



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/129548/>

Version: Accepted Version

Article:

Chen, X, Wang, M, Hicks, MA et al. (2018) A new matrix for multiphase couplings in a membrane porous medium. *International Journal for Numerical and Analytical Methods in Geomechanics*, 42 (10). pp. 1144-1153. ISSN: 0363-9061

<https://doi.org/10.1002/nag.2783>

© 2018 John Wiley & Sons, Ltd. This is the peer reviewed version of the following article: Chen, X, Wang, M, Hicks, MA et al. (2018) A new matrix for multiphase couplings in a membrane porous medium. *International Journal for Numerical and Analytical Methods in Geomechanics*. ISSN 0363-9061, which has been published in final form at <https://doi.org/10.1002/nag.2783>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

A new matrix for multiphase couplings in a membrane porous medium

Xiaohui Chen^{1,*†}, Manhui Wang^{2,‡}, Michael A. Hicks³ and Hywel R. Thomas²

¹School of Civil Engineering, University of Leeds, LS2 9JT, UK

²Geoenvironmental Research Centre, School of Engineering, Cardiff University,
Cardiff CF24 3AA, UK

³Section of Geo-Engineering, Faculty of Civil Engineering and Geosciences, Delft
University of Technology, P.O. Box 5048, 2600 GA Delft, the Netherlands

* Correspondence to: X. Chen, School of Civil Engineering, University of Leeds, LS2 9JT, UK

† E-mail: x.chen@leeds.ac.uk

‡ Present address: Computing Services Department, University of Liverpool, Brownlow Hill, Liverpool
L69 3GG, UK

Abstract

The empirical Darcy's Law of water transport in porous media, Fick's Law of chemical diffusion and Fourier's Law of thermal transport have been widely used in Geophysics/Geochemistry for over 150 years. However, the strong couplings between water, temperature and chemicals in a membrane porous medium have made these laws inapplicable, and present a significant hurdle to the understanding of multiphase flow in such a material. Extensive experiments over the past century have observed chemical osmosis and thermal osmosis, but a model for understanding their underlying physico-chemical basis has remained unavailable, due to the highly cross-disciplinary and multiscale-multiphase nature of the coupling. Based on the fundamental principles of non-equilibrium thermodynamics and Mixture Coupling Theory, a rigorously theoretical and mathematical framework is proposed and a general model accounting for all of the coupled influences is developed. This leads to a simple and robust mathematical matrix for studying multiphase couplings in a membrane porous medium when all chemical components are electrically neutral.

Key words: Coupling, Membrane Porous Media, Mixture Coupling Theory, Multiphase

1. Introduction

In 1856, Henry Darcy developed a constitutive equation that describes the flow of a fluid through a porous medium based on the results of experiments on the flow of water through beds of sand. It is known as Darcy's Law¹, and has been widely used in earth and environmental sciences (e.g. hydrogeology, groundwater pollution), civil engineering (e.g. geotechnical engineering and energy geotechnics), and so on. In 1855, Adolf Fick developed a constitutive equation describing how chemical diffusion is driven by the concentration gradient, known as Fick's Law². It is widely used in geoscience (e.g. geochemistry), pharmacy (e.g. pharmaceuticals), materials science (e.g. radioactive materials), biological sciences (e.g. transport in biological tissues), and so on. In 1822, Joseph Fourier formed the constitutive equation that describes the relationship between the conduction rate in a material and the temperature gradient in the direction of energy flow³, known as Fourier's Law. It is widely used in engineering science (e.g. geothermal energy).

However, since these three laws are based on the common assumption that no strong coupling exists with other physical/chemical fields, all the three laws become invalid in very low permeability porous media (e.g. when the permeability $k \leq 10^{-11}$ m/s) in which strong couplings between the multiphases/multiscales normally exist⁴. For example, Figure 1 shows the water transport in, and deformation of, a porous medium at the macro-scale, down to the mesoscale of a membrane porous medium to limit the transport of large molecules, and further down to the molecular scale of chemical diffusion. In this illustration, the multiphases include water, heat, and chemicals. When a water pressure gradient ($grad p$), a chemical mass fraction gradient ($grad c$), and a temperature gradient ($grad T$) are applied across the mixture in a porous medium, the following situations are involved: (1) The pressure gradient causes the water molecules to migrate (usually from high pressure to lower pressure) with a mass flux of $\mathbf{u} = -(k/\nu) grad p$, in which k is the permeability of the porous medium, ν is the viscosity of the fluid, and \mathbf{u} is the Darcy flux; (2) This water flow will be affected simultaneously by the chemical ($\mathbf{J} = \rho_f D grad c$, where ρ_f is the fluid mass density, D is the diffusion coefficient, and \mathbf{J} is the diffusion flux) and thermal ($\mathbf{I}'_q = \lambda grad T$, in which λ is the thermal conduction coefficient, and \mathbf{I}'_q is the thermal flux) transport flows, and vice versa; (3) The secondary or tertiary coupled driving force may become the major driving force of the flow in some circumstances (e.g. $grad c$ becomes the major driving force of water flow rather than $grad p$ for chemical osmosis in a membrane porous medium⁵); (4) Overall, the 3 flows (water, chemical, and thermal) and 3 driving forces ($grad p$, $grad c$ and $grad T$) present a 3 x 3 matrix describing the cross-couplings between each other (Figure 2), which is the realistic condition of the multiphase porous medium system. Extensive experiments have been conducted in recent decades^{6,7}, but little has been achieved regarding theoretical development in a strict mathematical way.

