Cronfa - Swansea University Open Access Repository

_____

This is an author produced version of a paper published in:
International Journal of Numerical Methods for Heat and Fluid Flow

Cronfa URL for this paper:
http://cronfa.swan.ac.uk/Record/cronfa32120

_____

Paper:

Di Fraia, S., Massarotti, N. & Nithiarasu, P. Modelling electro-osmotic flow in porous media: a review. *International Journal of Numerical Methods for Heat and Fluid Flow*
http://dx.doi.org/10.1108/HFF-11-2016-0437

_____

International Journal of Numerical Methods for Heat and Fluid Flow

Modelling electro-osmotic flow in porous media: a review

Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.

Revised submission.rar

SCHOLARONE™
Manuscripts

Modelling electro-osmotic flow in porous media: a review

S. Di Fraia[1], N. Massarotti[1], and P. Nithiarasu[2]

[1]Department of Engineering, University of Naples 'Parthenope', Centro Direzionale Isola C4, 80143, Naples, Italy
[2]Biomedical Engineering and Rheology Group, Zienkiewicz Centre for Computational Engineering, Swansea University, Swansea SA2 8PP, United-Kingdom

Abstract

Purpose - This paper aims to provide a comprehensive literature review on modelling electro-osmotic flow in porous media.

Design/methodology/approach - Modelling electro-osmosis in fluid systems without solid particles has been firstly introduced. Then, after a brief description of the existing approaches for porous media modelling, EOF in porous media has been considered by analysing the main contributions to the development of this topic.

Findings - The analysis of literature has highlighted the absence of an universal model to analyse electro-osmosis in porous media, whereas many different methods and assumptions are used.

Originality/value - For the first time, the existing approaches for modelling electro-osmotic flow in porous have been collected and analysed in order to provide detailed indications for future works concerning this topic.

Paper type - Literature review

Keywords: Numerical methods, Electro-osmosis, Charged particles, Generalised model.

1   INTRODUCTION

Electroosmotic phenomena were first observed in porous materials at the beginning of 19th century, when Reuss discovered that water contained in clays, if subjected to an applied electric field, migrates towards a cathode (Probstein, 2005). Due to their mineral composition and physical features, clay soil particles are characterized by net negative charge and high specific surface (Nicholson, 2014). Therefore, they tend to attract positive ions, such as the dissociated salts that are commonly present in water, with the formation of a high concentration region close to the charged surface (Probstein, 2005), the so-called diffuse double layer (Asadi et al., 2013). The application of an external electric field involves the movement of the counter ions of the diffuse layer in excess (Sheu et al., 2012), that drag the nearby ions with them (Probstein, 2005) because of the fluid viscosity (Huang et al., 2009). This drag force is the main reason for Electro-Osmotic Flow (EOF) (Asadi et al., 2013). Such a phenomenon is shown in Figure 1.

Address correspondence to: simona.difraia@uniparthenope.it

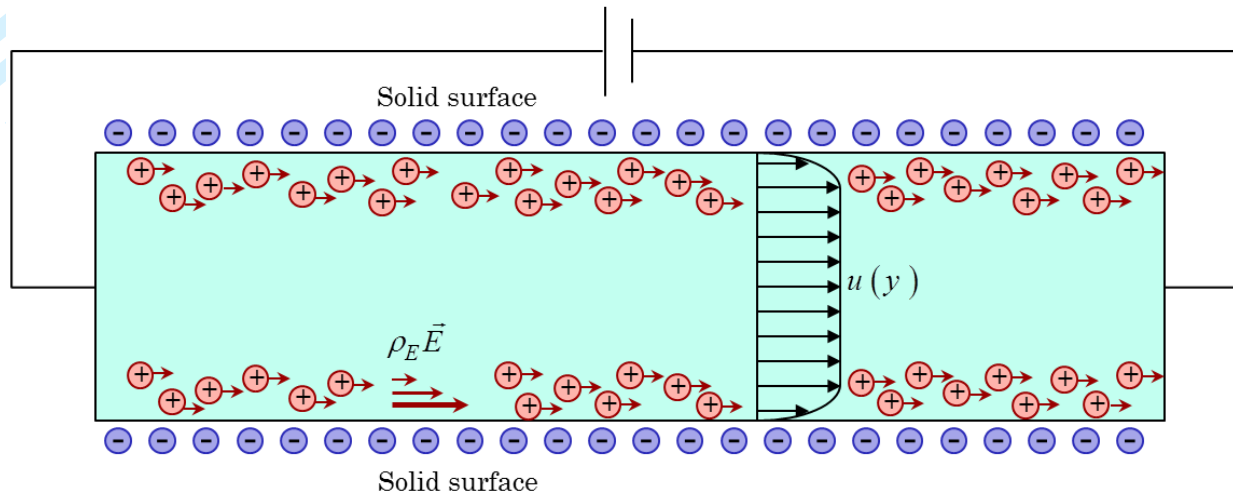Modelling electro-osmotic flow in porous media: a review

Figure 1: Electro-kinetic effects in the electrical double layer induce the fluid flow, that is approximately uniform outside the electrical double layer. (The thickness of the electrical double layer is enlarged for the sake of clarity).

