two schemes are identical upon making equivalences between our  $\mathbf{g}(\mathbf{R})$  field and the  $\mathbf{B}(\mathbf{R})$  field of macrotransport theory (cf. e.g. (5.22)–(5.24)). Thus, the electrical conductivity scalar  $\sigma(\mathbf{r})$  in the present problem finds an equivalent in the diffusivity dyadic  $\mathbf{D}(\mathbf{r})$  of the macrotransport diffusion scheme, whereas the surface charge convection term  $(-\rho_d^s \varepsilon_f \zeta / \mu_f)$  possesses an equivalent in the surface diffusivity  $D_s$  (see §8 for further discussion of this analogy).



#### 4. Determination of the microscale velocity field

The equations governing fluid flow within the interstices of the porous medium are assumed at the microscale level to be those of Stokes flow (without a body force  $\rho_u \mathbf{E}$ , whose absence owes to the extreme thinness of electrical double layers)

$$\mu_f \nabla^2 \mathbf{v} = \nabla p \quad (\mathbf{R} \in V_f), \quad (4.1)$$

with the continuity condition

$$\nabla \cdot \mathbf{v} = 0 \quad (\mathbf{R} \in V_f), \quad (4.2)$$

subject to the tangential slip condition (cf. (3.3b))

$$\mathbf{n} \cdot \mathbf{v} = 0, \quad \mathbf{I}_s \cdot \mathbf{v} = -\frac{\varepsilon_f}{\mu_f} \zeta \mathbf{E}_s \quad (\mathbf{R} \in s_p). \quad (4.3)$$

The mean, homogeneous, Darcy-scale seepage velocity vector

$$\bar{\mathbf{v}} \stackrel{\text{def}}{=} \frac{1}{\tau_o} \int_{\tau_f} \mathbf{v} \, dV \quad (4.4)$$

is assumed to be spatially uniform. Owing to the spatial periodicity of the medium, this constancy belies the fact that

$$\mathbf{v} \equiv \mathbf{v}(\mathbf{r}) \quad (4.5)$$

whence, from (4.1) it is evident that the microscale pressure gradient field  $\nabla p$  is spatially periodic. As in the decompositions (3.17) and (3.28), it follows that,

$$p(\mathbf{R}) = \tilde{p}(\mathbf{r}) + \mathbf{R} \cdot \bar{\nabla} \bar{p}, \quad (4.6)$$

where

$$\bar{\nabla} \bar{p} \stackrel{\text{def}}{=} \frac{1}{\tau_o} \int_{\partial \tau_o} \, ds \, p \quad (4.7)$$

is a lattice constant, having an interpretation as the mean, Darcy-scale pressure gradient.

Substitution of (4.6) into (4.1)–(4.3) furnishes the following boundary value problem for determination of the spatially periodic fields  $(\mathbf{v}, \tilde{p})$ :

$$\mu_f \nabla^2 \mathbf{v} = \nabla \tilde{p} + \bar{\nabla} \bar{p} \quad (\mathbf{r} \in \tau_f), \quad (4.8)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (\mathbf{r} \in \tau_f), \quad (4.9)$$

$$\mathbf{n} \cdot \mathbf{v} = 0, \quad \mathbf{I}_s \cdot \mathbf{v} = \frac{\varepsilon_f}{\mu_f} \zeta \mathbf{I}_s \cdot (\nabla \tilde{\Phi} - \bar{\mathbf{E}}) \quad (\mathbf{r} \in s_p). \quad (4.10)$$

Owing to the linearity of the problem defined by (4.8)–(4.10), we may decompose  $(\mathbf{v}, \tilde{p})$  as

$$\mathbf{v} = \frac{1}{\mu_f} \mathbf{V} \cdot \bar{\nabla} \bar{p} + \frac{1}{\mu_f} \mathbf{V}^E \cdot \bar{\mathbf{E}}, \quad (4.11)$$

$$\tilde{p} = \mathbf{\Pi} \cdot \bar{\nabla} \bar{p} + \mathbf{\Pi}^E \cdot \bar{\mathbf{E}}, \quad (4.12)$$

where  $[\mathbf{V}(\mathbf{R}), \mathbf{\Pi}(\mathbf{R})]$  and  $[\mathbf{V}^E(\mathbf{R}), \mathbf{\Pi}^E(\mathbf{R})]$  are spatially periodic (dyadic and vector) fields, dependent upon the geometry of the medium and its physicochemical constitution, independent of  $\bar{\nabla} \bar{p}$  and  $\bar{\mathbf{E}}$  (as established below).

The fields  $(\mathbf{V}, \mathbf{\Pi})$  and  $(\mathbf{V}^E, \mathbf{\Pi}^E)$  are to be obtained by solution of the following

pair of configuration-specific, cellular, boundary-value problems, obtained by substituting (4.11) and (4.12) into (4.8)–(4.10) with (3.46) and (3.47):

(i) *V*-problem

$$\nabla^2 \mathbf{V} = \nabla \mathbf{H} + \mathbf{I} \quad (\mathbf{r} \in \tau_f), \quad (4.13)$$

$$\nabla \cdot \mathbf{V} = \mathbf{0} \quad (\mathbf{r} \in \tau_f), \quad (4.14)$$

$$\mathbf{n} \cdot \mathbf{V} = \mathbf{0}, \quad \mathbf{I}_s \cdot \mathbf{V} = \frac{\varepsilon_f \zeta}{\sigma_f} \nabla_s \mathbf{h} \quad (\mathbf{r} \in s_p), \quad (4.15a)$$

$$\mathbf{V}, \nabla \mathbf{V} \quad \text{spatially periodic}, \quad (4.15b)$$

and

(ii) *V<sup>E</sup>* problem

$$\nabla^2 \mathbf{V}^E = \nabla \mathbf{H}^E \quad (\mathbf{r} \in \tau_f), \quad (4.16)$$

$$\nabla \cdot \mathbf{V}^E = \mathbf{0} \quad (\mathbf{r} \in \tau_f), \quad (4.17)$$

$$\mathbf{n} \cdot \mathbf{V}^E = \mathbf{0}, \quad \mathbf{I}_s \cdot \mathbf{V}^E = \varepsilon_f \zeta (\nabla_s \tilde{\mathbf{g}} - \mathbf{I}_s) \quad (\mathbf{r} \in s_p), \quad (4.18a)$$

$$\mathbf{V}^E, \nabla \mathbf{V}^E \quad \text{spatially periodic}. \quad (4.18b)$$

Upon substitution of (4.11) into (4.4) we obtain the generalized Darcy's law

$$\bar{\mathbf{v}} = -\frac{1}{\mu_f} \bar{\mathbf{K}} \cdot \nabla \bar{p} - \frac{1}{\mu_f} \bar{\mathbf{K}}_E^c \cdot \bar{\mathbf{E}}, \quad (4.19)$$

where we have defined

$$\bar{\mathbf{K}} \stackrel{\text{def}}{=} -\frac{1}{\tau_o} \int_{\tau_f} \mathbf{V} \, dV, \quad (4.20a)$$

or, alternatively (upon use of (4.14) and (4.15a))

$$\bar{\mathbf{K}} = -\frac{1}{\tau_o} \int_{\partial \tau_o} \mathbf{r} \, ds \cdot \mathbf{V} \quad (4.20b)$$

as the (hydraulic) permeability dyadic ( $\text{m}^2$ ) and

$$\bar{\mathbf{K}}_E^c \stackrel{\text{def}}{=} -\frac{1}{\tau_o} \int_{\tau_i} \mathbf{V}^E \, dV \quad (4.21a)$$

or, alternatively (upon use of (4.17) and (4.18a))

$$\bar{\mathbf{K}}_E^c = -\frac{1}{\tau_o} \int_{\partial \tau_o} \mathbf{r} \, ds \cdot \mathbf{V}^E \quad (4.21b)$$

as the (electroosmotic) transduction coupling dyadic ( $\text{N s m}^{-2}$ ).

The dyadics  $\bar{\mathbf{K}}$  and  $\bar{\mathbf{K}}_E^c$  represent the permeabilities of the medium associated respectively, with applied pressure-gradient  $\nabla \bar{p}$  and electric  $\bar{\mathbf{E}}$  fields. They are lattice constants of the medium, independent of the manner of apportioning the medium into unit cells and of the applied  $\nabla \bar{p}$  and  $\bar{\mathbf{E}}$  fields, as follows from the integrands of (4.20) and (4.21), taken with (4.13) to (4.18). Further discussion of these dyadics is provided in §8.