The focus of this paper is to develop a general constitutive equation for thermo-hydro-chemical coupled transport in a porous medium and thereby modify centuries of understanding. The attention is limited to a transient flow, with a steady state of non-reactive chemical transport and a restriction to electrically neutral components, in a

membrane porous medium, and does not consider the deformation of the medium (e.g. soil compaction can drive water out).

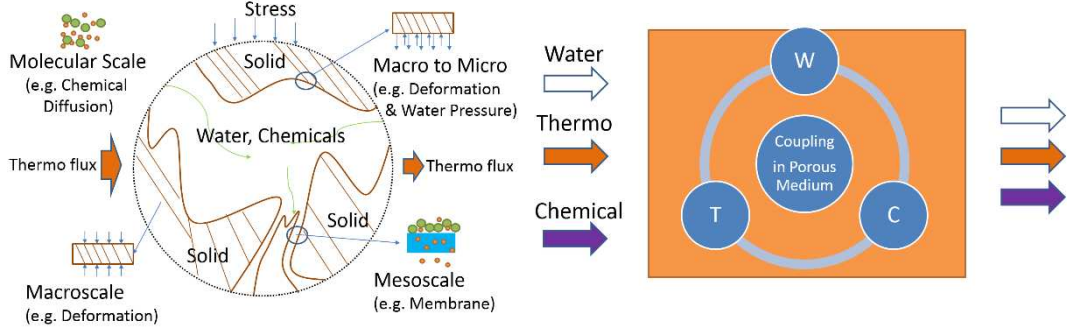


Figure 1 Multiphase-multiscale porous medium **Figure 2** Water (W), Thermo (T) and Chemical (C) couplings

2. Overall dissipation function

In a multiphase-multiscale porous medium, the dynamic movement of the mixture causes dissipation. For example, the friction between solids and fluids slows down the water transport. Such dissipation can be expressed using entropy production (γ) through the expression $T\gamma$, in which T is the temperature. The entropy production may be defined as the sum of the products of the flows with their conjugated forces ⁸,

$$0 \leq \gamma = \mathbf{I}_q \cdot \text{grad} \left(\frac{1}{T} \right) + \sum_{i=1}^N \mathbf{I}_i \cdot \text{grad} \left(-\frac{\mu_i}{T} \right) \quad (1)$$

where \mathbf{I}_q is the thermal flux; N is the total number of chemical components; $\mathbf{I}_i = \rho_i(\mathbf{v}_i - \mathbf{v}_m)$ is the i th ($i=1, \dots, N$) chemical flux, in which ρ_i and \mathbf{v}_i are the mass density and velocity of the i th chemical, respectively, and \mathbf{v}_m is the velocity of the solid matrix; and μ_i is the chemical potential of the i th chemical. In equation (1), the driving force of \mathbf{I}_q is $\text{grad} \left(\frac{1}{T} \right)$ and the driving force of \mathbf{I}_i is $\text{grad} \left(-\frac{\mu_i}{T} \right)$.

