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A Phenomenological Approach to Modeling Transport in Porous Media

Jacob Bear^{1,2} and Leonid G. Fel¹

1) Dept. of Civil & Environmental Engineering, Technion-IIT, Haifa, Israel

2) Kinneret College on the Sea of Galilee, Zemach, Israel

Abstract

The objective of this article is to make use of the phenomenological approach in order to construct models for the transport of extensive quantities, such as mass of a fluid phase, mass of a component of a fluid phase, momentum of a phase and energy, in porous medium domains. Special attention is devoted to express the fluxes of these extensive quantities, especially the non-advective ones, as functions of their relevant driving forces, obeying the principle of minimum entropy production. It is shown that for each extensive quantity, we have a linear diffusive flux term, a non-linear diffusive term and a dispersive flux term. The latter is shown to be proportional to the velocity squared. In each case, the number of moduli that describe fluid and porous matrix properties is determined. The momentum balance equation for a porous medium domain, which is the "motion equation", is analyzed and simplified for special cases, leading to Darcy's law and to Brinkman's equation.

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List of main symbols

c^γ	Concentration of γ -chemical species.	T	Temperature.
\mathcal{D}	Molecular diffusivity.	t	time.
\mathcal{D}^*	Molecular diffusivity in a pm.	\mathbf{W}	$= \nabla \mathbf{V} + (\nabla \mathbf{V})^T$.
E	Extensive quantity (e.g., m , m^γ , \mathbf{M} , \mathcal{E}).	\mathbf{V}^E	Velocity of E .
\mathcal{E}	Energy.	\mathbf{V}	Velocity ($\equiv \mathbf{V}^m$).
e	Intensive quantity of E .	z	Vertical coordinate (pos. upward) .
\mathbf{F}	Force.	α	Subscript for α -phase.
$f_{\alpha \rightarrow \beta}^E$	Rate of transfer of E from α to β , per unit volume of pm.	$\boldsymbol{\tau}$	Shear stress.
f	Subscript for fluid.	Γ^E	Source of E per unit mass.
I	Internal energy per unit mass.	γ	Superscript for γ -species.
\mathbf{j}^E	Microscopic flux of E (...per unit flu. area).	Δ	Hydraulic radius.
\mathbf{J}^E	Macroscopic flux of E (...per unit flu. area).	θ_α	Volumetric fraction of α -phase.
\mathbf{J}_{pm}^E	Macroscopic flux of E (...per unit pm area).	λ	Thermal conductivity.
\mathbf{k}	Permeability.	λ_{pm}	Thermal conductivity of pm.
\mathbf{M}	Momentum ($= \rho \mathbf{V}$).	μ	Fluid viscosity.
m	Mass.	ρ	Density.
		$\boldsymbol{\sigma}$	Stress.

p	Pressure.	ϕ, ϕ^A	Porosity and areal porosity, respectively.
\dot{S}	Rate of entropy production.	ω^γ	Mass fraction of γ in fluid ($= \rho^\gamma/\rho$).
s	Subscript for solid		

1 Introduction

The phenomenological approach considered here involves the construction of macroscopic continuum models of phenomena in porous media on the basis of observable macroscopic variables only, avoiding their derivation from microscopic equations. Its aim is to provide an appropriate explanation of experimental observations of phenomena in the most simple way. This approach also ensures that the developed models are thermodynamically correct.

Here, we use of the phenomenological approach for the construction of *mathematical models* that describe phenomena of transport of *extensive quantities*, such as mass, momentum and energy of phases and phase components in a *porous medium* (henceforth, pm) *domain*. The latter, regarded as a single *continuum*, is composed of a *solid matrix* and a *void space*, with both subdomains distributed all over the pm domain. The void space is occupied by one or more fluids.

With no attempt to present a historical review, let us highlight a few points. Since Darcy's (1856) famous experiments in Dijon, that led to Darcy's law, models of transport of extensive quantities have been proposed and used. In earlier years, the focus was on single-phase mass flow. In later years, and nowadays, the efforts involve modeling of multi-transport phenomena, e.g., multiple phases, multiple (possibly) interacting chemical species, non-isothermal conditions and deformable porous media, often simultaneously. Various methods have been used to construct such models, written at the *porous medium* ($=$ *macroscopic*) *level*, starting from what happens at the *pore* ($=$ *microscopic*) *level*. Homogenization and REV averaging are examples. Our objective in this paper is to show how such models can be achieved by the *phenomenological approach*.

The phenomenological approach is not new. In fact, Darcy's law, obtained on the basis of sand column experiments, is a phenomenological law. In the area of groundwater flow, Dupuit (1848, 1863), Forchheimer (1886, 1901) and Boussinesq (1904), and many others, followed the same path. Richards (1931) extended Darcy's to unsaturated flow. In petroleum engineering, Muskat (1949) wrote the classical book on Physical Principles of Oil Production, in which Darcy's law was extended to two phase flow. Bear *et al* (1968, Sec. 1.6) presented a brief historical review on the development of the theory and applications of phenomena of transport in porous media. Most of the developments were based on the phenomenological approach. Approaches based on mixture

theory, REV averaging and homogenization started only around the a 1950's.

Even in earlier years, it was obvious that the core of any flow model is the balance equation of the fluid's mass. Accordingly, the development of any flow and transport model starts from the general balance equation for a considered extensive quantity, E , of a fluid in a spatial domain \mathcal{U} , bounded by a closed surface \mathcal{S} (*microscopic* level of description):

$$\left\{ \begin{array}{l} \text{Quantity of } E \\ \text{accumulating} \\ \text{in } \mathcal{U} \text{ during } \cdot \Delta t \end{array} \right\} = \left\{ \begin{array}{l} \text{Net quantity of } E \\ \text{entering } \mathcal{U} \\ \text{through } \mathcal{S} \text{ during } \cdot \Delta t \end{array} \right\} + \left\{ \begin{array}{l} \text{Net production of } E \\ \text{in } \mathcal{U} \\ \text{during } \Delta t \end{array} \right\}. \quad (1)$$

Written for an α -phase that occupies a volumetric fraction $\theta_\alpha (= \mathcal{U}_\alpha/\mathcal{U})$ of a control volume \mathcal{U} of a pm domain, and with the possibility that the considered E_α can cross any $\alpha - \beta$ interface, the above expression can be written in the form

$$\left\{ \begin{array}{l} \text{Quantity of} \\ E_\alpha \text{ accumulating} \\ \text{in } \mathcal{U} \\ \text{during } \Delta t \end{array} \right\} = \left\{ \begin{array}{l} \text{Net quantity of} \\ E_\alpha \text{ entering } \mathcal{U} \\ \text{through } \mathcal{S} \\ \text{during } \Delta t \end{array} \right\} + \left\{ \begin{array}{l} \text{Net quantity of} \\ E_\alpha \text{ entering } \mathcal{U}_\alpha \\ \text{through } \mathcal{S}_{\alpha\beta} \\ \text{during } \Delta t \end{array} \right\} + \left\{ \begin{array}{l} \text{Net production} \\ \text{of } E_\alpha \text{ in } \mathcal{U}_\alpha \\ \text{during } \Delta t \end{array} \right\} \quad (2)$$

When the last form of the balance equation is written for a small (e.g., parallelepiped) volume in a pm domain around a point, and for a small time interval, and then letting the volume and the time interval shrink to zero, the equation takes the form of a *partial differential equation* (PDE) that expresses the balance of E at a (*i.e., any*) point within the pm domain:

$$\frac{\partial \theta_\alpha e_\alpha}{\partial t} = -\nabla \cdot \theta_\alpha \mathbf{J}_{\alpha,tot}^E + f_{\beta \rightarrow \alpha}^E + \theta_\alpha \rho_\alpha \Gamma^E, \quad (3)$$

where e_α denotes E_α per unit volume of fluid α -phase. In this equation $\mathbf{J}_{\alpha,tot}^E$ denotes the *total* flux of E , *with* and *in* the moving α -phase, per unit phase area, $f_{\beta \rightarrow \alpha}^E$ denotes the rate at which E is transferred into the α -phase from all other (β -)phases, per unit volume of pm, and Γ_α^E is the rate of production of E per unit mass of the α -phase. This balance equation, obtained *phenomenologically*, describes the transport of any extensive quantity in an α -phase that occupies the entire void space or part of it, in a pm domain. Equation (3) is referred to as the *macroscopic* level. Appropriate expressions have to be provided for the flux, the transfer and the source terms. The term "flux" is used here to denote the quantity of E passing through a unit phase area per unit time.