## 5. Convective–dispersive description

### (a) Pore-level description

Since the dimensions of the flexible Brownian cluster depicted in figure 1 are exceedingly small relative to the dimensions of the interstices of the porous medium, it effectively convects with the local fluid velocity  $\mathbf{V}(\mathbf{R})$  at each cellular-space point  $\mathbf{R}$  in the interstices of the porous medium. As discussed on qualitative grounds in §2, diffusive transport of the cluster arises from both forced and Brownian mechanisms. Specifically, we assume the transport of a ‘tracer’ cluster to be governed by Smoluchowski’s equation

$$\frac{\partial P}{\partial t} + \nabla \cdot \mathbf{J} = \delta(\mathbf{R} - \mathbf{R}')\delta(t) \quad (\mathbf{R} \in V_f), \quad (5.1)$$

where the convective–diffusive flux of tracer probability is assumed given by

$$\mathbf{J} = \mathbf{v}P + \mathbf{M}_E \cdot \mathbf{E}P - \mathbf{D} \cdot \nabla P, \quad (5.2)$$

subject to 
$$\mathbf{J} = \mathbf{0} \quad (\mathbf{R} \in s_p) \quad (5.3)$$

on the fixed-bed surfaces  $s_p$ , and

$$(P, \mathbf{J}) |\mathbf{R} - \mathbf{R}'|^m \rightarrow (0, \mathbf{0}) \quad (m = 0, 1, 2, \dots) \quad \text{as } |\mathbf{R} - \mathbf{R}'| \rightarrow \infty \quad (5.4)$$

far from the point  $\mathbf{R}'$  at which the Brownian tracer was introduced into the system. Here,

$$P d^3 \mathbf{R} \equiv P(\mathbf{R}, t | \mathbf{R}') d^3 \mathbf{R} \quad (5.5)$$

denotes the conditional probability that the tracer is located at the interstitial point  $\mathbf{R}$  at time  $t$ , given that it was introduced at  $t = 0$  at  $\mathbf{R}'$ .

From knowledge of  $P$ , we may determine the pointwise concentration field  $C(\mathbf{R}, t)$  by means of the superposition theorem

$$C(\mathbf{R}, t) = \int_{V_0} C_0(\mathbf{R}', 0) P(\mathbf{R}, t | \mathbf{R}') d^3 \mathbf{R}', \quad (5.6)$$

where  $C_0(\mathbf{R}', 0)$  denotes the initial concentration profile of solute particles (or clusters).

The electrophoretic mobility  $\mathbf{M}(\mathbf{R})$  of the tracer, as well as its diffusivity  $\mathbf{D}(\mathbf{R})$ , are presumed to be known phenomenological functions calculable from the particular microstructure of the (effectively point-size) tracer. In the simplest case of a spherical Brownian particle of radius  $a$ , with a uniform zeta potential,  $\zeta_B = \text{const.}$ , we have†

$$\mathbf{M}_E = \mathbf{I} \frac{\varepsilon_f \zeta_B}{\mu_f}, \quad \mathbf{D} = \mathbf{I} \frac{kT}{6\pi\mu_f a}. \quad (5.7a, b)$$

The former of these relations is the classical Smoluchowski result for the electrophoretic mobility of a sphere in the absence of surface current (Levich 1962). The latter is the classical Stokes–Einstein diffusivity of a spherical Brownian particle. Non-spherical particles possessing uniform zeta potential,  $\zeta_B = \text{const.}$ , are characterized

† In applications involving charged molecules, rather than charged colloidal particles, the electrophoretic mobility  $\mathbf{M}_E$  is to be interpreted as an ionic mobility. For further consideration of this physical scenario, see Edwards & Langer (1994).

by

$$\mathbf{M}_E = \mathbf{I} \frac{\varepsilon_f \zeta_B}{\mu_f}, \quad \mathbf{D} = kT\mathbf{M}, \quad (5.8a, b)$$

where  $\mathbf{M}$  is the hydrodynamic mobility dyadic of the particle, to be determined by calculating the hydrodynamic force acting upon the non-spherical particle in a uniform, zero-Reynolds number streaming flow (Happel & Brenner 1983). The fact that the electrophoretic mobility  $\mathbf{M}_E$  is identical for spherical and non-spherical particles has been established by Morrison (1970). This, however, is true only for particles exhibiting a uniform zeta potential  $\zeta_B = \text{const.}$  (Anderson 1985) and negligible surface current (Levich 1962).

In the more general case of a flexible, Brownian cluster composed of two or more charged, rigid Brownian particles bound together by attractive/repulsive potentials, the mean electrophoretic mobility and diffusivity may be obtained by a suitable coarse-graining over all of the cluster's internal configurations in the course of its translation, extension and rotation within a uniform electric field (this scenario being appropriate for the present case of a cluster whose dimensions are very small relative to the pore-space scale and the length-scale of spatial gradients in  $\mathbf{E}(\mathbf{R})$ ). Such a coarse-graining theory exists in the form of macrotransport analysis, as first outlined by Brenner *et al.* (1987). The unique feature here is the fact that the individual forced-diffusive motions of each rigid particle in the cluster are related to that particle's electrophoretic, rather than hydrodynamic, mobility.

In general, the mean electrophoretic mobility  $\mathbf{M}_E$  of the cluster will be non-isotropic and dependent upon the orientation of the applied electric field. An explicit example in this context is the calculation of Fair & Anderson (1990) of the electrophoretic motion of a charged dumbbell. Likewise, the 'diffusivity'  $\mathbf{D}$  of the cluster will combine Brownian diffusive and convective-diffusive contributions, the latter following from the fact that, in general, the cluster will move at different particle velocities depending upon its instantaneous configuration in the applied electric field. The calculation of Nadim & Brenner (1989) for a flexible Brownian dumbbell in an external field provides an explicit example, although their use of hydrodynamic mobilities in representing the convection of the cluster in the external field must in the present context be replaced by use of electrophoretic mobilities.

Interestingly, in the case of a flexible cluster of charged, Brownian particles for which the zeta potential of each individual particle of the cluster is identical and uniform, the mean electrophoretic mobility dyadic of the cluster is simply (Fair & Anderson 1990) that given in (5.7a), and the cluster's diffusion dyadic is simply the mean Brownian diffusion dyadic of the cluster. In other words, there is no convective contribution to the cluster's diffusion dyadic  $\mathbf{D}(\mathbf{R})$  unless the zeta potentials of the individual particles comprising the cluster are either unequal or non-uniform on each particle's surface. A further possibility, not addressed by Fair & Anderson (1990), is that there exists a surface current on each particle surface, in which case a convective contribution to  $\mathbf{D}(\mathbf{R})$  can generally be expected.

#### (b) Darcy-scale description

The theory of macrotransport processes† for discontinuous systems may be directly applied to the preceding scenario to develop the effective, Darcy-scale description

† The text of Brenner & Edwards (1993) may be consulted for a thorough discussion of the derivation, interpretation and specific application of the theoretical material reviewed in this subsection.

in terms of coarse-scale phenomenological coefficients. In particular, as originally established by Brenner (1980), in the long-time limit

$$t \gg \tau_0^{2/3}/|D|, \quad (5.9)$$

the mean conditional probability scalar

$$\bar{P}(\mathbf{R}_n - \mathbf{R}'_n, t | \mathbf{r}') \stackrel{\text{def}}{=} \frac{1}{\tau_0} \int_{\tau_0\{\mathbf{n}\}} P(\mathbf{R}_n - \mathbf{R}'_n, \mathbf{r}, t | \mathbf{r}') d^3\mathbf{r}, \quad (5.10)$$

obtains an asymptotic limit (cf. (3.21*b*))

$$\bar{P}(\bar{\mathbf{R}}, t | \bar{\mathbf{R}}', \mathbf{r}') \approx \bar{P}(\bar{\mathbf{R}}, t | \bar{\mathbf{R}}'), \quad (5.11)$$

independent of initial local-scale conditions  $\mathbf{r}'$ , satisfying the following Darcy-scale description:

$$\frac{\partial \bar{P}}{\partial t} + \bar{\nabla} \cdot \bar{\mathbf{J}} = \delta(\bar{\mathbf{R}} - \bar{\mathbf{R}}') \delta(t), \quad (5.12)$$

$$\bar{\mathbf{J}} = \bar{\mathbf{U}}^* \bar{P} - \bar{\mathbf{D}}^* \cdot \bar{\nabla} \bar{P}, \quad (5.13)$$

subject to  $(\bar{P}, \bar{\mathbf{J}}) \rightarrow (0, \mathbf{0})$   $\left| \bar{\mathbf{R}} - \bar{\mathbf{R}}' \right| \rightarrow \infty$ . (5.14)

(The above description is easily converted into concentration variables, as in (2.9)–(2.11), upon use of the superposition theorem (5.6).) Here,  $\bar{\mathbf{U}}^*$  and  $\bar{\mathbf{D}}^*$  denote the Brownian particle's mean velocity and dispersivity, respectively. They are defined in terms of the microscale data by the pair of relations,

$$\bar{\mathbf{D}}^* = \int_{\tau_0} P_0^\infty (\nabla \mathbf{B})^\dagger \cdot (\text{sym } \mathbf{D}) \cdot \nabla \mathbf{B} d^3\mathbf{r} \quad (5.15)$$

and  $\bar{\mathbf{U}}^* = \int_{\tau_0} \mathbf{J}_0^\infty d^3\mathbf{r}$ . (5.16)