The term $\text{grad} \left(-\frac{\mu_i}{T} \right)$ in equation (1) may be transformed following the rules of ordinary differentiation as

$$\text{grad} \left(-\frac{\mu_i}{T} \right) = \frac{1}{T} \text{grad}(-\mu_i) - \mu_i \text{grad} \left(\frac{1}{T} \right) \quad (2)$$

in which $\text{grad} \mu_i$ may be denoted as ⁸

$$\text{grad} \mu_i = -\bar{S}_i \text{grad}(T) + \text{grad}(\mu_i^c) + \bar{V}_i \text{grad}(p) \quad (3)$$

where $\bar{S}_i = \frac{\partial S}{\partial n_i}$ is the partial molar entropy of the i th component (in which S denotes

entropy and n_i is the number of moles of the i th component); and $\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_j}$ is the

partial molar volume of the i th component (in which V denotes volume, while n_j is the number of moles of the j th chemical). Note that, for the convenience of the cross-disciplinary expression, both mass quantity and molar quantity have been used. These two types of quantities can be directly linked with each other through a simple equation:

i.e. the mass fraction of the i th chemical c_i can be obtained from $c_i = n_i M_i / \left(\sum_{i=1}^N n_i M_i \right)$,

where M_i is the molar mass of the i th component; and μ_i^c is the concentration dependent part of μ_i , which is usually written as $\mu_i^c = RT \ln a_i$ (in which a_i is the chemical activity, which equals the solute mole fraction in the case of an ideal solution). If the system is assumed to be in mechanical equilibrium, which leads to $grad(p) = 0$ (p is the pore fluid pressure), equation (3) can then be simplified as

$$grad \mu_i = -\bar{S}_i grad(T) + grad(\mu_i^c) \quad (4)$$

The relationship between entropy \bar{S}_i and enthalpy \bar{H}_i is⁹

$$\bar{H}_i = T\bar{S}_i + \mu_i \quad (5)$$

By introducing equations (4) and (5) into equation (3), it leads to

$$grad\left(\frac{-\mu_i}{T}\right) = -\bar{H}_i grad\left(\frac{1}{T}\right) - \frac{1}{T} grad(\mu_i^c) \quad (6)$$

Then, by substituting equation (6) into equation (1), the entropy function can be written as

$$\begin{aligned} \gamma &= (\mathbf{I}_q - \sum_{i=1}^N \bar{H}_i \mathbf{I}_i) \cdot grad\left(\frac{1}{T}\right) + \sum_{i=1}^N \mathbf{I}_i \cdot \frac{grad(-\mu_i^c)}{T} \\ &= \mathbf{I}'_q \cdot grad\left(\frac{1}{T}\right) + \sum_{i=1}^N \mathbf{I}_i \cdot \frac{grad(-\mu_i^c)}{T} \end{aligned} \quad (7)$$

where $\mathbf{I}'_q = \mathbf{I}_q - \sum_{i=1}^N \bar{H}_i \mathbf{I}_i$, which can be defined as the difference between the ‘total’ heat flow \mathbf{I}_q and that caused by the flows of mass transport $\sum_{i=1}^N \bar{H}_i \mathbf{I}_i$. Following the rules of ordinary differentiation, $grad\left(\frac{1}{T}\right)$ in equation (7) may be written as

$$grad\left(\frac{1}{T}\right) = -\frac{1}{T^2} grad T$$

By substituting this expression into equation (7), the dissipation function $T\gamma$ can be written as

$$\begin{aligned} T\gamma &= \mathbf{I}'_q \cdot \frac{grad(-T)}{T} + \sum_{i=1}^N \mathbf{I}_i \cdot grad(-\mu_i^c) \\ &= T\gamma_q + T\gamma_{che} \end{aligned} \quad (8)$$

where γ_q and γ_{che} are the entropy production of heat and chemical, respectively.

3. Local iso-thermal dissipation function

In a micro-scale local region within a porous medium, it can be assumed that the temperature is constant, and then $grad(-T)$ becomes zero in equation (4) and equation (8). This leads to $grad(-\mu_i) = grad(-\mu_i^c)$ and $\gamma = \gamma_{che}$. To focus on the interactions between chemicals and water, equation (1) can be written as

$$0 \leq \gamma_{che} = \sum_{i=1}^N \mathbf{I}_i \cdot \frac{grad(-\mu_i)}{T} \quad (9)$$

The dissipation function is then

$$T\gamma_{che} = \sum_{i=1}^N \mathbf{I}_i \cdot \text{grad}(-\mu_i) \quad (10)$$

The flux \mathbf{I}_i defines the mass flow relative to the solid mass for the i th chemical. However, it may be more convenient to use the diffusion flux \mathbf{J}_i , which describes the mass flow relative to the mixture's barycentric velocity.