For a specific E and α , this PDE is then written and solved for a specified pm domain geometry and initial and boundary conditions.

We wish to emphasize that every term in (3), as in all balance equations in this article, expresses what happens in the vicinity of a point in the pm domain (regarded as a continuum), in terms of values of state variables, that may be regarded as average values for some small domain around the

point, and coefficients that represent various aspects of the effects of the solid matrix configuration in that small domain.

As stated earlier, the objective of this paper is to write this equation for the specific cases of mass of a fluid phase, mass of a component of a fluid phase, momentum of a fluid phase, and energy of the pm as a whole, and, especially, to use the phenomenological approach in order to express the various fluxes, transfer and source terms that appear in these equations in terms of the *observable variables* of the transport problem. Here, variables are the density, the concentration of a chemical species, the pressure, and the temperature, and measurements or observations are implemented via appropriate instruments that provide the values of these variable "at a point", meaning "an average of the vicinity of the point". This is certainly true as the spatial variations of the values of these variables in the vicinity of any point can be approximated as linear. Furthermore, any local change in pressure, concentration and temperature tends to propagate quickly in the immediate vicinity, so that the measurement by an instrument provides a representative value at the point.

2 Specific Balance Equations

Based on the phenomenological macroscopic E -balance equation (3), following is a number of specific cases.

2.1 Mass of a fluid phase

For the mass of an α -fluid phase (density ρ_α) that occupies part the void space, at the volumetric fraction θ_α , since there are no α -mass sources *within* an α -phase, i.e., $\Gamma_\alpha^m = 0$, the α -fluid macroscopic mass balance equation takes the form

$$\frac{\partial \theta_\alpha \rho_\alpha}{\partial t} = -\nabla \cdot \theta_\alpha^A \mathbf{J}_{\alpha,tot}^m + f_{\beta \rightarrow \alpha}^m, \quad (4)$$

where $\mathbf{J}_{\alpha,tot}^m$ denotes the total α -mass flux (= mass per per unit time per unit area of α -phase), θ_α^A denotes the areal fraction of α in a cross-section, and $f_{\beta \rightarrow \alpha}^m$, denotes the rate of mass transfer from all β -phases to the α -phase, e.g., by evaporation or condensation, per unit volume of pm.

Note that we have made a distinction between the *porosity*, ϕ (= volume of void space per unit volume of pm), and the areal porosity, ϕ^A (= area of void in a planar cross-section, per unit area of cross section), and in the case of multiple phases between θ_α and θ_α^A , with $\phi^A = \phi^A(\nu_1, \nu_2, \nu_3)$, in which ν_1, ν_2, ν_3 denote the components of the unit vector, $\boldsymbol{\nu}$, normal to the considered cross-section. Nevertheless, it is usually assumed (as we shall do below) that $\phi \approx \phi^A$.

2.2 Mass of a chemical species in a fluid phase

We consider a chemical γ -species present in a fluid α -phase, occupying part of the void space. From (3), we obtain

$$\frac{\partial \theta_\alpha \rho_\alpha^\gamma}{\partial t} = -\nabla \cdot \theta_\alpha^A \mathbf{J}_{\alpha, tot}^{m^\gamma} + f_{\beta \rightarrow \alpha}^{m^\gamma} + \theta_\alpha \rho_\alpha \Gamma_\alpha^{m^\gamma}, \quad (5)$$

in which $\mathbf{J}_{\alpha, tot}^{m^\gamma}$ denotes the total flux of mass of γ with and in α , $f_{\beta \rightarrow \alpha}^{m^\gamma}$ denotes the rate of transfer of m^γ to the α -phase from the solid, and from another fluid phase, if present in the void space, across a fluid-fluid interface, e.g., by volatilization of γ , and $\Gamma_\alpha^{m^\gamma}$ may include such phenomena as radioactive decay or chemical reactions *within* the α -phase, in which γ is produced.

2.3 Momentum of a fluid phase

For the linear momentum, \mathbf{M} , of a fluid phase (f) that occupies the entire void space, the momentum balance equation takes the form:

$$\frac{\partial \phi \rho \mathbf{V}}{\partial t} = -\nabla \cdot \phi_\alpha^A \mathbf{J}_{tot}^{\mathbf{M}} + \mathbf{f}_{s \rightarrow f}^{\mathbf{M}} + \phi \rho \mathbf{\Gamma}^{\mathbf{M}}, \quad (6)$$

with $\mathbf{J}_{tot}^{\mathbf{M}}$ denoting the flux of momentum (per unit α -area), and $\mathbf{f}_{s \rightarrow f}^{\mathbf{M}}$ denoting the rate at which momentum is transferred from the solid phase to the fluid, across their common interface, per unit volume of pm. In the above equation, the source of momentum, $\mathbf{\Gamma}^{\mathbf{M}}$, is due to body (and other) forces (per unit mass of the phase). Note that the velocity, \mathbf{V} , has the meaning of *momentum per unit mass of the phase*.

If we are interested in the momentum balance equation for the pm as a whole, say in single phase flow, we write one equation for the fluid and one for the solid, and add them. The momentum exchange terms, $\mathbf{f}^{\mathbf{M}}$, will then vanish. Actually, in the phenomenological approach, we can write the momentum balance equation directly for the pm as a whole.

2.4 Energy of a fluid phase

For E representing the energy of a fluid that occupies the entire void space, $e = \rho (I + \frac{1}{2}V^2)$, i.e., the sum of the internal energy and the kinetic energy of the fluid, per unit fluid volume, but not potential energy, the energy balance equation is

$$\frac{\partial}{\partial t} \{ \phi \rho (I + \frac{1}{2}V^2) \} = -\nabla \cdot \phi^A \mathbf{J}_{tot}^{\mathcal{E}} + f_{s \rightarrow f}^{\mathcal{E}} + \phi \rho \Gamma^{\mathcal{E}}, \quad (7)$$

in which $\phi^A \mathbf{J}_{tot}^{\mathcal{E}}$ denotes the total energy flux carried *in and by* the fluid, by advection diffusion (\equiv heat conduction) and dispersion (per unit area of pm), $f_{s \rightarrow f}^{\mathcal{E}}$ denotes the energy (= heat) transferred

from the solid to the fluid across their common interface, per unit volume of pm, and $\phi\rho\Gamma^\varepsilon$ denotes the source of energy *within* the fluid (per unit volume of pm and per unit time).