The concept of Electric Double Layer (EDL) was introduced by Helmholtz, who realized that, if a charged metal surface is immersed into an electrolyte, a compact layer of ions forms on its surface (Stojek, 2010). Von Helmholtz (1879) derived an analytical relation for EOF in capillary tubes that was extended by von Smoluchowski (1921*b*) to describe EO velocity. Following this Gouy (1910) and Chapman (1913) presented the first theory for diffuse double layer model in the presence of a flat charged surface. They assumed that the ion concentration depends on the distance from the charged surface and can be described through a Boltzmann distribution. A similar approach was used by Debye and Hückel to describe the electrical potential around a spherical particle (Verwey and Overbeek, 1948). In 1924, Stern combined the above mentioned theories and introduced a model of solid-liquid interface that includes both the Helmholtz layer, constituted by the ions adsorbed on the charged surface, and the diffuse layer of Gouy and Chapman (Stojek, 2010). The Gouy-Chapman-Stern model is shown in Figure 2.

The use of porous media in electro-osmotic systems is very attractive. EOF is effective in low porosity media (Anderson and Keith Idol, 1985) and more advantageous than pressure-driven flow (Tallarek et al., 2002; Hlushkou et al., 2005). First applications dealt with chromatography techniques: in Capillary ElectroChromatography (CEC), electro-osmosis is employed to drive flow in packed capillary columns (Rathore and Horváth, 1997; Li and Remcho, 1997; Wan, 1997; Liapis and Grimes, 2000; Tallarek et al., 2002; Hlushkou et al., 2005, 2006). The main application for electro-osmosis in porous media is micro-pumping (Zeng et al., 2001; Yao and Santiago, 2003; Kang et al., 2004*a*; Tripp et al., 2004; Wang, Chen and Chang, 2006; Wang, Wang, Chen and Pan, 2006; Yao et al., 2006; Kang et al., 2007; Wang and Chen, 2007; Chen et al., 2008; Ai et al., 2010; Kwon et al., 2012): EO pumps are used in several fields such as cooling of electronic components (Berrouche et al., 2009; Cheema et al., 2013), oil exploration, chemical engineering and biomedical engineering (Wang and Chen, 2007; Tang et al., 2010; Chen et al., 2014), fuel cells (Cheema et al., 2013; Bennacer et al., 2007; Mahmud Hasan et al., 2011), dehumidification or dehydration (Li, Zhou, Yan and Tian, 2013; Li, Zhou, Yan, Han and Ren, 2013), chemical remediation of contaminated soil (Shapiro and Probstein, 1993; Wu and Papadopoulos, 2000; Tallarek et al., 2002; Cameselle, 2015), filter cakes (Anderson and Keith Idol, 1985), wastewater sludge (Hlushkou et al., 2005) and soil (Lewis and Garner, 1972; Lewis and Humpheson, 1973) dewatering and fluid reabsorption in the kidney (McLaughlin and Mathias, 1985). In fluid systems with no obstructions only the charge of channel surfaces affects EOF, while when porous

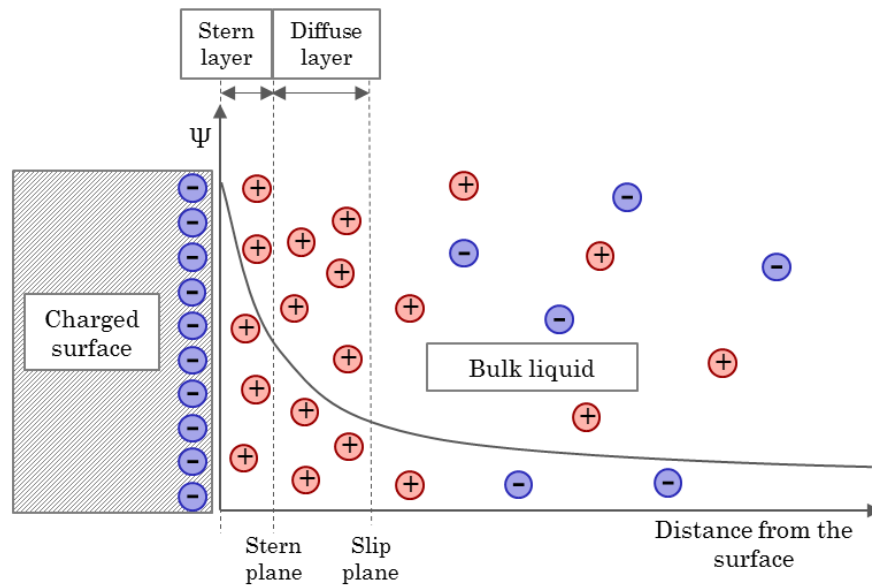Modelling electro-osmotic flow in porous media: a review