For the fluid, the total fluid mass density is

$$\rho_f = \sum_{i=1}^N \rho_i$$

where ρ_i is the mass density of the i th chemical. The mixture's barycentric velocity is

$$\mathbf{v}_f = \sum_{i=1}^N (\rho_i / \rho_f) \mathbf{v}_i$$

The diffusion flux can be defined as

$$\mathbf{J}_i = \mathbf{I}_i - \rho_i (\mathbf{v}_f - \mathbf{v}_m) = \rho_i (\mathbf{v}_i - \mathbf{v}_f)$$

The Gibbs-Duhem equation¹⁰, which describes the relationship between changes in chemical potential for components in a thermodynamical system, is

$$l df + S dT - V_{pore} dp + \sum_{i=1}^N m_i d\mu_i = 0$$

where V_{pore} is the pore space volume, m_i is the mass of the i th chemical, S is the entropy, f is an external force and l is the distance over which it acts. To simplify the problem, it is assumed that $df = 0$ and $dT = 0$, so that the equation can be written as

$$-V_{pore} dp + \sum_{i=1}^N m_i d\mu_i = 0$$

The relationship between pressure and chemical potential may then be derived as

$$\sum_{i=1}^N \bar{\rho}_i \cdot \text{grad} \mu_i = \text{grad} p$$

where $\bar{\rho}_i = \rho_i / \phi$, in which ϕ is the porosity of the medium and the fluid mass density ρ_i is expressed relative to the unit volume of the fluid-solid mixture.

The dissipation function (10) can now be rearranged as

$$\begin{aligned} T\gamma_{che} &= -\phi (\mathbf{v}_f - \mathbf{v}_m) \cdot \sum_{i=1}^N \bar{\rho}_i \cdot \text{grad} \mu_i - \sum_{i=1}^N [\mathbf{I}_i - \rho_i (\mathbf{v}_f - \mathbf{v}_m)] \cdot \text{grad}(\mu_i) \\ &= -\phi (\mathbf{v}_f - \mathbf{v}_m) \cdot \text{grad} p - \sum_{i=1}^N \mathbf{J}_i \cdot \text{grad}(\mu_i) \end{aligned} \quad (11)$$

As Darcy's velocity can be defined as

$$\mathbf{u} = \phi (\mathbf{v}_f - \mathbf{v}_m) \quad (12)$$

by introducing equation (12) into equation (11), the dissipation function becomes

$$T\gamma_{che} = -\mathbf{u} \cdot \text{grad} p - \sum_{i=1}^N \mathbf{J}_i \cdot \text{grad}(\mu_i) \quad (13)$$

Equation (13) summarizes the driving forces of Darcy flux (i.e. water pressure) and the diffusion flux (i.e. chemical potential).

If it is assumed that the fluid comprises a solute (subscript s) and a diluent (subscript d), $\sum_{i=1}^N \mathbf{J}_i$ can then be simplified as

$$\begin{aligned}\sum_{i=1}^N \mathbf{J}_i &= \mathbf{J}_s + \mathbf{J}_d = \rho_s(\mathbf{v}_s - \mathbf{v}_f) + \rho_d(\mathbf{v}_d - \mathbf{v}_f) \\ &= \rho_s \mathbf{v}_s + \rho_d \mathbf{v}_d - (\rho_s + \rho_d) \mathbf{v}_f\end{aligned}\quad (14)$$

The term $(\rho_s + \rho_d) \mathbf{v}_f$ in equation (14) can be rearranged as

$$\begin{aligned}(\rho_s + \rho_d) \mathbf{v}_f &= (\rho_s + \rho_d) \sum_{i=1}^N (\rho_i / \rho_f) \mathbf{v}_i \\ &= (\rho_s + \rho_d) \left(\frac{\rho_s \mathbf{v}_s}{\rho_s + \rho_d} + \frac{\rho_d \mathbf{v}_d}{\rho_s + \rho_d} \right) = \rho_s \mathbf{v}_s + \rho_d \mathbf{v}_d\end{aligned}\quad (15)$$

By substituting equation (15) into equation (14), it can be concluded that \mathbf{J}_s and \mathbf{J}_d are interdependent, and that there is only one independent diffusion flux,

$$\sum_{i=1}^N \mathbf{J}_i = \mathbf{J}_s + \mathbf{J}_d = \mathbf{0}\quad (16)$$

Thus the term $\sum_{i=1}^N \mathbf{J}_i \text{grad}(\mu_i)$ in equation (13) can be converted into only one diffusion flux \mathbf{J}_s as follows:

$$\begin{aligned}\sum_{i=1}^N \mathbf{J}_i \text{grad}(\mu_i) &= \mathbf{J}_s \text{grad}(\mu_s) + \mathbf{J}_d \text{grad}(\mu_d) \\ &= \mathbf{J}_s \text{grad}(\mu_s) - \mathbf{J}_s \text{grad}(\mu_d) = \mathbf{J}_s [\text{grad}(\mu_s) - \text{grad}(\mu_d)]\end{aligned}\quad (17)$$

Thus, by introducing equation (17), the dissipation function (13) can be written as

$$T\gamma_{che} = -\mathbf{u} \text{grad} p - \mathbf{J}_s \cdot \text{grad}(\mu_s - \mu_d)\quad (18)$$

The driving force of the diffusion flux \mathbf{J}_s becomes the difference between the chemical potential of the solute and that of the diluent (water in this case).