Note that the potential energy is not included as we assume that gravity is the only body force.

Since we are interested in the energy balance equation for the pm as a whole, we can write (7) once for the fluid (f) and once for the solid (s) and sum up the two equations. The total interphase energy transfer term will vanish, and we shall obtain:

$$\frac{\partial}{\partial t} \sum_{(f,s)} \{ \theta_\alpha \rho_\alpha (I_\alpha + \frac{1}{2} V_\alpha^2) \} = -\nabla \cdot \mathbf{J}_{pm,tot}^\varepsilon + \sum_{(f,s)} \theta_\alpha \rho_\alpha \Gamma_\alpha^\varepsilon, \quad \mathbf{J}_{pm,tot}^\varepsilon = \sum_{(f,s)} \theta_\alpha^A \mathbf{J}_{\alpha,tot}^\varepsilon. \quad (8)$$

All (macroscopic) balance equations in this section have been obtained strictly by phenomenological considerations, without resorting to any averaging technique. They contain fluxes, rates of interphase transfers and sources of the considered E 's, which will now be discussed in detail.

3 Fluxes

At the microscopic level of description, the total flux of E , \mathbf{j}_{tot}^E , is defined as $\mathbf{j}_{tot}^E = e\mathbf{V}^E$. This flux can be decomposed:

$$\mathbf{j}_{tot}^E = e\mathbf{V}^E = e\mathbf{V} + e(\mathbf{V}^E - \mathbf{V}) = \mathbf{j}_{adv}^E + \mathbf{j}_{dif}^E, \quad \rho\mathbf{V} = \sum_{(\gamma)} \rho^\gamma \mathbf{V}_\alpha^\gamma,$$

i.e., the sum of an *advective flux* carrying E at the fluid's (mass weighted) velocity, $\mathbf{V} (\equiv \mathbf{V}^m)$, and a *diffusive flux*, resulting from molecular motion, associated with the difference $(\mathbf{V}^E - \mathbf{V})$.

3.1 Advective fluxes

At the macroscopic level, with $\mathbf{V} (\equiv \mathbf{V}_f)$ denoting the fluid's average mass weighted velocity, the advective fluxes in a pm domain (per unit area of fluid phase), associated with the movement of the fluid, but not with any other driving force, are:

- **Mass of a fluid phase:** $e = \rho$, $\mathbf{J}_{adv}^m = \rho\mathbf{V}$. We may regard \mathbf{V} as a *momentum per unit mass*. Then it is a state variable, like ρ and ρ^γ and we need to include the momentum balance equation in the set of equations to be solved for these variables. Another option is to regard $\mathbf{J}^m (\equiv \rho\mathbf{V})$ as a flux driven by the force ∇p . Then, we use the generic terms in the polynomial representation of \mathbf{J}_{adv}^m

$$\mathbf{J}_{adv,i}^m = a'_{ij} \nabla_j p + b'_{ijk} \nabla_i p \nabla_k p + \dots, \quad (9)$$

where the coefficients are functions of the fluid properties ρ, μ and of the geometry of the void space. For sufficiently small ∇p , only the first term on the r.h.s. is significant, leading to the linear Darcy's law. For higher values of ∇p , the second term is added and we obtain an expression which is analogous to the Dupuit(1863)–Forchheimer (1930) non-linear flux law (actually, they wrote $\nabla p = a\phi\mathbf{V} + b(\phi\mathbf{V})^2$). The option of \mathbf{V} as a momentum density is considered in this article.

- **Mass of a chemical species in a fluid phase:** $e = \rho^\gamma, \mathbf{J}_{adv}^{m^\gamma} = \rho^\gamma\mathbf{V}$.
- **Momentum of a fluid phase** $e = \rho\mathbf{V}, \mathbf{J}_{adv}^M = \rho\mathbf{V}\mathbf{V}$.
- **Energy of a pm:** Assuming that only the fluid phase in motion, we have:

$$\mathbf{J}_{adv}^\varepsilon = \rho \left(I + \frac{1}{2}V^2 \right) \mathbf{V}.$$

3.2 Diffusive fluxes

For the macroscopic diffusive fluxes, we have:

- **Mass of a fluid phase:** $e = \rho, \mathbf{J}_{dif}^m = \rho(\mathbf{V} - \mathbf{V}) \equiv 0$, i.e., no diffusion of the total mass.
- **Mass of a chemical species in a fluid phase:** $e = \rho^\gamma$. In analogy to Fick's law in a fluid, and with a driving force, which is the gradient of (average) species concentration, expressed by the mass fraction of the species, $\omega^\gamma (\equiv \rho^\gamma/\rho)$, the macroscopic diffusive flux is $\mathbf{J}_{dif}^{m^\gamma} = -\rho\mathcal{D}_{pm}\nabla\omega^\gamma$, in which \mathcal{D}_{pm} denotes the *macroscopic coefficient of molecular diffusion*. It is a second rank tensor that can be expressed, for example, as the product of the scalar molecular diffusivity in a fluid continuum, and a void space geometrical property, \mathbf{T} , often called *tortuosity*, which is a second rank tensor, $\mathcal{D}_{pm} = \mathbf{T}\mathcal{D}$
- **Momentum of a fluid phase:** $e = \rho\mathbf{V}, \mathbf{J}_{dif}^M = \rho\mathbf{V}(\mathbf{V}^M - \mathbf{V}) = -\boldsymbol{\sigma}$, in which $\boldsymbol{\sigma} (\equiv \boldsymbol{\tau} - p\boldsymbol{\delta})$ denotes the stress in the fluid, $\boldsymbol{\tau}$ is the *shear or deviatoric stress* in the fluid phase, p is pressure and $\boldsymbol{\delta}$ denotes the *unit tensor*.

In the momentum balance equation (6), we can express the first term on the r.h.s. in the form

$$\nabla \cdot \phi^A \mathbf{J}_{adv+dif}^M \equiv \nabla \cdot \phi^A (\rho\mathbf{V}\mathbf{V} - \boldsymbol{\tau}) + \nabla \cdot \phi^A p\boldsymbol{\delta},$$

in which the $-\phi^A\boldsymbol{\tau}$ expresses the *diffusive flux of momentum*. since only $\boldsymbol{\tau}$ is contributing to the dissipation of energy.

- **Energy of a fluid phase:** $e_f = \rho_f(I_f + \frac{1}{2}\rho_f V_f^2), \mathbf{J}_{f,dif}^\varepsilon = \rho_f \left(I_f + \frac{1}{2}V_f^2 \right) (\mathbf{V}_f^\varepsilon - \mathbf{V}_f)$. At the microscopic level, i.e., in a phase continuum, the *diffusive* (\equiv *conductive*) energy flux is expressed by Fourier's law, $\mathbf{j}_{f,dif}^\varepsilon \equiv e^\varepsilon(\mathbf{V}_f^\varepsilon - \mathbf{V}) = -\lambda\nabla T$, in which T denotes the temperature, and λ denotes the thermal conductivity of the phase. By the phenomenological approach, at the macroscopic level,

in the fluid, the diffusive energy flux, driven by ∇T takes the form $\mathbf{J}_{f,dif}^E = -\boldsymbol{\lambda}_f^* \cdot \nabla T$, in which the $\boldsymbol{\lambda}_f^*$ denotes the macroscopic thermal conductivity within the fluid phase inside the void space.