The quantities  $P_0^\infty(\mathbf{R})$  and  $\mathbf{B}(\mathbf{R})$  are spatially varying microscale fields to be determined from knowledge of the local system by solving a pair of unit-cell, boundary-value problems. The  $P_0^\infty(\mathbf{R})$  field satisfies

$$\nabla \cdot \mathbf{J}_0^\infty = 0 \quad (\mathbf{r} \in \tau_f), \quad (5.17)$$

$$\mathbf{J}_0^\infty = \mathbf{U} P_0^\infty - \mathbf{D} \cdot \nabla P_0^\infty, \quad (5.18)$$

$$\mathbf{U} = \mathbf{v} + \mathbf{M}_E \cdot \mathbf{E}, \quad (5.19a)$$

$$\mathbf{n} \cdot \mathbf{J}_0^\infty = 0 \quad (\mathbf{r} \in s_p), \quad (5.19b)$$

$$P_0^\infty, \nabla P_0^\infty \quad \text{spatially periodic} \quad (5.20a, b)$$

and  $\int_{\tau_f} P_0^\infty d^3\mathbf{r} = 1$ . (5.21)

With  $P_0^\infty(\mathbf{R})$  known, a convenient method for obtaining the  $\mathbf{B}(\mathbf{R})$  field involves defining the spatially periodic field

$$\tilde{\mathbf{B}}(\mathbf{r}) \stackrel{\text{def}}{=} \mathbf{B}(\mathbf{R}) + \mathbf{R},$$

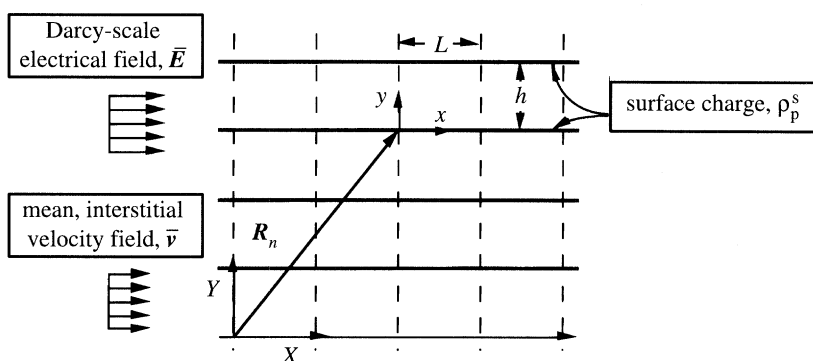


Figure 3. A two-dimensional porous medium composed of vanishingly thin, uniformly charged plates between which flows a Newtonian liquid, parallel to the plates, with mean interstitial velocity  $\bar{\mathbf{v}}$ . An electric field acts, with Darcy-scale mean  $\bar{\mathbf{E}}$ .

which represents the solution of the boundary-value problem

$$\nabla \cdot (P_0^\infty \mathbf{D} \cdot \nabla \tilde{\mathbf{B}}) - \mathbf{J}_0^\infty \cdot \nabla \tilde{\mathbf{B}} = P_0^\infty (\bar{\mathbf{U}}^* - \mathbf{U} + \nabla \cdot \mathbf{D}) + 2(\text{sym } \mathbf{D}) \cdot \nabla P_0^\infty \quad (\mathbf{r} \in \tau_f), \quad (5.22)$$

$$P_0^\infty \mathbf{n} \cdot (\mathbf{D} \cdot \nabla \tilde{\mathbf{B}} - \mathbf{D}) = \mathbf{0} \quad (\mathbf{r} \in s_p), \quad (5.23)$$

$$\tilde{\mathbf{B}} \text{ is continuous across } s_p$$

and 
$$\tilde{\mathbf{B}}, \nabla \tilde{\mathbf{B}} \text{ spatially periodic.} \quad (5.24)$$

As previously discussed following (3.53), the  $\mathbf{B}$ -field is directly analogous to the  $\mathbf{g}$ -field appearing in the mean electrical conductivity definition (3.40a). Similarly,  $\tilde{\mathbf{B}}$  is analogous to  $\tilde{\mathbf{g}}$ . Like the vector  $\tilde{\mathbf{g}}$ , the vector  $\tilde{\mathbf{B}}$  is defined by (5.22)–(5.24) only to within an arbitrary, physically irrelevant constant vector.

## 6. Example 1: layered medium of charged parallel plates

As a first explicit example of the foregoing theory, consider the scenario depicted in figure 3. A homogeneous electric field

$$\bar{\mathbf{E}} = \mathbf{i}_x \bar{E} \quad (6.1)$$

is applied in a direction parallel to a two-dimensional porous medium consisting of an infinite number of very thin solid plates whose uniform surface charge (on either side of the plates) is  $\rho_p^s$ . Sandwiched between the plates are parallel layers of thickness  $h$  of a Newtonian fluid of viscosity  $\mu_f$  and electrical properties  $(\epsilon_f, \sigma_f)$ . In addition to the field  $\bar{\mathbf{E}}$ , a Darcy-scale pressure gradient

$$\bar{\nabla} \bar{p} = \mathbf{i}_x d\bar{p}/dx \quad (6.2)$$

is applied to the layered medium.

A dilute collection of charged, Brownian spheres, each of radius  $a$  and possessing a uniform zeta potential  $\zeta_B$ , is placed within the interstices of the medium. Each of the spheres is characterized by the electrophoretic mobility and diffusivity relations provided by (5.7a, b).

In order to cast this problem in terms of the theory define the ‘volume’ (literally, surface area) of a unit cell by

$$\tau_o = hL, \quad (6.3)$$

where  $L$  is an arbitrary length measured parallel to the solid surfaces. Since the plates are infinitesimally thin,

$$\tau_o = \tau_f, \quad \tau_p = 0. \quad (6.4a, b)$$

Choose the local, cellular position vector  $\mathbf{R}$  as originating at the edge of a unit cell, as shown in the figure. Then,

$$\mathbf{r} = \mathbf{i}_x x + \mathbf{i}_y y \quad (0 \leq x < L, 0 \leq y < h). \quad (6.5)$$

(a) *Determination of the electric field*

For the circumstances of (6.1), we begin with the *a priori* postulate

$$\mathbf{E} = \mathbf{i}_x E(y), \quad (6.6)$$

whence, from (3.7), we have that

$$E(y) = -\frac{d}{dX} \Phi(X, y), \quad (6.7)$$

where  $\mathbf{R} = \mathbf{i}_x X + \mathbf{i}_y Y \quad (-\infty \leq X \leq \infty, -\infty \leq Y \leq \infty) \quad (6.8)$

is a global position vector defined in the global coordinate system  $(X, Y)$  originating at the zero cell  $\{\mathbf{0}\}$ . According to (3.17),

$$\Phi(X, y) = \tilde{\Phi}(x, y) - X \mathbf{i}_x \cdot \bar{\mathbf{E}}. \quad (6.9)$$

Given the current geometry, we additionally assume, subject to *a posteriori* verification, that

$$\tilde{\Phi} \equiv \tilde{\Phi}(y). \quad (6.10)$$

Next, use (3.22)–(3.25) to obtain the following boundary-value problem for determination of  $\tilde{\Phi}$ :

$$\frac{d^2 \tilde{\Phi}}{dy^2} = 0 \quad (0 \leq y < h), \quad (6.11)$$

$$\tilde{\Phi} = \text{const.}, \quad y = 0, h, \quad (6.12)$$

$$-\varepsilon_f \frac{d\tilde{\Phi}}{dy} = \rho_v^s, \quad y = 0, h, \quad (6.13)$$

$$-\sigma_f \frac{d\tilde{\Phi}}{dy} = 0, \quad y = 0, h. \quad (6.14)$$

The solution to the problem posed by (6.11)–(6.14) is simply

$$\tilde{\Phi} = \text{const.} \quad (0 \leq y < h). \quad (6.15)$$

In combination, (6.1), (6.9) and (6.10) give, with (6.15), the result

$$E(y) = \bar{E} = \text{const.} \quad (6.16)$$

This constitutes our solution for the microscale electric field. Note, for subsequent purposes, that, from (6.13),

$$\rho_u^s = 0. \quad (6.17)$$

(b) *Effective electrical conductivity*

To calculate the effective electrical conductivity  $\bar{\sigma}$  of the medium, we choose to solve the spatially periodic boundary-value problem (3.48) to (3.51), and subsequently to use (3.47) to obtain a solution for  $\bar{\sigma}$  via (3.40a). Equations (3.48) to (3.51) simplify considerably with the *a priori* postulate

$$\tilde{\mathbf{g}} = \mathbf{i}_y \tilde{g}(y). \quad (6.18)$$

In particular,

$$\frac{d^2 \tilde{g}}{dy^2} = 0 \quad (0 \leq y < h), \quad (6.19)$$

$$\frac{d\tilde{g}}{dy} = 1, \quad y = 0, h. \quad (6.20)$$

The solution to this problem is simply

$$\tilde{g} = y + \text{const.} \quad (0 \leq y < h). \quad (6.21)$$

From (3.47) we obtain (for fixed  $\{\mathbf{n}\}$ )

$$\mathbf{g} = -\mathbf{i}_x x, \quad (6.22)$$

to within a (physically arbitrary) constant. Finally, from (3.40a), we have

$$\bar{\sigma} = \mathbf{i}_x \mathbf{i}_x \left( \sigma_f - 2 \frac{\rho_d^s \varepsilon_f \zeta}{\mu_f h} \right). \quad (6.23)$$

This expression reveals that the effective electrical conductivity  $\bar{\sigma}$  is a combination of the electrical conductivity  $\sigma_f$  of the fluid and the surface current term  $\rho_d^s \varepsilon_f \zeta / \mu_f h$ . As the spacing  $h$  between layers diminishes, the contribution from the surface current to the overall conductivity of the medium increases as a consequence of the diminished specific surface (i.e. surface-to-volume ratio)  $1/h$ . Observe that a factor of 2 enters into the above expression for the effective electrical conductivity  $\bar{\sigma}$  of the medium by virtue of there being two double layers associated with each layer of interstitial fluid in the layered medium.