The chemical potential can be described as

$$d\mu = \frac{\partial \mu}{\partial T} dT + \frac{\partial \mu}{\partial p} dp + \frac{\partial \mu}{\partial c} dc\quad (19)$$

Therefore, by substituting equation (19) into the term $\text{grad}(\mu_s - \mu_d)$ in equation (18), it leads to

$$\text{grad}(\mu_s - \mu_d) = \left(\frac{\partial \mu_s}{\partial p} - \frac{\partial \mu_d}{\partial p} \right) \text{grad}(p) + \left(\frac{\partial \mu_s}{\partial c_s} - \frac{\partial \mu_d}{\partial c_s} \right) \text{grad}(c_s) + \left(\frac{\partial \mu_s}{\partial T} - \frac{\partial \mu_d}{\partial T} \right) \text{grad}(T)\quad (20)$$

in which $\left(\frac{\partial \mu_s}{\partial p} - \frac{\partial \mu_d}{\partial p} \right)$ can be further simplified through the following steps¹¹:

$$\frac{\partial \mu_s}{\partial p} = \frac{\partial V}{\partial c_s} = \bar{V}_s, \quad \bar{V}_s = \frac{\partial(\bar{\rho}_s)}{\partial c_s}$$

and

$$\frac{\partial \mu_d}{\partial p} = \frac{\partial V}{\partial c_d} = \bar{V}_d, \quad \bar{V}_d = \frac{\partial(\bar{\rho}_d)}{\partial c_d}$$

where \bar{V}_s and \bar{V}_d denote the partial mass volumes of the solute and diluent, respectively.

These quantities satisfy the thermodynamic identities¹². Thus, $\left(\frac{\partial \mu_s}{\partial p} - \frac{\partial \mu_d}{\partial p} \right)$ can be assumed to equal zero.

Regarding the term $\frac{\partial\mu_s}{\partial T} - \frac{\partial\mu_d}{\partial T}$ in equation (20),

$$\frac{\partial\mu_s}{\partial T} = -\bar{s}_s, \quad \frac{\partial\mu_d}{\partial T} = -\bar{s}_d$$

where \bar{s}_s and \bar{s}_d denote the partial mass entropy of the solute and diluent, respectively. To simplify the discussion it can be assumed that $\bar{\rho}_f(\bar{v}_s - \bar{v}_d) \ll 1$, which leads to $\bar{\rho}_f(\bar{s}_s - \bar{s}_d) \ll 1$, and thereby $\frac{\partial\mu_s}{\partial T} - \frac{\partial\mu_d}{\partial T}$ can be assumed to equal zero.

For the term $\frac{\partial\mu_s}{\partial c_s} - \frac{\partial\mu_d}{\partial c_s}$ in equation (20), at constant temperature and pressure in a local region, the relationship may be described as ⁸

$$c_s d\mu_s = -c_d d\mu_d$$

$$d\mu_d = -\frac{c_s}{c_d} d\mu_s$$

$$\frac{\partial\mu_d}{\partial c_s} = -\frac{c_s}{c_d} \frac{\partial\mu_s}{\partial c_s}$$

Thus,

$$\frac{\partial\mu_s}{\partial c_s} - \frac{\partial\mu_d}{\partial c_s} = \frac{\partial\mu_s}{\partial c_s} + \frac{c_s}{c_d} \frac{\partial\mu_s}{\partial c_s} = \frac{(c_s + c_d)}{c_d} \frac{\partial\mu_s}{\partial c_s} = \frac{1}{c_d} \frac{\partial\mu_s}{\partial c_s}$$

From the discussion above, equation (20) can be further simplified as

$$\text{grad}(\mu_s - \mu_d) = \frac{1}{c_d} \frac{\partial\mu_s}{\partial c_s} \text{grad}(c_s) \quad (21)$$

and the dissipation function (18) can be rewritten as ¹¹

$$T\gamma_{che} = -\mathbf{u} \text{grad } p - \mathbf{J}_s \cdot \left[\frac{1}{c_d} \frac{\partial\mu_s}{\partial c_s} \text{grad}(c_s) \right] \quad (22)$$