For the pm as a whole, the diffusive flux of energy is expressed as $\mathbf{J}_{pm,dif}^E = -\boldsymbol{\lambda}_{pm} \cdot \nabla T$, in which $\boldsymbol{\lambda}_{pm}$ denotes the thermal conductivity for the pm as a whole, i.e., through the *composite material* composed of the solid matrix and the fluid occupying the void space. Thus, $\boldsymbol{\lambda}_{pm}$ depends on both λ_f and λ_s and on the configuration of the two phases in the pm domain.

Altogether, we have 3 driving forces: $\nabla\omega^\gamma$ for the diffusive mass of a species, $\nabla\mathbf{V} + (\nabla\mathbf{V})^T$ (see below) for the diffusive flux of momentum and ∇T for the diffusive flux of energy.

3.3 Dispersive fluxes

Around the 1950's, mainly in dealing with the quality of groundwater in aquifers, as associated with dissolved chemical species, it was noted (e.g., summary in Bear, 1972, Sec. 10.3), both in field experiments and in laboratory experiments, that a dissolved species is transported in a pm domain, both in the general direction of the flow and also normal to it, in a way that *could not be explained merely by the movement of the fluid at its average velocity and by molecular diffusion*. This phenomenon was called *dispersion*. To bridge the discrepancy, an additional flux was introduced at the macroscopic level—the *dispersive flux*. It became obvious that this additional flux is not a real flux, like the two fluxes—advective and diffusive—discussed above; *it does not exist at the microscopic level. It is a flux that has to be added in order to compensate for the fact that the advective transport of the solute at the macroscopic level is described in terms of the volume averaged velocity (and this was done because Darcy's law provides this velocity), while, actually, within the void space, the solute is transported at every (microscopic) point by the local microscopic velocity*. All this is in addition to molecular diffusion, which is also included in the macroscopic description. Altogether, the *total macroscopic flux* of a solute is expressed as the sum:

$$\mathbf{J}^{m^\gamma} = \mathbf{J}_{adv}^{m^\gamma} + \mathbf{J}_{dis}^{m^\gamma} + \mathbf{J}_{dif}^{m^\gamma}. \quad (10)$$

The dispersive flux will be considered below.

Although (10) is written for $E = m^\gamma$, it is applicable for any E .

• Dispersive flux of a solute

Over the years, research, using a variety of models, has led to various expressions that describe the dispersive flux of a solute; not much research efforts have been devoted to the dispersion of momentum and energy, although, in principle, this kind of flux should be present in the respective (macroscopic) balance equation models.

The term Fickian expression has often been used, because of its resemblance to Ficks law for molecular diffusion, i.e., a flux proportional to the gradient of concentration. In recent years, some researchers, on the basis of field observations of plume development in aquifers, have proposed various non-Fickian alternative approaches to the determination of plume shape.

In what follows, we shall employ the phenomenological approach to suggest an expression for the dispersive flux, based on the observation that this flux must depend on the velocity (no dispersion if $\mathbf{V} = 0$) and on the driving force $\nabla\omega^\gamma$ (no dispersion if $\nabla\omega^\gamma = 0$).

Although the discussion in this section has been devoted to the dispersive flux of a solute, the same phenomenon of dispersive flux is present also in the cases of transport of energy and of momentum.

3.4 Non-advective fluxes

Within the framework of the phenomenological approach to modeling transport in pm, we shall now derive expressions for the fluxes of extensive quantities, *other than the advective fluxes*; these are the diffusive and dispersive fluxes mentioned above. We shall start with the flux of a solute. The same approach will then be applied to the fluxes of other extensive quantities.

• Non-advective solute flux

We make use of the generic terms in the *polynomial representation* of the total (macroscopic) flux of a γ -species in a fluid phase. The total non-advective flux of γ , \mathbf{J}^γ , is produced by (1) the velocity of the fluid phase, \mathbf{V} , and (2) the *driving force* represented by $-\nabla\omega^\gamma$; the two are *independent* of each other. The flux is, thus, a smooth function of these two, factors, $\mathbf{J}^\gamma = \mathbf{J}^\gamma(\rho, \mathbf{V}, \nabla\omega^\gamma)$.

Developing this functional relationship in a power series, up to third order terms, we obtain:

$$\begin{aligned} J_i^\gamma(\rho, \nabla\omega^\gamma, \mathbf{V}) &= A_{ik} \nabla_k \omega^\gamma + B_{ikl} \nabla_k \omega^\gamma \nabla_l \omega^\gamma + C_{ikl} V_l \nabla_k \omega^\gamma \\ &+ D_{iklm} \nabla_k \omega^\gamma \nabla_l \omega^\gamma \nabla_m \omega^\gamma + E_{iklm} V_k \nabla_l \omega^\gamma \nabla_m \omega^\gamma + G_{iklm} V_l V_m \nabla_k \omega^\gamma, \end{aligned} \quad (11)$$

in which the various coefficients (A_{ik}, B_{ikl} , etc.) include the effect of ρ . As everywhere else, the Einstein summation convention is employed (e.g., $A_{ik} \nabla_k \omega^\gamma \equiv \sum_{(k)} A_{ik} \nabla_k \omega^\gamma$). The various $A, B, \dots G$'s are tensorial coefficients that are associated with fluid and pm properties, i.e, the geometry of the void space configuration; in multiphase flow these coefficients depend also on fluid saturation.

In thermodynamics, the *rate of entropy production*, $\dot{\mathcal{S}}$, is related to the *thermodynamic driving force*, \mathbf{X} , and to the *thermodynamic flux*, \mathbf{Y} by $\dot{\mathcal{S}} = Y_i X_i$ (De Groot and Mazur, 1962, p. 65). Furthermore, the rate of entropy production must be positive, i.e., $\dot{\mathcal{S}} \geq 0$. Here, the solute flux,

\mathbf{J}^γ is driven by $-\nabla\omega^\gamma$, which acts as a "driving force". Thus, in this case, $\mathbf{X} = -\nabla\omega^\gamma$, and its conjugate flux is $\mathbf{Y} = -\mathbf{J}^\gamma$. Altogether, we have

$$\begin{aligned} \dot{\mathcal{S}}(\rho, \nabla\omega^\gamma, \mathbf{V}) &= A_{ik} \nabla_i \omega^\gamma \nabla_k \omega^\gamma + B_{ikl} \nabla_i \omega^\gamma \nabla_k \omega^\gamma \nabla_l \omega^\gamma + C_{ikl} \nabla_i \omega^\gamma \nabla_k \omega^\gamma V_l \\ &+ D_{iklm} \nabla_i \omega^\gamma \nabla_k \omega^\gamma \nabla_l \omega^\gamma \nabla_m \omega^\gamma + E_{iklm} \nabla_i \omega^\gamma \nabla_k \omega^\gamma \nabla_l \omega^\gamma V_m + G_{iklm} \nabla_i \omega^\gamma \nabla_k \omega^\gamma V_l V_m. \end{aligned} \quad (12)$$

Note that we have extended the construction of $\dot{\mathcal{S}}$, as proposed by de Groot and Mazur (1962), for a flux linearly proportional to a driving force, to the nonlinear case considered here.