According to (3.1c), for a positively charged particulate surface ( $\zeta > 0$ ),  $\rho_d^s$  is negative, whence surface current amplifies the overall conductivity by an amount  $|2\rho_d^s \varepsilon_f \zeta / \mu_f h|$ . In fact, the effective electrical conductivity  $\bar{\sigma}$  is amplified by surface current effects regardless of the sign of the fixed surface charge, since  $\rho_d^s \varepsilon_f \zeta / \mu_f h \leq 0$  for both positively and negatively charged solid surfaces.

(c) *Determination of the velocity field*

The spatially periodic velocity and pressure fields follow from (4.11) and (4.12). In the present case, we assume

$$\mathbf{V} = \mathbf{i}_x \mathbf{i}_x V(y); \quad \mathbf{V}^E = \mathbf{i}_x \mathbf{i}_x V^E(y), \quad (6.24a, b)$$

$$\mathbf{\Pi} = \mathbf{i}_y \mathbf{\Pi}(y); \quad \mathbf{\Pi}^E = \mathbf{i}_y \mathbf{\Pi}^E(y). \quad (6.25a, b)$$



Substituting the above postulates into (4.13) to (4.15) yields (upon utilizing the fact that  $\mathbf{h} = \text{const.}$ , as follows from (3.44)–(3.45))

$$\frac{d^2V}{dy^2} = 1 \quad (0 \leq y < h), \quad (6.26)$$

$$\frac{d\Pi}{dy} = -1 \quad (0 \leq y < h), \quad (6.27)$$

$$V = 0 \quad y = 0, h. \quad (6.28)$$

Likewise, (4.16) to (4.18) give (with (6.21)),

$$\frac{d^2V^E}{dy^2} = 0 \quad (0 \leq y < h), \quad (6.29)$$

$$\frac{d\Pi^E}{dy} = 0 \quad (0 \leq y < h), \quad (6.30)$$

$$V^E = -\varepsilon_f \zeta \quad y = 0, h. \quad (6.31)$$

Equations (6.26)–(6.28) furnish the solutions

$$V = \frac{1}{2}(y^2 - hy) \quad (0 \leq y < h), \quad (6.32)$$

$$\Pi = -y + \text{const.} \quad (0 \leq y < h) \quad (6.33)$$

and (6.29)–(6.31) give

$$V^E = -\varepsilon_f \zeta \quad (0 \leq y < h), \quad (6.34)$$

$$\Pi^E = \text{const.} \quad (0 \leq y < h). \quad (6.35)$$

Upon combining (6.32)–(6.35) with (6.24) and (6.25), we obtain the following solution for the microscale velocity field (cf. (4.11)):

$$\mathbf{v} = \frac{1}{2\mu_f}(y^2 - yh)\nabla\bar{p} - \frac{\varepsilon_f\zeta}{\mu_f}\bar{\mathbf{E}}. \quad (6.36)$$

The first term in the above relation is the standard result (Bird *et al.* 1960) for Poiseuille flow between parallel plates, whereas the second is the usual result (Levich 1962) for electroosmosis between charged flat plates.

(d) *Effective permeability and electrokinetic cross-coupling properties*

Finally, (upon utilizing the fact that  $\mathbf{h} = \text{const.}$ ), we may use (3.40b), (4.20) and (4.21) with the results (6.24), (6.32) and (6.34) to obtain

$$\bar{\mathbf{K}} = \mathbf{i}_x \mathbf{i}_x (h^2/12) \quad (6.37)$$

for the hydraulic permeability of the medium and

$$\bar{\mathbf{K}}_P^c = \bar{\mathbf{K}}_E^c = \mathbf{i}_x \mathbf{i}_x (\varepsilon_f \zeta) \quad (6.38a, b)$$

for the electrokinetic transductive coupling dyadics. Once again, these two expressions are in agreement with those appearing in the literature (see Bird *et al.* 1960; Levich 1962). We note that the equivalence between the streaming-potential ( $\bar{\mathbf{K}}_P^c$ ) and electroosmotic ( $\bar{\mathbf{K}}_E^c$ ) cross-coupling dyadics is in accord with non-equilibrium thermodynamic considerations (DeGroot & Mazur 1969) (cf. (8.1)). The expressions

(6.37), (6.38a), (6.38b) give simply the results for the hydraulic permeability, streaming potential current and electroosmotic permeability for the case of Poiseuille flow between charged parallel plates in the presence of a homogeneous electric field.

(e) *Convective dispersion*

Equations (5.17)–(5.21) are solved in the present circumstances by

$$P_0^\infty = \frac{1}{\tau_0} \equiv \frac{1}{hL}. \quad (6.39)$$

Thus, 
$$\mathbf{J}_0^\infty = \frac{1}{hL}(\mathbf{v} + \mathbf{M}_E \cdot \mathbf{E}). \quad (6.40)$$

Substitute (5.7a), (6.2), (6.6), (6.16) and (6.36) into the above to obtain

$$\mathbf{J}_0^\infty = \mathbf{i}_x \frac{1}{hL} \left[ \frac{1}{2\mu_f} (y^2 - yh) \frac{d\bar{p}}{dx} - \frac{\varepsilon_f \zeta}{\mu_f} \bar{E} \left( 1 - \frac{\zeta_B}{\zeta} \right) \right]. \quad (6.41)$$

With use of the definition (5.16), the preceding expression affords the result

$$\bar{\mathbf{U}}^* = \bar{\mathbf{v}} + \bar{\mathbf{M}} \cdot \bar{\mathbf{E}}, \quad (6.42)$$

where (cf. (4.19), (6.37) and (6.38b))

$$\bar{\mathbf{v}} = -\mathbf{i}_x \left( \frac{h^2}{12\mu_f} \frac{d\bar{p}}{dx} + \frac{\varepsilon_f \zeta}{\mu_f} \bar{E} \right) \quad (6.43)$$

is the mean fluid velocity and

$$\bar{\mathbf{M}} = \mathbf{I} \varepsilon_f \zeta_B / \mu_f \quad (6.44)$$

the mean electrophoretic mobility of the charged sphere through the porous medium. This is the classical Smoluchowski formula (cf. (5.7a)).

The equations for the  $\mathbf{B}$ -field may be simplified by the *a priori* assumption:

$$\mathbf{B} = \mathbf{i}_x B(y) - (\mathbf{i}_x x + \mathbf{i}_y y). \quad (6.45)$$

Hence, from (5.22) to (5.24), we have, with the preceding findings,

$$D \frac{d^2 B}{dy^2} = - \left[ \frac{h^2}{12\mu_f} + \frac{1}{2\mu_f} (y^2 - yh) \right] \frac{d\bar{p}}{dx}, \quad (6.46)$$

subject to 
$$dB/dy = 0 \quad y = 0, h. \quad (6.47)$$

Here, we have used

$$\mathbf{D} = \mathbf{I} D, \quad D = \frac{kT}{6\pi\mu_f a}. \quad (6.48)$$

Equations (6.46) and (6.47) furnish the solution

$$\frac{dB}{dy} = - \frac{h^2}{D\mu_f} \left[ \frac{y}{12} + \frac{1}{2} \left( \frac{y^3}{3h^2} - \frac{y^2}{2h} \right) \right] \frac{d\bar{p}}{dx}. \quad (6.49)$$

Substitution of the above into (5.15) yields the known (Brenner & Edwards 1993) result

$$\bar{\mathbf{D}}^* = \mathbf{I} D + \mathbf{i}_x \mathbf{i}_x \frac{h^2}{210D} \left( \frac{h^2}{12\mu_f} \frac{d\bar{p}}{dx} \right)^2 \quad (6.50)$$

for the effective dispersivity dyadic of the solute through the layered medium. The

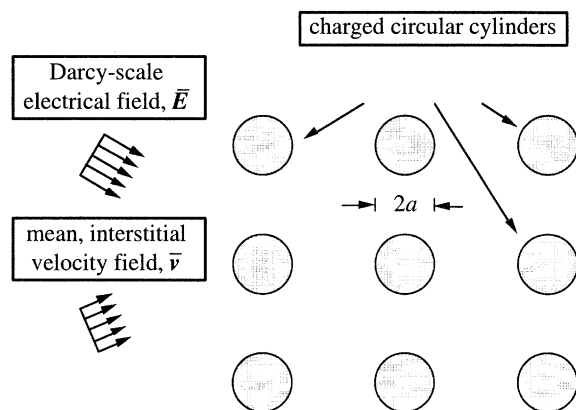


Figure 4. A two-dimensional porous medium composed of charged circular cylinders in a square array. A Newtonian liquid flows through the interstices with mean interstitial velocity  $\bar{v}$ . An electric field acts throughout the medium with Darcy-scale mean  $\bar{E}$ . The fields  $\bar{v}$  and  $\bar{E}$  are directed at arbitrary angles in the perpendicular plane to the axes of the cylinders.

absence of an electrical contribution to the above result for the effective dispersivity of the charged species through the porous medium owes to the homogeneity of the electrical-field-induced convective motion of the particle. This result is peculiar to the present problem. In particular, since the portion of the velocity field (cf. (6.32)) produced by the  $E$ -field does not depend upon local position within the porous medium,  $E$  fails to produce a dispersive effect, as mobile, charged particles will travel with the same  $E$ -driven velocities irrespective of their location within the medium.