4. Phenomenological equations

By introducing equation (22) into equation(8), the dissipation function can be summarized as

$$T\gamma = \mathbf{I}'_q \cdot \frac{\text{grad}(-T)}{T} - \mathbf{u} \text{grad } p - \mathbf{J}_s \left[\text{grad}(\mu_s - \mu_d) \right] \quad (23)$$

Since \mathbf{u} is velocity, the term $\mathbf{u} \text{grad } p$ should be rewritten as

$$\mathbf{u} \text{grad } p = (\rho_f \mathbf{u}) \left(\frac{\text{grad } p}{\rho_f} \right)$$

Also, by considering equation (21), the term $\mathbf{J}_s \left[\text{grad}(\mu_s - \mu_d) \right]$ can be rewritten as

$$\mathbf{J}_s \left[\text{grad}(\mu_s - \mu_d) \right] = \mathbf{J}_s \left[\frac{1}{c_d} \frac{\partial\mu_s}{\partial c_s} \text{grad}(c_s) \right]$$

Thus, the dissipation function is defined as

$$T\gamma = -(\rho_f \mathbf{u}) \left(\frac{\text{grad } p}{\rho_f} \right) - \mathbf{J}_s \left[\frac{1}{c_d} \frac{\partial\mu_s}{\partial c_s} \text{grad}(c_s) \right] - \mathbf{I}'_q \cdot \frac{\text{grad}(T)}{T} \quad (24)$$

Using phenomenological expressions ⁹ in equation (24), to give linear relationships between the driving forces and fluxes, leads to

$$\bar{\rho}_f \mathbf{u} = -L^{11} \left(\frac{\text{grad } p}{\rho_f} \right) - L^{12} \left(\frac{1}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) - L^{13} \left(\frac{\text{grad}(T)}{T} \right) \quad (25)$$

$$\mathbf{J}_s = -L^{21} \left(\frac{\text{grad } p}{\rho_f} \right) - L^{22} \left(\frac{1}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) - L^{23} \left(\frac{\text{grad}(T)}{T} \right) \quad (26)$$

$$\mathbf{I}'_q = -L^{31} \left(\frac{\text{grad } p}{\rho_f} \right) - L^{32} \left(\frac{1}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) - L^{33} \left(\frac{\text{grad}(T)}{T} \right) \quad (27)$$

where each flux has three driving forces, and the L^{ij} denote a set of phenomenological coefficients.

Equation (25) describes the fluid flux (previously Darcy flux), which can be further reorganized in terms of familiar earth science coefficients obtained from experimental study ¹³ as

$$\begin{aligned} \mathbf{u} &= -\frac{L^{11}}{\bar{\rho}_f^2} (\text{grad } p) - \frac{L^{12}}{\bar{\rho}_f} \left(\frac{1}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) - \frac{L^{13}}{\bar{\rho}_f} \frac{\text{grad}(T)}{T} \\ &= -\left(\frac{L^{11}}{\bar{\rho}_f^2} \right) \left[\text{grad } p + \left(\frac{L^{12}}{L^{11}} \right) \left(\frac{\bar{\rho}_f}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) + \left(\frac{L^{13}}{L^{11}} \right) \frac{\bar{\rho}_f \text{grad}(T)}{T} \right] \end{aligned} \quad (28)$$

By comparing with Darcy's law, $\mathbf{u} = -\frac{k}{v} \text{grad } p$, the coefficients can be further elaborated as

- $\frac{k}{v} = \frac{L^{11}}{\bar{\rho}_f^2}$, in which k is the permeability and v is the fluid viscosity.
- $r_f = \frac{L^{12}}{L^{11}}$, the chemical reflection coefficient, which serves as a measure of the efficiency of the osmotic transport ^{11,14}.
- $r_q = \frac{L^{13}}{L^{11}}$, the thermal reflection coefficient, which serves as a measure of the efficiency of the osmotic transport. ¹⁵

Thus, Darcy's Law can be extended to give

$$\mathbf{u} = -\frac{k}{v} \left[\text{grad } p + r_f \left(\frac{\bar{\rho}_f}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) + r_q \frac{\bar{\rho}_f \text{grad}(T)}{T} \right] \quad (29)$$

Equation (26) describes the chemical transport, which can be further defined in terms of coefficients obtained from experimental study as

$$\begin{aligned} \mathbf{J}_s &= -L^{21} \left(\frac{\text{grad } p}{\rho_f} \right) - L^{22} \left(\frac{1}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) - L^{23} \left(\frac{\text{grad}(T)}{T} \right) \\ &= -\frac{L^{21} p}{\rho_f^2} \frac{\text{grad } p}{p} - \rho_f \frac{L^{22}}{c_d \rho_f} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) - L^{23} \left(\frac{\text{grad}(T)}{T} \right) \end{aligned} \quad (30)$$

where

- $L = \frac{L^{21} p}{\rho_f^2}$, the pressure diffusion coefficient for chemical transport.
- $D = \frac{L^{22}}{c_d \rho_f} \frac{\partial \mu_s}{\partial c_s}$, the dispersion-diffusion coefficient for chemical transport.