The requirement that $\dot{\mathcal{S}}$ be positive definite, i.e., $\dot{\mathcal{S}} \geq 0$, leaves in (12) only the quadratic and the two quartic terms,

$$\dot{\mathcal{S}}(\rho, \nabla\omega^\gamma, \mathbf{V}) = A_{ik} \nabla_i \omega^\gamma \nabla_k \omega^\gamma + D_{iklm} \nabla_i \omega^\gamma \nabla_k \omega^\gamma \nabla_l \omega^\gamma \nabla_m \omega^\gamma + G_{iklm} \nabla_i \omega^\gamma \nabla_k \omega^\gamma V_l V_m \geq 0. \quad (13)$$

In (13), we note that certain symmetries exist in the three tensors \mathbf{A} , \mathbf{D} and \mathbf{G} :

$$A_{ik} = A_{ki}^1, \quad D_{iklm} = D_{kilm} = \dots = D_{ilmk}, \quad G_{iklm} = G_{kilm} = G_{ikml} = G_{lmik}, \quad (14)$$

where the tensor D_{iklm} is invariant under every permutation of the full *symmetric group* \mathcal{S}_4 .

Thus, with (13), and since

$$\dot{\mathcal{S}} = \langle \mathbf{J}^\gamma, \nabla\omega^\gamma \rangle, \quad (15)$$

in which $\langle \mathbf{V}_1, \mathbf{V}_2 \rangle$ denotes the scalar product of the vectors \mathbf{V}_1 and \mathbf{V}_2 , it follows that the non-advective flux is expressed as

$$J_{non-adv,i}^\gamma = -A_{ik} \nabla_k \omega^\gamma - D_{iklm} \nabla_k \omega^\gamma \nabla_l \omega^\gamma \nabla_m \omega^\gamma - G_{iklm} \nabla_k \omega^\gamma V_l V_m. \quad (16)$$

The first two terms on the r.h.s. of (16) do not involve the velocity. They describe *diffusion*. The first term is actually the diffusive flux expressed by Fick's law, with $A_{ik} \equiv \rho \mathcal{D}_{ij}^*$. The second term represents a non-linear, or "non-Fickian" diffusive flux. The last term expresses the *dispersive flux* discussed above, with $-\nabla\omega^\gamma$ as the driving force, but with a proportionality to V^2 . This may be still considered a "Fickian" law, but it is different from the Fickian expression mentioned in Sec. 3.3, in that here the flux depend on V^2 . It may be interesting to mention that in one of the earliest works on dispersion, the work of Taylor (1953), concerning dispersion in a capillary tube, the dispersive flux was also proportional to V^2 .

A detailed analysis of the tensors \mathbf{A} , \mathbf{D} and \mathbf{G} in a 3-dimensional pm domain with a prescribed symmetry (e.g., isotropic, axisymmetric) shows that the increase in symmetry towards isotropy causes a reduction in the number of independent moduli associated with these tensorial coefficients.

For an isotropic pm – highest symmetry – we need *four* moduli for the description of the three tensorial coefficients:

$$A_{ik} = a\delta_{ik}, \quad D_{iklm} = \frac{d}{3}(\delta_{ik}\delta_{lm} + \delta_{il}\delta_{km} + \delta_{im}\delta_{kl}), \quad G_{iklm} = g_1\delta_{ik}\delta_{lm} + \frac{g_2}{2}(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl}), \quad (17)$$

$$\dot{\mathcal{S}}(\rho, \nabla\omega^\gamma, \mathbf{V}) = a(\nabla\omega^\gamma)^2 + d(\nabla\omega^\gamma)^4 + g_1(\nabla\omega^\gamma)^2\mathbf{V}^2 + g_2\langle\nabla\omega^\gamma, \mathbf{V}\rangle^2, \quad (18)$$

with $a, d, g_1, g_2 > 0$, and the non-advective flux presented above as (16) taking the form

$$J_{non-adv,i}^\gamma(\nabla\omega^\gamma, \mathbf{V}) = -a\nabla_i\omega^\gamma - d(\nabla\omega^\gamma)^2\nabla_i\omega^\gamma - (g_1\mathbf{V}^2\nabla_i\omega^\gamma + g_2\langle\nabla\omega^\gamma, \mathbf{V}\rangle V_i). \quad (19)$$

Again, in this equation, the first term expresses linear diffusion, the second term expresses non-linear diffusion, and the last term expresses the dispersive flux of γ . In (19), we note the driving force, $\nabla\omega^\gamma$ and the dependence on V^2 .

For *axisymmetric* pm domains, with the axis of symmetry indicated by the unit vector \mathbf{e} , we need *eleven* (2+3+6) moduli to describe these 3 tensorial coefficients

$$\begin{aligned} \dot{\mathcal{S}}(\rho, \nabla\omega^\gamma, \mathbf{V}, \mathbf{e}) &= a_1(\nabla\omega^\gamma)^2 + a_2\langle\nabla\omega^\gamma, \mathbf{e}\rangle^2 + d_1(\nabla\omega^\gamma)^4 + 2d_2(\nabla\omega^\gamma)^2\langle\nabla\omega^\gamma, \mathbf{e}\rangle^2 + d_3\langle\nabla\omega^\gamma, \mathbf{e}\rangle^4 \\ &+ g_1\mathbf{V}^2(\nabla\omega^\gamma)^2 + g_2\langle\nabla\omega^\gamma, \mathbf{V}\rangle^2 + g_3\mathbf{V}^2\langle\nabla\omega^\gamma, \mathbf{e}\rangle^2 + g_4\langle\mathbf{e}, \mathbf{V}\rangle^2(\nabla\omega^\gamma)^2 \\ &+ g_5\langle\mathbf{e}, \mathbf{V}\rangle\langle\mathbf{V}, \nabla\omega^\gamma\rangle\langle\nabla\omega^\gamma, \mathbf{e}\rangle + g_6\langle\mathbf{e}, \mathbf{V}\rangle^2\langle\mathbf{e}, \nabla\omega^\gamma\rangle^2, \end{aligned} \quad (20)$$

with the following thermodynamic constraints imposed on the eleven moduli:

$$a_1, a_2 > 0, \quad d_1, d_3 > 0, \quad d_1d_3 > (d_2)^2,$$

and, similar to the results obtained in Fel and Bear (2010),

$$g_1 > 0, \quad g_1 + g_2 > 0, \quad g_1 + g_3 > 0, \quad g_1 + g_4 > 0, \quad g_1 + g_2 + g_3 + g_4 + g_5 + g_6 > 0,$$

$$(g_1)^2 + g_1(3g_2 + g_3 + g_4 + g_5 + g_6) + 2g_2(g_3 + g_4 + g_6) > \frac{1}{2}(g_5)^2.$$

The non-advective momentum flux is:

$$\begin{aligned} J_{non-adv,i}^\gamma(\rho, \nabla\omega^\gamma, \mathbf{V}, \mathbf{e}) &= a_1\nabla_i\omega^\gamma + a_2\langle\nabla\omega^\gamma, \mathbf{e}\rangle e_i \\ &+ d_1(\nabla\omega^\gamma)^2\nabla_i\omega^\gamma + d_2((\nabla\omega^\gamma)^2e_i + \langle\nabla\omega^\gamma, \mathbf{e}\rangle^2\nabla_i\omega^\gamma) + d_3\langle\nabla\omega^\gamma, \mathbf{e}\rangle^3e_i \\ &+ g_1\mathbf{V}^2\nabla_i\omega^\gamma + g_2\langle\nabla\omega^\gamma, \mathbf{e}\rangle V_i + g_3\mathbf{V}^2\langle\nabla\omega^\gamma, \mathbf{e}\rangle e_i + g_4\langle\mathbf{e}, \mathbf{V}\rangle^2\nabla_i\omega^\gamma \\ &+ g_5\langle\mathbf{e}, \mathbf{V}\rangle(\langle\mathbf{V}, \nabla\phi\rangle e_i + \langle\nabla\omega^\gamma, \mathbf{e}\rangle V_i) + g_6\langle\mathbf{e}, \mathbf{V}\rangle^2\langle\mathbf{e}, \nabla\omega^\gamma\rangle e_i, \end{aligned} \quad (21)$$

in which the first two terms describe the linear diffusive flux, with the tensorial coefficient of diffusion depending on two scalar moduli, a_1, a_2 . The next three terms, with moduli d_1, d_2 and d_3 ,

describe the nonlinear diffusive flux components. The remaining terms describe the dispersive flux. We note that for this axially symmetric pm, the dispersivity coefficient is defined by six dispersivity moduli, g_1, \dots, g_6 .