## 7. Example 2: two-dimensional array of circular cylinders

This example possesses particular relevance to electrokinetic transductive phenomena in cartilagenous tissues (Frank & Grodzinsky 1987*a, b*), and offers an opportunity for direct comparison with the results of Eisenberg & Grodzinsky (1988).

Consider the two-dimensional porous medium depicted in figure 4, composed of non-conducting circular cylinders of radius  $a$  fixed within a spatially periodic array. For definiteness, the array is depicted as being square, though the manner of arrangement is unimportant for the dilute conditions of interest, i.e. for which the volume fraction of the cylindrical bed-particles  $\phi$  is very small,

$$\phi \ll 1. \quad (7.1)$$

The particles are presumed to be non-conducting, with uniform surface charge. Occupying the interstitial space is a conducting Newtonian fluid. The electrochemical double layers at the cylindrical particle surfaces are taken to be extremely thin, consistent with the preceding analysis. At the gross, Darcy-scale of the medium, uniform electrical  $\bar{E}$  and pressure-gradient  $\bar{\nabla} \bar{p}$  fields are applied.

Our aim is to calculate the Darcy-scale electromechanical properties ( $\bar{\sigma}$ ,  $\bar{K}$ ,  $\bar{K}_P^c$ ,  $\bar{K}_E^c$ ) of the medium to leading order in the bed-particle volume fraction  $\phi$ . This task proves more challenging (and illuminating) than the prior example owing to the complexity of the medium and the greater degree of transductive coupling that occurs. Because of the explicit separation that is made in the present theory between  $\bar{E}$ -induced and  $\bar{\nabla} \bar{p}$ -induced transport, combined with the configuration-specific na-

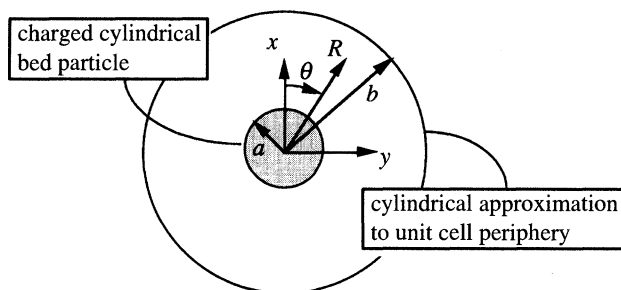


Figure 5. The unit cell periphery  $\partial\tau_0$  is approximated as being cylindrical, with the center of the cylindrical bed particle coinciding with the center of the cell.

ture of the microfields ( $\mathbf{g}$ ,  $\mathbf{h}$ ,  $\mathbf{V}$ ,  $\mathbf{V}^E$ ) appearing in the integrals (3.40a), (3.40b), (4.20) and (4.21), it is possible to solve for the dyadic quantities ( $\overline{\boldsymbol{\sigma}}$ ,  $\overline{\mathbf{K}}$ ,  $\overline{\mathbf{K}}_P^c$ ,  $\overline{\mathbf{K}}_E^c$ ) for arbitrarily oriented ( $\overline{\mathbf{E}}$ ,  $\overline{\nabla p}$ ), without specifying their magnitudes. This contrasts with the less formal scheme of Eisenberg & Grodzinsky (1988), to which comparison is to be frequently made in the subsequent analysis.

Owing to the smallness of the volume fraction  $\phi$ , the precise nature of the unit cell boundary  $\partial\tau_0$  is unimportant, at least to leading order in  $\phi$ . This affords a considerably simplified treatment of the various boundary-value problems encountered in the theory. In particular, it is useful to imagine the boundary of a unit cell to be cylindrical, of radius  $b$ . This configuration is shown in figure 5. We note that,

$$\phi = (a/b)^2. \quad (7.2)$$

#### (a) Determination of $\mathbf{V}(\mathbf{r})$ and $\overline{\mathbf{K}}$

Owing to the nature of ( $\boldsymbol{\Pi}$ ,  $\mathbf{V}$ ) as configuration-specific fields, independent of the orientation of any applied external field, and given the isotropic nature of the array, we have

$$\boldsymbol{\Pi}(\mathbf{r}) = \mathbf{0}, \quad (7.3)$$

$$\mathbf{V}(\mathbf{r}) = i_R i_R V_{RR}(R) + i_\phi i_\phi V_{\phi\phi}(R), \quad (7.4)$$

at least to leading order in  $\phi$ . Here, ( $i_R$ ,  $i_\phi$ ) represent unit vectors associated with the circular cylindrical coordinate system ( $R$ ,  $\phi$ ) shown in figure 5. Equations (4.13)–(4.15) therefore reduce to

$$\nabla^2 \mathbf{V} = \mathbf{I}, \quad (7.5)$$

$$\nabla \cdot \mathbf{V} = \mathbf{0}, \quad (7.6)$$

$$\mathbf{V} = \frac{\varepsilon_f \zeta}{\sigma_f} \nabla_s \mathbf{h} \quad \text{at } R = a, \quad (7.7)$$

$$\overline{\mathbf{K}} = -\frac{1}{\pi} \int_0^{2\pi} i_R i_R \cdot \mathbf{V} d\phi \quad \text{at } R = b. \quad (7.8)$$

The last condition at the periphery of the unit cell follows from the integral condition (4.20b): the integral condition itself derives from the spatially periodic character of  $\mathbf{V}$ , and effectively serves to replace the explicit condition (4.15b) in the present approximation.

In component form, (7.5)–(7.8) are found to reduce to the respective equations

$$\frac{d^2 V_{RR}}{dR^2} + \frac{1}{R} \frac{dV_{RR}}{dR} - \frac{2}{R^2} (V_{RR} - V_{\phi\phi}) = 1, \quad (7.9)$$

$$\frac{d^2 V_{\phi\phi}}{dR^2} + \frac{1}{R} \frac{dV_{\phi\phi}}{dR} + \frac{2}{R^2} (V_{RR} - V_{\phi\phi}) = 1, \quad (7.10)$$

$$\frac{dV_{RR}}{dR} + \frac{1}{R} (V_{RR} - V_{\phi\phi}) = 0, \quad (7.11)$$

$$V_{RR} = 0, \quad V_{\phi\phi} = \frac{\varepsilon_f \zeta}{\sigma_f a} h_R(a) \quad \text{at } R = a, \quad (7.12)$$

$$V_{RR} + V_{\phi\phi} = -2\bar{K} \quad \text{at } R = b. \quad (7.13)$$

(To obtain the condition (7.13) from (7.8) it is necessary to use the continuity condition (7.11) and maintain only the leading order term resulting from the integrand of (7.8).) Here,  $\bar{K} = |\bar{\mathbf{K}}|$ , and  $h_R(R)$  is a scalar field to be encountered (cf. (7.26)–(7.28)). Given the forms of these equations, it is useful to define the quantity

$$\eta \stackrel{\text{def}}{=} V_{RR} + V_{\phi\phi}. \quad (7.14)$$

Substitution into (7.9)–(7.13) reveals that the field  $\eta(R)$  satisfies the boundary value problem

$$\frac{d^2 \eta}{dR^2} + \frac{1}{R} \frac{d\eta}{dR} = 2, \quad (7.15)$$

$$\eta = \frac{\varepsilon_f \zeta}{\sigma_f a} h_R(a) \quad \text{at } R = a, \quad (7.16)$$

$$\eta = -2\bar{K} \quad \text{at } R = b, \quad (7.17)$$

possessing the solution

$$\eta = - \left[ \frac{2\bar{K} + \frac{1}{2}(a^2 + b^2) + \varepsilon_f \zeta h_R(a) / \sigma_f a}{\ln(b/a)} \right] \ln \left( \frac{R}{a} \right) + \frac{1}{2} (R^2 - a^2) + \frac{\varepsilon_f \zeta}{\sigma_f a} h_R(a). \quad (7.18)$$

Now, substitute (7.4) into (4.20) for the Darcy-scale permeability dyadic, and use the relations

$$\mathbf{i}_R = \mathbf{i}_x \cos \phi + \mathbf{i}_y \sin \phi, \quad \mathbf{i}_\phi = -\mathbf{i}_x \sin \phi + \mathbf{i}_y \cos \phi,$$

with  $(\mathbf{i}_x, \mathbf{i}_y)$  unit Cartesian basis vectors, to obtain

$$\bar{\mathbf{K}} = \mathbf{i}_x \mathbf{i}_x \bar{K}_{xx} + \mathbf{i}_y \mathbf{i}_y \bar{K}_{yy}, \quad (7.19)$$

where 
$$\bar{K}_{xx} = \bar{K}_{yy} \equiv \bar{K} = -\frac{1}{b^2} \int_a^b \eta(R) R dR. \quad (7.20)$$

Substitute (7.18) into the above expression to find (with, now,  $\phi$  the solid fraction defined by (7.2))

$$\bar{\mathbf{K}} \approx \frac{1}{4} b^2 [\ln(b/a) - 1] + O(\phi \ln \phi^{-1}). \quad (7.21)$$

The above result for the hydraulic permeability of the medium agrees with the leading-order result of Happel (1959). It agrees as well, to  $o(\phi \ln \phi^{-1})$ , with Eisenberg & Grodzinsky (1988), in the limiting cases of the latter study wherein there is no

surface conduction and the double layers are extremely thin. Higher-order deviations from the circular-cell results of Happel (1959) and Eisenberg & Grodzinsky (1988) are presumed to reflect the approximate nature of the cylindrical cell assumption used in theirs and our analyses.