Figure 2: Model of electrical double layer: the potential drop is more pronounced in the region very close to the charged surface, the so-called Stern or Helmholtz layer, than in the diffuse or Gouy-Chapman layer. As the distance from the charged surface increases the ionic concentration tends to that of the bulk and the potential tends to zero.

media are introduced, the contribution of charged solid particles has to be taken into account. In previous works concerning numerical modelling of EOF in porous media, several simplifying hypotheses have been considered (Wang, 2012). In the past decades most authors have just considered the charge of channel walls and neglected the charge of solid particles, both in the equation governing the internal potential and in the momentum equation for fluid flow. Recently some authors have tried to consider the contribution of charged solid particles to EOF. Some of them have employed a microscopic approach and solved the problem by using the Lattice Boltzmann Method (LBM) (Wang, Wang, Chen and Pan, 2006; Wang and Chen, 2007; Wang et al., 2007; Wang, 2012; Li, Zhou, Yan and Tian, 2013; Li, Zhou, Yan, Han and Ren, 2013). Others have used a generalized model for porous media. In this latter case, the momentum equation has been modified by adding a source term depending on the charge density of porous medium and the applied electrical field, while the internal potential equation has not been changed (Scales and Tait, 2006; Tang et al., 2010). Moreover, EDL thickness is often considered to be much smaller than pore diameters: in micro- and nanopores the scale of these lengths is quite similar (Wang, 2012), there this is a considerable approximation.

The paper is organised as follows: in Section 2 modelling of electro-osmosis in fluid systems without solid particles has been introduced. In Section 3, EOF in porous media is considered: after a brief description of the existing approaches for porous media modelling, the most recent works on EOF in porous media have been analysed.

2 THEORETICAL BACKGROUND

2.1 Electroosmosis

As introduced by Gouy (1910) and Chapman (1913), the Electric Double Layer (EDL) potential, ψ, for a planar surface can be described by the Poisson equation:

$$\frac{\partial^2 \psi}{\partial x_i^2} = -\frac{\rho_E}{\varepsilon \varepsilon_0} \tag{1}$$

where ε is the dielectric constant of the electrolyte, ε_0 is the permittivity of vacuum and ρ_E is the net charge density, dependent on the distance from the wall. If the charged surface is positive, it will attract and accumulate negative ions, while positive ions are repelled. By assuming the hypothesis of thermal equilibrium, Boltzmann distribution can be used to predict the ionic number concentration (Hu et al., 1999):

$$n^+ = n_0 e^{-\left(\frac{ze\psi}{k_B T}\right)}; \qquad n^- = n_0 e^{\left(\frac{ze\psi}{k_B T}\right)}; \tag{2}$$

where n^+ and n^- represent the number of positive and negative ions, respectively, n_0 is the ionic number concentration in the bulk solution, z is the valance of the ions, e is the elementary charge, k_B is the Boltzmann's constant, and T is the temperature measured in kelvin. This assumption consists in considering the average concentration of ions at a given point to be dependent on the average value of the electric potential at the same point (Verwey and Overbeek, 1948). Due to the boundary conditions used to derive the Eq. (2), it is valid only if the planar surface is immersed in an infinitely large liquid phase, or if there are two surfaces separated from each other by an infinitely liquid phase (Qu and Li, 2000). Dirichlet and Neumann conditions can be used to describe the boundaries (Wang and Chen, 2008); the choice usually depends on the numerical method employed to solve the problem. The bulk ionic concentration n_0 can be obtained as

$$n_0 = cN_A \tag{3}$$

where c is the concentration of electrolyte in Moles and N_A is the Avogadro constant. The net charge density can be defined as

$$\rho_E = ze\left(n^+ - n^-\right) \tag{4}$$

Substituting Eq. (2) and reorganising,

$$\rho_E = -2n_0 ze \sinh\left(\frac{ze\psi}{k_B T}\right) \tag{5}$$

The non-linear Poisson-Boltzmann equation, obtained by substituting Eq. (5) into Eq. (1), allows to determine the EDL potential distribution for a symmetrical ionic solution:

$$\frac{\partial^2 \psi}{\partial x_i^2} = \frac{2n_0 ze}{\varepsilon \varepsilon_0} \sinh\left(\frac{ze\psi}{k_B T}\right) \tag{6}$$