• **Non-advective momentum flux**

At the microscopic level, i.e., in a fluid continuum, the deviatoric stress, τ_{ij} , which expresses the dissipative part of the diffusive momentum flux, is related to the driving force $W_{ij} (\equiv \nabla_i V_j + \nabla_j V_i)$, which is a symmetric 2nd rank tensor. With this in mind, at the macroscopic level, the non-advective flux of momentum depends on the fluid's velocity, \mathbf{V} , and on a driving force, \mathbf{W} , by the general constitutive relation

$$\tau_{ij} = \tau_{ij}(\mathbf{W}, \mathbf{V}) = M_{ijkl} W_{kl} + N_{ijklpstr} W_{kl} W_{ps} W_{tr} + L_{ijklps} W_{kl} V_p V_s, \quad (22)$$

where $M_{ijkl} = M_{jikl} = M_{jilk} = M_{ijlk}$, $N_{ijklpstr} = N_{jiklpstr} = \dots = N_{trijklps}$ and $L_{ijklps} = L_{jiklps} = L_{ijklps} = L_{klijps} = L_{ijklsp}$ are tensorial coefficients that depend on fluid and void-space properties.

The first term on the r.h.s. represents the linear diffusive flux of momentum, with the 4th rank tensor M_{ijkl} standing for the usual fluid viscosity for a Newtonian fluid. The second term, with the 8th rank tensorial coefficient, $N_{ijklpstr}$, is responsible for non-linear viscous effects. The dispersive part of the non-advective momentum flux involves the 6th rank tensorial coefficient L_{ijklps} .

The corresponding rate of entropy production is:

$$\dot{S}(\mathbf{W}, \mathbf{V}) = \tau_{ij} W_{ij} = M_{ijkl} W_{ij} W_{kl} + N_{ijklpstr} W_{ij} W_{kl} W_{ps} W_{tr} + L_{ijklps} W_{ij} W_{kl} V_p V_s. \quad (23)$$

To facilitate the presentation of (23) for an isotropic pm, we introduce the following notations for operations with the \mathbf{W} -tensor,

$$\begin{aligned} \langle \mathbf{W}, \boldsymbol{\delta} \rangle &\equiv W_{ii}, & \langle \mathbf{W}, \mathbf{W} \rangle &\equiv W_{ij} W_{ji}, & \langle \mathbf{W}, \mathbf{W}, \mathbf{W} \rangle &\equiv W_{ij} W_{jk} W_{ki}, \\ \langle \mathbf{W}, \mathbf{W}, \mathbf{W}, \mathbf{W} \rangle &\equiv W_{ij} W_{jk} W_{kl} W_{li}, & \langle \mathbf{WV}, \mathbf{WV} \rangle &\equiv W_{ij} V_j W_{ik} V_k. \end{aligned} \quad (24)$$

With this notation, we get *eleven* (2+5+4) viscous moduli,

$$\begin{aligned} \dot{S}(\mathbf{W}, \mathbf{V}) &= M_1 \langle \mathbf{W}, \mathbf{W} \rangle + M_2 \langle \mathbf{W}, \boldsymbol{\delta} \rangle^2 \\ &+ N_1 \langle \mathbf{W}, \mathbf{W} \rangle^2 + N_2 \langle \mathbf{W}, \mathbf{W}, \mathbf{W}, \mathbf{W} \rangle + N_3 \langle \mathbf{W}, \mathbf{W}, \mathbf{W} \rangle \langle \mathbf{W}, \boldsymbol{\delta} \rangle + N_4 \langle \mathbf{W}, \mathbf{W} \rangle \langle \mathbf{W}, \boldsymbol{\delta} \rangle^2 \\ &+ N_5 \langle \mathbf{W}, \boldsymbol{\delta} \rangle^4 + L_1 \langle \mathbf{W}, \mathbf{W} \rangle \mathbf{V}^2 + L_2 \langle \mathbf{WV}, \mathbf{WV} \rangle + L_3 \langle \mathbf{V}, \mathbf{W}, \mathbf{V} \rangle \langle \mathbf{W}, \boldsymbol{\delta} \rangle + L_4 \langle \mathbf{W}, \boldsymbol{\delta} \rangle^2 \mathbf{V}^2. \end{aligned} \quad (25)$$

When $\langle \mathbf{W}, \boldsymbol{\delta} \rangle = 0$, equivalent to $\nabla \cdot \mathbf{V} = 0$, i.e., *isochoric flow*, we are left for the isotropic case, with only five (1+2+2) moduli:

$$\begin{aligned} \dot{S}(\mathbf{W}, \mathbf{V}) &= M_1 \langle \mathbf{W}, \mathbf{W} \rangle + N_1 \langle \mathbf{W}, \mathbf{W} \rangle^2 \\ &+ N_2 \langle \mathbf{W}, \mathbf{W}, \mathbf{W}, \mathbf{W} \rangle + L_1 \langle \mathbf{W}, \mathbf{W} \rangle \mathbf{V}^2 + L_2 \langle \mathbf{WV}, \mathbf{WV} \rangle. \end{aligned} \quad (26)$$

The corresponding non-advective momentum flux is

$$\mathbf{J}_{non-adv,ij}^M = M_1 W_{ij} + N_1 \langle \mathbf{W}, \mathbf{W} \rangle W_{ij} + N_2 W_{ik} W_{kl} W_{lj} + L_1 \mathbf{V}^2 W_{ij} + L_2 W_{ik} V_k V_j. \quad (27)$$

The first term expresses the diffusive flux of fluid momentum. The next two terms express the nonlinear momentum flux. The last two terms express the dispersive flux of momentum (proportional to V^2). For a Newtonian fluid, $M_1 \equiv \mu$, i.e., the fluid's viscosity.

• **Non-advective heat flux**

We consider the entire pm, i.e., a rigid stationary solid matrix and a void space occupied by a single fluid, with both solid and fluid phases at thermal equilibrium, i.e., a single temperature T . The development of the expressions for the non-advective fluxes of heat are similar to those of solute, except that in this case, the diffusive flux has to take into account the heat transported in both fluid and solid phases. Altogether, (16) through (21) are valid, except that the numerical values of the various coefficients are different, and the thermal diffusivity of the pm depends on the porosity, and on the thermal conductivities of the two phases, but not on their densities.

For example, for an isotropic pm, we may express the non-advective heat flux in the form (16), replacing ω^γ by T , A_{ik} by $\lambda_{pm,ik}^*$ and omitting the nonlinear diffusive term. We obtain:

$$J_{non-adv,i}^H = -\lambda_{pm,ik}^* \nabla_k T - G_{iklm}^H V_l V_m \nabla_k T, \quad (28)$$

i.e., the sum of a diffusive term and a dispersive one.