(b) *Determination of  $\mathbf{h}(\mathbf{r})$  and  $\overline{\mathbf{K}}_P^c$*

The explicit solutions for  $V_{RR}$  and  $V_{\phi\phi}$  derive from substitution of the permeability result (7.21) into (7.18), followed by use of the decomposition (7.14), the continuity equation (7.11) and the boundary condition (7.12). This gives,

$$V_{RR} = -\frac{1}{4}(b^2 + a^2) \left[ \ln(R/a) - \frac{1}{2} \right] + \frac{1}{8}(R^2 - 2a^2) - \frac{1}{8}b^2a^2/R^2, \quad (7.22)$$

$$V_{\phi\phi} = -\frac{1}{4}(b^2 + a^2) \left[ \ln(R/a) + \frac{1}{2} \right] + \frac{1}{8}(3R^2 - 2a^2) + \frac{1}{8}(b^2a^2/R^2) + (\varepsilon_f \zeta h_R(a)/\sigma_f a). \quad (7.23)$$

The surface dyadic  $\mathbf{V}_s$ , whose definition is provided by (3.3d), may then be seen to possess the solution

$$\mathbf{V}_s = -i_\phi i_\phi \left[ \frac{1}{2a}(b^2 - a^2) + \frac{\rho_d^s}{\sigma_f a} h_R(a) \right] \quad (7.24)$$

by use of (7.4) with (3.1c), (7.22) and (7.23). This result enters the boundary condition (3.45b) for the  $\mathbf{h}(\mathbf{R})$  field. The latter is found to possess the form

$$\mathbf{h} = i_R h_R(R), \quad (7.25)$$

such that (3.44)–(3.45), with also (7.24) reduce to the respective equations

$$\frac{1}{R} \frac{d}{dR} \left( R \frac{dh_R}{dR} \right) - \frac{h_R}{R^2} = 0, \quad (7.26)$$

$$-\frac{dh_R}{dR} = \frac{\varepsilon_f \zeta}{a \mu_f} \left[ \frac{1}{2a}(b^2 - a^2) + \frac{\rho_d^s}{\sigma_f a} h_R(a) \right] \quad \text{at } R = a, \quad (7.27)$$

$$h_R = 0 \quad \text{at } R = b. \quad (7.28)$$

The latter condition follows from the integral condition (3.45d) (cf. (7.8) and the discussion thereof).

Equations (7.26)–(7.28) exhibit the solution

$$h_R = -\frac{\varepsilon_f \zeta}{2\mu_f} \left[ \frac{b^2 - a^2}{b^2(1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a) + a^2(1 + \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a)} \right] b \left( -\frac{b}{R} + \frac{R}{b} \right). \quad (7.29)$$

Substituting this result into (3.40b) and utilizing also (7.24) furnishes

$$\overline{\mathbf{K}}_P^c = i_x i_x \overline{\mathbf{K}}_{Pxx}^c + i_y i_y \overline{\mathbf{K}}_{Pyy}^c, \quad (7.30)$$

where 
$$\overline{\mathbf{K}}_{Pxx}^c = \overline{\mathbf{K}}_{Pyy}^c \approx \frac{\varepsilon_f \zeta}{1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a} + O(\phi). \quad (7.31)$$

This constitutes a leading-order approximate solution to the streaming-potential electromechanical coupling dyadic. As with (7.21), this result is found to be in leading-order agreement with the (zero surface conduction, very thin double layer) result of Eisenberg & Grodzinsky (1988) (observe that they report their results in terms of the fixed surface charge  $\rho_p^s$ , rather than the double-layer charge  $\rho_d^s$ , resulting in a sign flip in accordance with (3.1b, c)).

(c) Determination of  $\tilde{\mathbf{g}}(\mathbf{r})$  and  $\bar{\boldsymbol{\sigma}}$ 

We begin with the *a priori* postulate

$$\tilde{\mathbf{g}} = \mathbf{i}_R \tilde{g}_R(R), \quad (7.32)$$

such that (3.48)–(3.51) simplify to the respective equations

$$\frac{1}{R} \frac{d}{dR} \left( R \frac{d\tilde{g}_R}{dR} \right) - \frac{\tilde{g}_R}{R^2} = 0, \quad (7.33)$$

$$\frac{d\tilde{g}_R}{dR} + \left( \frac{\rho_d^s \varepsilon_f \zeta}{\mu_f \sigma_f a} \right) \tilde{g}_R = 1 + \frac{\rho_d^s \varepsilon_f \zeta}{\mu_f \sigma_f a} \quad \text{at } R = a, \quad (7.34)$$

$$\tilde{g}_R = 0 \quad \text{at } R = b. \quad (7.35)$$

The condition at the outer cell surface ( $R = b$ ), similar to condition (7.28), replaces the condition of spatial periodicity and is a direct consequence of (3.52).

Equations (7.33)–(7.35) have as their solution

$$\tilde{g}_R = \phi \left[ \frac{1 + \rho_d^s \varepsilon_f \zeta / \sigma_f \mu_f a}{1 - \rho_d^s \varepsilon_f \zeta / \sigma_f \mu_f a} \right] \left( -\frac{b^2}{R} + R \right) + O(\phi^2). \quad (7.36)$$

We note that

$$\nabla_s \tilde{\mathbf{g}} = \mathbf{i}_\phi \mathbf{i}_\phi \tilde{g}_R(a)/a,$$

whence, substitution of (7.36) into (3.53) is found to give

$$\bar{\boldsymbol{\sigma}} = \mathbf{i}_x \mathbf{i}_x \bar{\boldsymbol{\sigma}}_{xx} + \mathbf{i}_y \mathbf{i}_y \bar{\boldsymbol{\sigma}}_{yy}, \quad (7.37)$$

with

$$\bar{\boldsymbol{\sigma}}_{xx} = \bar{\boldsymbol{\sigma}}_{yy} \approx \sigma_f \left[ 1 - 2\phi \left( \frac{1 + \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a}{1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a} \right) \right] + O(\phi^2). \quad (7.38)$$

Equation (7.38) agrees, once again, with the comparable result of Eisenberg & Grodzinsky (1988) to terms of the indicated order.

(d) Determination of  $\mathbf{V}^E(\mathbf{r})$  and  $\bar{\mathbf{K}}_E^c$ 

The calculation of the electromechanical coupling dyadic  $\bar{\mathbf{K}}_E^c$  requires evaluation of the microscale dyadic  $\mathbf{V}(\mathbf{r})$ . As in (7.3) and (7.4), we begin with the initial, leading-order postulates

$$\boldsymbol{\Pi}^E(\mathbf{r}) = \mathbf{0}, \quad (7.39)$$

$$\mathbf{V}^E(\mathbf{r}) = \mathbf{i}_R \mathbf{i}_R V_{RR}^E(R) + \mathbf{i}_\phi \mathbf{i}_\phi V_{\phi\phi}^E(R). \quad (7.40)$$

Upon substituting the above into (4.16)–(4.18), we find

$$\frac{d^2 V_{RR}^E}{dR^2} + \frac{1}{R} \frac{dV_{RR}^E}{dR} - \frac{2}{R^2} (V_{RR}^E - V_{\phi\phi}^E) = 0, \quad (7.41)$$

$$\frac{d^2 V_{\phi\phi}^E}{dR^2} + \frac{1}{R} \frac{dV_{\phi\phi}^E}{dR} + \frac{2}{R^2} (V_{RR}^E - V_{\phi\phi}^E) = 0, \quad (7.42)$$

$$\frac{dV_{RR}^E}{dR} + \frac{1}{R} (V_{RR}^E - V_{\phi\phi}^E) = 0, \quad (7.43)$$

$$V_{RR}^E = 0 \quad \text{at } R = a, \quad (7.44a)$$

$$V_{\phi\phi}^E = -\varepsilon_f \zeta \left[ 1 + \frac{1 + \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a}{1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a} \right] \quad \text{at } R = a, \quad (7.44b)$$

$$V_{\phi\phi}^E + V_{RR}^E = -2\overline{K}_E^c \quad \text{at } R = b. \quad (7.45)$$