Thus, Fick's Law can be extended in the form

$$\mathbf{J}_s = -L \rho_f \frac{\text{grad } p}{p} - \rho_f D \text{grad}(c_s) - L^{23} \left(\frac{\text{grad}(T)}{T} \right) \quad (31)$$

Equation (27) describes the thermal transport and may be further rearranged as

$$\begin{aligned}
\mathbf{I}'_q &= -L^{31} \left(\frac{\text{grad } p}{\rho_f} \right) - L^{32} \left(\frac{1}{c_d} \frac{\partial \mu_s}{\partial c_s} \text{grad}(c_s) \right) - L^{33} \left(\frac{\text{grad}(T)}{T} \right) \\
&= - \left(\frac{L^{31} p}{\rho_f^2} \right) \left(\rho_f \frac{\text{grad } p}{p} \right) - \rho_f \left(\frac{L^{32}}{c_d \rho_f} \frac{\partial \mu_s}{\partial c_s} \right) \text{grad}(c_s) - L^{33} \left(\frac{\text{grad}(T)}{T} \right) \\
&= -L_q \left(\rho_f \frac{\text{grad } p}{p} \right) - \rho_f D_q \text{grad}(c_s) - \lambda \text{grad}(T)
\end{aligned} \tag{32}$$

where

- $L_q = \left(\frac{L^{31} p}{\rho_f^2} \right)$, the pressure diffusion coefficient for thermal transport.
- $D_q = \left(\frac{L^{32}}{c_d \rho_f} \frac{\partial \mu_s}{\partial c_s} \right)$, the dispersion-diffusion coefficient for thermal transport.
- $\lambda = \frac{L^{33}}{T}$, the conduction coefficient.

Thus, equation (32) is an extension of Fourier's Law.

5. Coupling matrix and its evaluation

The final coupling matrix derived from equations (29), (31) and (32) may be described as follows:

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{J}_s \\ \mathbf{I}'_q \end{pmatrix} = - \begin{bmatrix} \frac{k}{v} & \frac{kr_f \bar{\rho}_f}{vc_d} \frac{\partial \mu_s}{\partial c_s} & \frac{kr_q \bar{\rho}_f}{vT} \\ \frac{L\rho_f}{p} & \rho_f D & \frac{L^{23}}{T} \\ \frac{L_q \rho_f}{p} & \rho_f D_q & \lambda \end{bmatrix} \begin{pmatrix} \text{grad } p \\ \text{grad } c_s \\ \text{grad } T \end{pmatrix} \tag{33}$$

This new equation describes the inter-dependence of water, chemical and thermal fluxes in a porous medium.

If only single phase transport is considered, then no coupling exists, which means that the coupled coefficients become zero. Thus, Darcy's Law, Fick's Law and Fourier's Law are special cases of matrix (33), i.e.

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{J}_s \\ \mathbf{I}'_q \end{pmatrix} = - \begin{bmatrix} \frac{k}{v} & 0 & 0 \\ 0 & \rho_f D & 0 \\ 0 & 0 & \lambda \end{bmatrix} \begin{pmatrix} \text{grad } p \\ \text{grad } c_s \\ \text{grad } T \end{pmatrix} \tag{34}$$

Furthermore, when considering only the coupling between Darcy's flux and chemical transport, equation (33) can be simplified as¹⁶

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{J}_s \end{pmatrix} = - \begin{bmatrix} \frac{k}{v} & \frac{kr_f \bar{\rho}_f}{vc_d} \frac{\partial \mu_s}{\partial c_s} \\ \frac{L\rho_f}{p} & \rho_f D \end{bmatrix} \begin{pmatrix} \text{grad } p \\ \text{grad } c_s \end{pmatrix} \tag{35}$$

If only the coupling between Darcy flux and thermal osmosis is considered, equation (33) can be simplified as ¹⁵