4 Interphase Transfers

Here, we consider the rate of transfer, $f_{\beta \rightarrow \alpha}^E$, of an extensive quantity, E , to an α -phase from all other β -phases, including the solid, within a pm domain.

• **Transfer of mass of a γ -species of a phase.** Such transfer across the interface between adjacent phases in the pm domain may be due to adsorption/desorption of γ , ion exchange, or solid dissolution. We shall not elaborate on this issue as it is well known and will detract attention from the main issue of this article.

• **Transfer of momentum of a phase, $\mathbf{f}_{f \rightarrow s}^M$.** We assume that (1) the fluid in the void space "sticks" to the solid surface (no-slip condition), and (2) the solid may be in motion (e.g., due to deformation). The \mathbf{M} -transfer, across the solid-fluid interface, is due to the fluid's velocity gradient at the solid microscopic surface, integrated over the entire fluid-solid interface area, per unit volume of porous medium. We assume that the fluid is *Newtonian*, and that at a point in

the porous medium domain, this transfer is (1) proportional to the difference in average velocity between the fluid and the solid matrix, (2) inversely proportional to some length characterizing the distance between these two subdomains, e.g., the length characterizing the size of a pore (we shall use the hydraulic radius, Δ , of the void space, equal to the volume of the void space divided by the interfacial solid-fluid area), (3) proportional to the total interfacial area between the phases, and (4) proportional to the fluid's viscosity. Thus,

$$(f_{f \rightarrow s}^M)_i = \phi R_{ij} \mu \frac{V_{j,f} - V_{j,s}}{\Delta^2}, \quad (29)$$

in which R_{ij} , a second rank symmetric tensor, is coefficients associated with the geometry of the void space. Note that the volume of void space per unit solid-void surface area is equal to the hydraulic radius of the void space.

- **Transfer of Energy of a phase.** There is no interphase energy transfer as we have assumed that all phases are at the same temperature.

5 Sources of Extensive Quantities

- **Source of mass of a phase.** There are no mass sources within a phase.
- **Source of mass of a component of a phase.** This source may be due to decay, or production of components due to chemical reactions. We shall not elaborate on this kind of source here.
- **Source of momentum of a phase.** We are considering sources only in the fluid (but per unit volume of pm). This source is due to forces acting on the fluid. In the case considered here, we have two sources of momentum per unit volume of porous medium. One is due to body forces, here due to gravity, $\Gamma^M = -\phi \rho g \nabla z$. The other is due to the pressure gradient in the fluid, $-\phi^A \nabla p$, where we have taken into account that the fluid occupies only (the fluid) part of any cross-sectional area through the pm.
- **Energy of a phase.** There are four sources of energy: (1) $\phi \rho \Gamma_{chem}^E \equiv \phi \rho \Gamma_{chem}^H$, due to heat generated by chemical reactions in the fluid phase (if such reactions exist), (2) $\mathbf{V} \cdot (\phi \rho \mathbf{F})$, due to the work, per unit volume of pm, by the body force \mathbf{F} ($= -g \nabla z$), (3) $-\nabla \cdot \{\mathbf{V} \cdot \phi^A (-\boldsymbol{\tau})\}$, resulting from the work of the viscous (shear) stress in the fluid, per unit volume of pm, and (4) $\nabla \cdot \mathbf{V} \cdot (p \boldsymbol{\delta})$ due to the work of the pressure, per unit unit volume of the porous medium.

6 Final Balance Equations

In this section, we shall insert the sources, the rates of transfer and the expressions for fluxes of E in the balance equations presented in Sec. 2, in order to obtain the specific balance equations in terms of the problem variables: $p, T, V, \rho^\gamma, \gamma = 1, 2, \dots, N$. We have not counted ρ as a variable because $\rho = \sum_{(\gamma)} \rho^\gamma$. Altogether we have $N+3$ variables, and $N+3$ equation: $N+2$ balance equations and one constitutive relation, $\rho = \rho(p, T, \rho^\gamma)$.

In this section, to simplify the presentation, we'll make the assumption that $\phi = \phi^A$.

6.1 Mass balance for a fluid phase

Inserting the advective mass flux in (4), replacing θ_α by $\phi (= \phi^A)$, i.e., single phase, we obtain:

$$\frac{\partial \phi \rho}{\partial t} = -\nabla \cdot (\phi \rho \mathbf{V}). \quad (30)$$

6.2 Mass balance for a chemical species

From (5), rewritten for a single fluid phase, we obtain

$$\frac{\partial \phi \rho \omega_\alpha^\gamma}{\partial t} = -\nabla \cdot \phi (\rho \omega^\gamma \mathbf{V} + \mathbf{J}_{diff}^{m\gamma} + \mathbf{J}_{disp}^{m\gamma}) + f_{\beta \rightarrow \alpha}^{m\gamma} + \phi \rho \Gamma^{m\gamma}, \quad (31)$$

into which we can now insert appropriate expressions for the non-advective γ -fluxes that appear in Subs. 3.4. As an example, we shall make use of (19) (for the isotropic case):

$$\frac{\partial \phi \rho \omega_\alpha^\gamma}{\partial t} = -\nabla \cdot \phi \{ \rho \omega^\gamma \mathbf{V} - a \nabla \omega^\gamma - 2d(\nabla \omega^\gamma)^2 \nabla \omega^\gamma - (g_1 \mathbf{V}^2 \nabla \omega^\gamma + g_2 \langle \nabla \omega^\gamma, \mathbf{V} \rangle \mathbf{V}) \} + f_{\beta \rightarrow \alpha}^{m\gamma} + \phi \rho \Gamma^{m\gamma}. \quad (32)$$

We note that the total γ -flux is made up of an advective flux, a (linear) diffusive flux, with a representing the (scalar) coefficient of diffusion in a pm, $\rho \mathcal{D}_{pm}^*$, a non-linear diffusive flux, and a dispersive flux, which is proportional to the fluid's velocity squared and depends on two (scalar) coefficients that represent the effect of the void space geometry.

6.3 Momentum balance

Based on the discussion up to this point, we may now write the momentum balance equation (6) in the form

$$\frac{\partial \phi \rho \mathbf{V}}{\partial t} + \nabla \cdot \phi \rho \mathbf{V} \mathbf{V} = \mathbf{G}, \quad \mathbf{G} = \nabla \cdot \phi \mathbf{J}_{diff}^M + \nabla \cdot \phi \mathbf{J}_{disp}^M - \phi \nabla p - \phi \rho g \nabla z + \mathbf{f}_{f \rightarrow s}^M. \quad (33)$$

By combining this equation with the mass balance equation (30), we obtain another form of the macroscopic momentum balance equation

$$\phi\rho\frac{D\mathbf{V}}{Dt} = \nabla \cdot \phi (\mathbf{J}_{diff}^M + \mathbf{J}_{disp}^M) - \phi\nabla p - \phi\rho g\nabla z + \mathbf{f}_{f\rightarrow s}^M. \quad (34)$$

or, in view of (29),

$$\phi\rho\frac{D\mathbf{V}}{Dt} = \nabla \cdot \phi (\mathbf{J}_{diff}^M + \mathbf{J}_{disp}^M) - \phi(\nabla p + \rho g\nabla z) - \phi\frac{\mu\mathbf{R}}{\Delta^2}(\mathbf{V}_f - \mathbf{V}_s). \quad (35)$$

In what follows, we shall (1) neglect the nonlinear diffusive flux of momentum, (2) neglect the dispersive flux of momentum, (3) assume a Newtonian fluid, and (4) express the diffusive flux of momentum by $\phi\mu\nabla\mathbf{V}$, i.e., assuming isochoric flow at the microscopic level. The momentum balance equation (35) then reduces to

$$\phi\rho\frac{D\mathbf{V}}{Dt} = \nabla \cdot \phi\mu\nabla\mathbf{V} - \phi(\nabla p + \rho g\nabla z) - \phi\frac{\mu\mathbf{R}}{\Delta^2}(\mathbf{V}_f - \mathbf{V}_s). \quad (36)$$

Sometimes, different μ 's are used in the first term and last terms on the r.h.s. of (36): The first μ is referred to as "turbulent viscosity", while the second μ is the "molecular viscosity".