As in (7.14), define the scalar field

$$\eta^E \stackrel{\text{def}}{=} V_{RR}^E + V_{\phi\phi}^E, \quad (7.46)$$

and substitute this into the above to arrive at the boundary value problem

$$\frac{d^2 \eta^E}{dR^2} + \frac{1}{R} \frac{d\eta^E}{dR} = 0, \quad (7.47)$$

$$\eta^E = -\varepsilon_f \zeta \left[ 1 + \frac{1 + \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a}{1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a} \right] \quad \text{at } R = a, \quad (7.48)$$

$$\eta^E = -2\overline{K}_E^c \quad \text{at } R = b. \quad (7.49)$$

These yield the solution

$$\eta^E = \left\{ \frac{-2\overline{K}_E^c + 2\varepsilon_f \zeta (1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a)^{-1}}{\ln(b/a)} \right\} \ln \frac{R}{a} - 2\varepsilon_f \zeta \left( 1 - \frac{\rho_d^s \varepsilon_f \zeta}{\mu_f \sigma_f a} \right)^{-1}, \quad (7.50)$$

from which, upon substitution into (4.21) we ultimately find

$$\overline{K}_E^c = \mathbf{i}_x \mathbf{i}_x \overline{K}_{E_{xx}}^c + \mathbf{i}_y \mathbf{i}_y \overline{K}_{E_{yy}}^c, \quad (7.51)$$

where

$$\begin{aligned} \overline{K}_{E_{xx}}^c &= \overline{K}_{E_{yy}}^c \equiv K_E^c = -\frac{1}{b^2} \int_a^b \eta^E(R) R \, dR. \\ &\approx \frac{\varepsilon_f \zeta}{1 - \rho_d^s \varepsilon_f \zeta / \mu_f \sigma_f a} + O(\phi \ln \phi^{-1}). \end{aligned} \quad (7.52)$$

To the specified order, this result is identical both with the comparable result of Eisenberg & Grodzinsky (1988) and with the streaming-potential coefficient (7.31) obtained previously. Thus, as in the previous example (cf. (6.38)), we find identical expressions for the cross-coupling electromechanical transduction dyadics, in accordance with non-equilibrium thermodynamic constraints (DeGroot & Mazur 1969).

## 8. Recapitulation and discussion

In §§2–5 we derived, starting from an exact, microscale, physicochemical characterization of the periodic porous medium, the Darcy-scale electrokinetic transduction matrix

$$\begin{bmatrix} \overline{\mathbf{J}}_u \\ \overline{\mathbf{v}} \end{bmatrix} = \begin{bmatrix} \overline{\boldsymbol{\sigma}} & -\mu_f^{-1} \overline{\mathbf{K}}_P^c \\ -\mu_f^{-1} \overline{\mathbf{K}}_E^c & \mu_f^{-1} \overline{\mathbf{K}} \end{bmatrix} \cdot \begin{bmatrix} \overline{\mathbf{E}} \\ -\nabla \overline{p} \end{bmatrix}, \quad (8.1)$$

relating macroscale current flux  $\overline{\mathbf{J}}_u$  and mean interstitial velocity  $\overline{\mathbf{v}}$  to the applied electric  $\overline{\mathbf{E}}$  and pressure-gradient  $\nabla \overline{p}$  fields. In addition, we have offered an explicit scheme for calculating the convective  $\overline{\mathbf{U}}^*$  and dispersive  $\overline{\mathbf{D}}^*$  properties of the macroscale transport equation (2.9) for a charged, Brownian particle constrained to the interstitial space of the porous medium.



The material dyadics ( $\bar{\sigma}$ ,  $\bar{\mathbf{K}}$ ,  $\bar{\mathbf{K}}_p^c$ ,  $\bar{\mathbf{K}}_E^c$ ) have been respectively defined by (3.40a), (3.40b), (4.21a) and (4.20a) in terms of the four spatially dependent microscale fields ( $\mathbf{g}$ ,  $\mathbf{h}$ ,  $\mathbf{V}$ ,  $\mathbf{V}^E$ ). These latter directed field quantities are to be obtained by solution of the respective boundary value problems (3.41)–(3.42); (3.44)–(3.45); (4.16)–(4.18); (4.13)–(4.15). Below, we offer discussions of various properties of the macroscale ( $\bar{\sigma}$ ,  $\bar{\mathbf{K}}$ ,  $\bar{\mathbf{K}}_p^c$ ,  $\bar{\mathbf{K}}_E^c$ ) and microscale ( $\mathbf{g}$ ,  $\mathbf{h}$ ,  $\mathbf{V}$ ,  $\mathbf{V}^E$ ) fields by reference to their defining equations as well as to the examples worked out in §§6 and 7. (The macroscale convective–dispersive properties ( $\bar{\mathbf{U}}^*$ ,  $\bar{\mathbf{D}}^*$ ), which are related to the microscale fields ( $P_0^\infty$ ,  $\mathbf{B}$ ) by their defining relations (5.15) and (5.16), have been discussed elsewhere (Brenner & Edwards 1993).)

(a) *Conduction problem ( $\bar{\sigma}$ ,  $\mathbf{g}$ )*

The non-periodic microscale field  $\mathbf{g}(\mathbf{R})$  describes the local dependence of the voltage potential  $\Phi(\mathbf{R})$  upon the macroscopically uniform, applied field  $\bar{\mathbf{E}}$ . This may be seen from (3.38). Note, moreover, from (3.7) and (3.17), that for a purely homogeneous medium,  $\mathbf{E}(\mathbf{R}) = \text{const.} = \bar{\mathbf{E}}$ , whence  $\hat{\Phi} = \text{const.}$ , or

$$\Phi(\mathbf{R}) = -\mathbf{R} \cdot \bar{\mathbf{E}}.$$

Thus, for a homogeneous continuum

$$\mathbf{g} = -\mathbf{R}.$$

Recognition of this limiting behaviour proves helpful in the solution of specific problems. Equation (3.41), which governs the  $\mathbf{g}$ -field in the bulk fluid and particulate domains, reflects the fact that the porous medium is electrically neutral, exhibiting zero volumetric charge density. The continuity (3.42a) of the tangential component of  $\nabla \mathbf{g}$  is equivalent to a stipulation that  $\mathbf{g}$  (i.e.  $\Phi$ ) be continuous across the particulate surfaces  $s_p$ , whereas the normal component of  $\nabla \mathbf{g}$  at the charged particulate surfaces  $s_p$  of the porous medium may exhibit discontinuities owing to a surface current flux (cf. (3.42c)) into the bulk domains or simply a discontinuity of electrical conductivity. The production of net surface-excess charge at  $s_p$  is governed by (3.42b).

Whereas  $\nabla \mathbf{g}$  is spatially periodic,  $\mathbf{g}$  itself is not. It is in principle straightforward to show (see Brenner & Adler 1982) that for a fixed cell  $\{\mathbf{n}\}$ , the appropriate condition to be imposed on  $\mathbf{g}$  at the boundary of the cell is

$$\mathbf{g}(\mathbf{R}_n, \mathbf{r} + \mathbf{l}_i)|_{P_{+i}} - \mathbf{g}(\mathbf{R}_n, \mathbf{r})|_{P_{-i}} = -\mathbf{r}|_{P_{+i}} + \mathbf{r}|_{P_{-i}}, \quad (8.2)$$

where  $P_{+i}$  and  $P_{-i}$  are congruent points on opposite cell faces and  $\mathbf{l}_i$  are the basis lattice vectors introduced in (2.5). This complicating feature of the boundary value problem (3.41)–(3.42) is avoided in the alternative  $\tilde{\mathbf{g}}$ -problem (3.48)–(3.51).

In the case of a non-conducting particulate phase

$$\sigma_p = 0,$$

(3.42c) reduces to

$$-\mathbf{n} \cdot \nabla \mathbf{g} = \frac{\varepsilon_f}{\mu_f \sigma_f} \nabla_s \cdot (\zeta \nabla_s \mathbf{g}) \quad (\mathbf{R} \in s_p).$$

Spatial gradients in  $\mathbf{g}$  persist in the particulate domain in this case, corresponding to finite  $\mathbf{E}$ . On the other hand, for a perfectly conducting (e.g. metallic) particulate medium,

$$\sigma_p \rightarrow \infty,$$

we have that  $\mathbf{E}(\mathbf{R}) \rightarrow \mathbf{0}$  ( $\mathbf{R} \in V_p$ ), whence

$$\nabla g \rightarrow \mathbf{0} \quad (\mathbf{R} \in V_p).$$

However,  $\sigma_p \nabla g$  may not vanish (barring the case of an ideally polarizable particulate phase (Levich 1962)), and it is possible in this limit that condition (3.42a) will be violated owing to sharp voltage potential gradients in the thin double layer zone.