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{I}'_q \end{pmatrix} = - \begin{bmatrix} \frac{k}{v} & \frac{kr_q \bar{\rho}_f}{vT} \\ \frac{L_q \rho_f}{p} & \lambda \end{bmatrix} \begin{pmatrix} grad p \\ grad T \end{pmatrix} \quad (36)$$

It can be seen that the matrices obtained in eqs. (33), (35) and (36) are asymmetric. Onsager's symmetry relationship has not been used to give a further "simplification", as it may not be applicable to continuum thermodynamics according to some experimental results¹⁷ and theoretical analyses^{18,19}. Membrane porous media present a unique environment in which the multi-scale influence may be important (e.g. the molecular-scale influence has a more significant impact on the macro transport/friction mechanism than in normal porous media)²⁰. These matrices provide a general description of the couplings between the multiphases to guide further experimental investigation.

6. Conclusion

This article has developed a new matrix equation (33), describing the couplings between three fluxes (water-thermo-chemical) and the combination of driving forces that may directly or indirectly affect the flux transport. Unlike the understanding of 150 years ago, which was that water flux is only driven by water gradient, in a more complicated membrane porous medium the coupled influence between water, chemical and heat becomes more and more important, especially for contemporary geoscience and geotechnical engineering applications, such as radioactive waste disposal, carbon capture and storage, shale gas, and landfill. The coupled matrix can also be used for highly cross-disciplinary applications, such as in chemistry/chemical engineering and biology/biological engineering.

Acknowledgments

The first author acknowledges the financial support by a University of Leeds Research Grant (40711500). The second and fourth authors acknowledge the financial support by the Welsh European Funding Office (WEFO) through the FLEXIS project.

References

1. Darcy H. *Les Fontaines Publiques de la Ville de Dijon*. Paris: Dalmont; 1856.
2. Fick A. Ueber diffusion. *Annalen der Physik*. 1855;170(1):59-86.
3. Fourier JBJ. *The analytical theory of heat*. The University Press; 1878.
4. Cath TY, Childress AE, Elimelech M. Forward osmosis: principles, applications, and recent developments. *Journal of Membrane Science*. 2006;281(1):70-87.

5. Chen X, Pao W, Thornton S, Small J. Unsaturated hydro-mechanical-chemical constitutive coupled model based on mixture coupling theory: Hydration swelling and chemical osmosis. *International Journal of Engineering Science*. 2016;104:97-109.
6. Graf DL. Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. *Geochim. Cosmochim. Acta*. 1982;46(8):1431-1448.
7. Sun X, Wu J, Shi X, Wu J. Experimental and numerical modeling of chemical osmosis in the clay samples of the aquitard in the North China Plain. *Environmental Earth Sciences*. 2016;75(1):1-12.
8. Katchalsky A, Curran PF. *Nonequilibrium thermodynamics in biophysics*. Cambridge, MA: Harvard University Press; 1965.
9. De Groot SR. *Thermodynamics of irreversible processes*. Vol 336: Amsterdam: North-Holland Pub. Company; 1951.
10. Parr RG. Density functional theory of atoms and molecules. *Horizons of Quantum Chemistry*: Springer; 1980:5-15.
11. Heidug WK, Wong SW. Hydration swelling of water-absorbing rocks: A constitutive model. *Int. J. Num. Anal. Meth. Geomech*. 1996;20:403-430.
12. Ito K, Moynihan CT, Angell CA. Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water. *Nature*. 1999;398(6727):492-495.
13. Lewis RW, Schrefler BA. *The finite-element method in deformation and consolidation of porous media*. New York: Wiley; 1987.
14. Staverman A. The theory of measurement of osmotic pressure. *Recueil des Travaux Chimiques des Pays-Bas*. 1951;70(4):344-352.
15. Chen X, Pao W, Li X. Coupled thermo-hydro-mechanical model with consideration of thermal-osmosis based on modified mixture theory. *International Journal of Engineering Science*. 2013;64(0):1-13.
16. Chen X, Hicks MA. Unsaturated hydro-mechanical-chemo coupled constitutive model with consideration of osmotic flow. *Computers and Geotechnics*. 2013;54:94-103.
17. Mason EA, Wendt RP, Bresler EH. Test of the Onsager relation for ideal gas transport in membranes. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*. 1972;68(0):1938-1950.
18. Truesdell C. *Rational thermodynamics*. Springer Science & Business Media; 2012.
19. Cussler EL. *Diffusion: mass transfer in fluid systems*. Cambridge University Press; 2009.
20. Bear J. *Dynamics of fluids in porous media*. Courier Corporation; 2013.