The above equation may be regarded as a generalized motion equation. Let us consider a number of simplifications:

CASE A.

We assume that the magnitude of the velocity is such that the viscous force, resisting the flow, due to the transfer of momentum at the fluid-solid interface is much larger than both the inertial force and the viscous resistance to the flow, i.e.,

$$\left| \phi\rho\frac{D\mathbf{V}}{Dt} \right| \ll \left| \phi\frac{\mu\mathbf{R}}{\Delta^2}(\mathbf{V}_f - \mathbf{V}_s) \right|, \quad \text{and} \quad \left| \nabla \cdot \phi\mu\nabla\mathbf{V} \right| \ll \left| \phi\frac{\mu\mathbf{R}}{\Delta^2}(\mathbf{V}_f - \mathbf{V}_s) \right|.$$

Then, the momentum balance equation reduces to

$$\phi(\mathbf{V}_f - \mathbf{V}_s) = -\frac{\mathbf{k}}{\mu}(\nabla p + \rho g\nabla z), \quad \mathbf{k} = \phi\Delta^2\mathbf{R}^T, \quad (37)$$

which is Darcy's law, with \mathbf{k} denoting the permeability. Thus, *Darcy's law, which is usually regarded as a flux equation, is nothing but a simplified form of the momentum balance equation.* The product $\phi\mathbf{V}_f$ is usually referred to as the *specific discharge* of the fluid.

CASE B

We neglect the inertial effects, but we maintain the internal viscous friction in the fluid. In this case,

$$\left| \phi \rho \frac{\partial \mathbf{V}}{\partial t} \right| \ll |\mathbf{V} \cdot \phi \mu \nabla \mathbf{V}|.$$

Then, (36) reduces to

$$\nabla \cdot \phi \mu \nabla \mathbf{V} - \phi (\nabla p + \rho g \nabla z) - \phi \frac{\mu \mathbf{R}}{\Delta^2} (\mathbf{V}_f - \mathbf{V}_s) = 0, \quad (38)$$

known as the *Brinkman equation*. In it, we note two viscous terms: one which is due to the momentum transfer from the solid to the fluid, and the other which is due to a fluid velocity gradient, unless the (macroscopic) velocity is uniform everywhere, i.e., $\mathbf{V} = \text{const.}$. It is possible that the viscosity, μ , is not the same in these two terms, with one in the first term on the r.h.s. of (38) depending also on the geometry of the void space. The Brinkman equation is usually employed when we deal with a saturated pm bounded by a body of free water.

CASE C

When the local acceleration, $\partial \mathbf{V} / \partial t$, cannot be neglected, e.g., when flow starts, or in oscillatory flow, the momentum balance equation takes the form

$$\phi \rho \frac{\partial \mathbf{V}}{\partial t} = \nabla \cdot \phi \mu \nabla \mathbf{V} - \phi (\nabla p + \rho g \nabla z) - \phi \frac{\mu \mathbf{R}}{\Delta^2} (\mathbf{V}_f - \mathbf{V}_s). \quad (39)$$

6.4 Energy balance

We start from the energy balance equation (7). For the total energy flux, in the case of an isotropic pm, we make use of (28), i.e., taking into account only the linear diffusive heat flux, and the "Fickian" dispersive flux. Energy per unit volume of pm is added by (1) the work done on the fluid phase by external body forces, e.g., gravity ($\mathbf{V} \cdot \phi \rho \mathbf{F} \equiv -\mathbf{V} \cdot \phi \rho g \nabla z$), (2) work done on the fluid by the stress within the fluid, composed of the work done by the viscous forces ($\nabla \cdot (\mathbf{V} \cdot \phi^A \boldsymbol{\tau})$) and by the pressure forces, ($\nabla \cdot (\mathbf{V} \cdot \phi^A p \boldsymbol{\delta})$), and (3) heat produced by chemical reactions within the fluid ($= \phi \rho \Gamma^H$). We obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \{ \phi \rho (I + \frac{1}{2} V^2) \} = & - \nabla \cdot \{ \phi^A \rho (I + \frac{1}{2} V^2) \mathbf{V} \} - \nabla \cdot \phi^A \mathbf{J}_{diff}^H - \nabla \cdot \phi^A \mathbf{J}_{disp}^H \\ & + \nabla \cdot \{ \mathbf{V} \cdot (\phi^A \boldsymbol{\tau}) \} - \nabla \cdot \{ \mathbf{V} \cdot (\phi^A p \boldsymbol{\delta}) \} - \mathbf{V} \cdot \phi \rho g \nabla z + \phi \rho \Gamma^H, \quad (40) \end{aligned}$$

in which the diffusive and dispersive fluxes of heat are defined by (28), and the shear stress, $\boldsymbol{\tau}$, can be expressed by (22). Note that there is no exchange of heat between solid and fluid, as we have assumed that both are at the same T .

7 Summary and conclusions

We have demonstrated how the phenomenological approach can be employed for the construction of mathematical models that describe the transport of mass, momentum and energy in porous medium domains. In this approach, the models are constructed on the basis of assuming the phenomena that occur at the macroscopic level envisioned as a continuum.

Several advantages can be mentioned: (1) there is no need for up-scaling (e.g., by averaging or homogenization), as the models are written directly at the macroscopic level, and only phenomena that are considered relevant are included, (2) the positive definitiveness of the entropy production is ensured, (3) all flux expressions are tensorially correct, (4) we obtain also non-linear diffusive flux expressions, and (5) we obtain expressions for the dispersive fluxes which arise because the models are written in terms of averaged fluid velocity, while the real advective transport is produced by the local (microscopic) velocities, which vary from point to point within the void space. We also obtain the correct number of coefficients that are related to void space geometry, with their correct number of moduli that represent various features of void-space geometry and symmetry characteristics. The transport models derived here have to be *validated experimentally*. The coefficients in these models have to be obtained *experimentally* for any given pm, making use of some inverse technique

Initial and boundary conditions can also be obtained phenomenologically, directly at the macroscopic level, based on the understanding of phenomena that occur on the boundaries (e.g., specified pressure or flux, or continuity of flux). Because each of the balance equations describes what happens at (i.e., in the vicinity of) a point, they are applicable to heterogeneous pm domains.

The same approach is also applicable to cases not included in this article, e.g., multiphase flow, non-elastic deformable porous medium (in which $\mathbf{V}_s \neq 0$), and non-Newtonian fluids. We recall that in the phenomenological approach we assume that the constitutive relationships of the solid matrix and the fluids that occupy the void space are assumed to have the same shape as at the microscopic level, but with different coefficients.

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