Observe the following equivalences between the macrotransport scheme (Brenner & Edwards 1993) for the effective diffusivity of an adsorbing solute in a spatially periodic porous medium and the electrical conduction problem characterized by (3.40a) and (3.41)–(3.42):

diffusion scheme microvariables	$\mathbf{b}(\mathbf{R})$	$D(\mathbf{R})$	$D_s(\mathbf{R})$	$\overline{\mathbf{D}}^*$
electrical conduction scheme microvariables	$\mathbf{g}(\mathbf{R})$	$\sigma(\mathbf{R})$	$-\rho_d^s(\mathbf{R})\varepsilon_f\zeta(\mathbf{R})/\mu_f$	$\overline{\sigma}$

Since  $-\rho_d^s\varepsilon_f\zeta/\mu_f$  is non-negative (cf. (3.1c)) for both positively and negatively charged surfaces, we may carry over the following conclusions for  $\overline{\sigma}$ , as described in detail by Brenner & Edwards (1993) for the diffusion equivalent  $\overline{\mathbf{D}}^*$ :

$$\left. \begin{array}{l} \overline{\sigma} \text{ symmetric} \quad (= \overline{\sigma}^\dagger) \\ \overline{\sigma} \text{ positive definite} \quad (\mathbf{u} \cdot \overline{\sigma} \cdot \mathbf{u} > 0). \end{array} \right\} \quad (8.3)$$

Here, the superscript  $\dagger$  denotes the transposition operator and  $\mathbf{u}$  is any non-zero vector.

(b) *Hydraulic permeability problem* ( $\overline{\mathbf{K}}, \mathbf{V}$ )

The microscale dyadic field  $\mathbf{V}(\mathbf{r})$ , from which the macroscale hydraulic permeability  $\overline{\mathbf{K}}$  is to be calculated via (4.20), is spatially periodic, satisfying the boundary-value problem (4.13)–(4.15). The field  $\mathbf{V}$  may be regarded as (the negative of) a local, pointwise-varying, microscale permeability, which for a completely homogeneous continuum is given, simply, by

$$\mathbf{V}(\mathbf{R}) = \text{const.} \equiv -\overline{\mathbf{K}}.$$

Particularly noteworthy is the boundary condition (4.15a), which corresponds to the ‘production’ of the micro-permeability quantity  $\mathbf{V}$  at the particulate surface. Physically, this condition reflects the fact that convection of fluid very near to the solid boundaries  $s_p$  owing to an applied pressure gradient, however minute this convection may be, gives rise to a finite surface current which in turn creates an appreciable ‘slip’ velocity near to the solid boundary in accordance with (3.3b).

The symmetry and positive-definiteness of  $\overline{\mathbf{K}}$  is easily established in the following manner. Dot multiply (4.13) with  $\mathbf{V}$  and utilize (4.14) to obtain

$$\mathbf{V} = \nabla \cdot [(\nabla \mathbf{V}) \cdot \mathbf{V}] - \nabla \mathbf{V} : \nabla \mathbf{V}^\dagger - \nabla \cdot (\mathbf{V} \mathbf{\Pi}).$$

Substitute this result into (4.20a) to find

$$\overline{\mathbf{K}} = \frac{1}{\tau_o} \int_{\tau_f} \nabla \mathbf{V} : \nabla \mathbf{V}^\dagger dV + \frac{1}{\tau_o} \int_{\tau_f} \nabla \cdot (\mathbf{V} \mathbf{\Pi}) \mathbf{V} dV - \frac{1}{\tau_o} \int_{\tau_f} \nabla \cdot [(\nabla \mathbf{V}) \cdot \mathbf{V}] dV.$$

Use the divergence theorem on the second and third integrals, use condition (4.15a)

and note the spatially periodic character of  $\mathbf{V}$  and  $\mathbf{\Pi}$  to deduce

$$\overline{\mathbf{K}} = \frac{1}{\tau_o} \int_{\tau_f} \nabla \mathbf{V} : \nabla \mathbf{V}^\dagger dV. \quad (8.4)$$

This result affords the immediate conclusion that

$$\left. \begin{array}{l} \overline{\mathbf{K}} \text{ symmetric} \quad (= \overline{\mathbf{K}}^\dagger) \\ \overline{\mathbf{K}} \text{ positive definite} \quad (\mathbf{u} \cdot \overline{\mathbf{K}} \cdot \mathbf{u} > 0). \end{array} \right\} \quad (8.5)$$

(c) *Electromechanical coupling problems* ( $\overline{\mathbf{K}}_P^c$ ,  $\mathbf{h}$ ) and ( $\overline{\mathbf{K}}_E^c$ ,  $\mathbf{V}^E$ )

Electromechanical coupling phenomena at the Darcy scale of the porous material, deriving from streaming current and/or electroosmotic phenomena at the micro-interstitial scale, are characterized by the dyadics ( $\overline{\mathbf{K}}_P^c$ ,  $\overline{\mathbf{K}}_E^c$ ), at the Darcy scale, and ( $\mathbf{h}$ ,  $\mathbf{V}^E$ ), at the microscale.

The spatially periodic vector field  $\mathbf{h}(\mathbf{R})$  satisfies (3.44)–(3.45). As follows from (3.38), it owes its existence to the susceptibility of the interstitial fluid phase to receive and conduct ‘streaming’ current away from the particulate surfaces (cf. (3.45*b*)). Streaming current refers to current induced by an applied pressure gradient owing to the convection of mobile double-layer ions. Even though the double layer is presumed in the analysis to be very thin, and, consequently, the (pressure-gradient-induced) velocity in this layer is very small, the double-layer excess charge (cf. (3.1*c*)) is inversely proportional to double-layer thickness  $1/\kappa$ , whence the surface-current ‘driving force’  $\mathbf{V}_s$  (cf. (3.3*d*)) is generally of finite magnitude. For a homogeneous medium, as well as in many applications (see e.g. §6), to within an arbitrary constant,

$$\mathbf{h}(\mathbf{r}) = \mathbf{0}.$$

The spatially periodic microscale dyadic field  $\mathbf{V}^E$  satisfies (4.16)–(4.18). Similar to the field  $\mathbf{V}$ , the dyadic  $\mathbf{V}^E$  may be viewed as a microscale electroosmotic permeability (note, however, the opposite sign), which for a completely homogeneous continuum is given by (cf. (4.21*a*))

$$\mathbf{V}^E(\mathbf{R}) = \text{const.} \equiv -\overline{\mathbf{K}}_E^c.$$

Electro-osmosis refers to the convection which accompanies the movement of double-layer ions owing to the action of an applied electric field.

On the basis of non-equilibrium-thermodynamic, Onsagger reciprocity (DeGroot & Mazur 1969), it has been argued (Frank & Grodzinsky 1987*b*) from a purely macroscopic point of view that

$$\overline{\mathbf{K}}_E^c = \overline{\mathbf{K}}_P^c.$$

While we have not succeeded in proving this equivalence in general, it is significant that for the two example problems outlined in §§6 and 7, this equivalence is in fact obeyed.

## 9. Future directions

We intend to use the present theory to calculate the electromechanical transductive properties ( $\overline{\boldsymbol{\sigma}}$ ,  $\overline{\mathbf{K}}$ ,  $\overline{\mathbf{K}}_P^c$ ,  $\overline{\mathbf{K}}_E^c$ ) for spherical-particle arrays in a future contribution. It is hoped to compare these results with the experimental measurements of Buschmann *et al.* (1992) for the streaming potential and hydraulic permeability of (approximately

spherical) chondrocyte cells, surrounded by charged, extracellular matrix, in agarose gels. Similar calculations for actual cartilage materials would appear to require an accurate microscale characterization of the cartilage medium, although the model of randomly oriented, charged cylinders – as suggested by Eisenberg & Grodzinsky (1988) – may provide a reasonable starting point.

Numerous practically significant extensions of the present article suggest themselves. Generalization to address the case of double layers of finite thickness is an obvious extension. Electrokinetic phenomena in cartilage material, for example, often involve separation distances between charged surfaces that are of the order of the Debye length (Grodzinsky 1983). A thorough examination of electrokinetic phenomena in cartilage material will, therefore, ultimately require consideration of the effects of finite double layers.

Charge-mediated transport of particles through a charged porous medium, as arises in the transport of macromolecules through the kidney's glomerular basement membrane, requires an extension of the theory either to include: (i) finite double layers; (ii) finite size of Brownian particle (cluster); (iii) a double layer thickness that is much smaller than the pore size, though larger or of the same order as the Brownian particle size. This latter extension, which introduces the possibility of the Brownian particle entering regions of non-zero charge density near charged, particulate surfaces, appears most straightforward to effect on the basis of the present article.

Application of the theory to the removal of waste materials from underground soils (Shapiro *et al.* 1989) entails a further extension to address the case of bulk and surface chemical reaction of the convecting/diffusing species. At least for the case of first-order irreversible chemical reactions, this extension may be accomplished by building upon the work of Shapiro & Brenner (1988).

A major application of the current theory is toward the elucidation of transdermal transport of charged and non-charged drugs in the presence of an electrical field. This application, which possesses large significance in regards to transdermal drug delivery (Langer 1990), has recently been pursued in the context of the present theory by Edwards & Langer (1994).

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