For small values of the electric potential, the electrostatic energy of charges, $ze\psi$, is much smaller than thermal energy, $k_B T$, and therefore (Rice and Whitehead, 1965)

$$\sinh\left(\frac{ze\psi}{k_B T}\right) \approx \left(\frac{ze\psi}{k_B T}\right) \tag{7}$$

Considering the room temperature, $T = 298K$, the above approximation could be considered valid only for $\psi \simeq 25mV$. However, it has been found to well describe the EDL potential distribution at a single plane

Modelling electro-osmotic flow in porous media: a review

surface for values of ψ up to 50 mV in case of univalent electrolytes (Rice and Whitehead, 1965); when noninteger symmetric electrolytes are considered, the simplified approach has been found to be valid up to a ψ value of 30mV (Flatt and Bowen, 2003). In these cases Eq. (6) can be linearised as follows

$$\frac{\partial^2 \psi}{\partial x_i^2} = \kappa^2 \psi \tag{8}$$

where κ^{-1}, known as Debye length, represents the EDL characteristic thickness and is generally a constant for a given solid-liquid interface (Patankar and Hu, 1998):

$$\kappa = \left(\frac{2n_0 z^2 e^2}{k_B T \varepsilon \varepsilon_0} \right)^{1/2}$$

Often the electro-kinetic radius, κa, where a is the channel diameter or width, is also used as one of the EOF parameters. EOF has been found to increase as κa is in the range of 1-100, and to be constant beyond this value (Rice and Whitehead, 1965; Yao and Santiago, 2003). When the channel width is much larger than the Debye length, the drag effect due to electro-kinetic forces of EDL decreases, and as a consequence EOF is reduced.

The influence of the electro-kinetic radius on the potential ψ is shown in Figure 3 where the non-dimensional ψ is plotted against the non-dimensional channel width, for different values of κa.
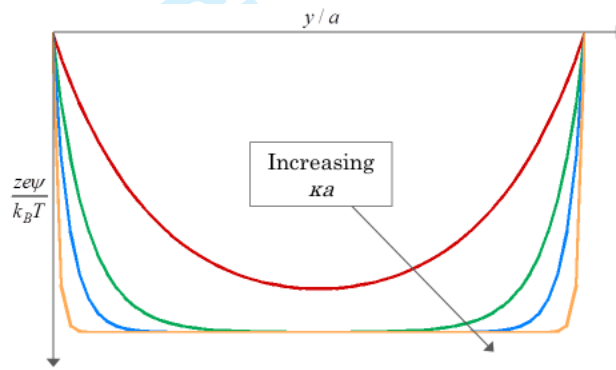

Figure 3: The effect of varying the electro-kinetic radius, κa, on the non-dimensional internal potential, $\frac{ze\psi}{k_B T}$.

The electric potential distribution, expressed in cylindrical coordinates can be described by Rice and Whitehead (1965)

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = \kappa^2 \psi \tag{9}$$

and in this case the reciprocate of Debye length is given by

$$\kappa = \left(\frac{8\pi n_0 z^2 e^2}{k_B T \varepsilon \varepsilon_0} \right)^{1/2}$$

The solution of Eq. (9) (Rice and Whitehead, 1965) is finite at $r = 0$ and equal to

$$\psi = B I_0 (\kappa r) \tag{10}$$

where I_0 is the zero-order modified Bessel function of the first kind. At $r = a$, $\psi = \psi_0$, therefore

$$\psi = \psi_0 \frac{I_0 (\kappa r)}{I_0 (\kappa a)} \tag{11}$$

Such analytical solutions are valid only for simple cases.

2.1.1 EDL overlapping

The Boltzmann distribution assumes that the solid charged surface involved in EO phenomena is immersed in an infinitely large aqueous phase. Under this assumption, at a certain distance from the surface, EDL potential is zero and the ionic concentration can be considered to be equal to the original bulk ionic concentration (Talapatra and Chakraborty, 2008). When the distance between two solid surfaces, such as two parallel plates or the walls of a channel, is of the same order of magnitude of EDL thickness, EDLs overlap. In this case, the Boltzmann distribution cannot properly describe EOF, since the ionic concentration is not equal to the original bulk concentration and, as a consequence, EDL potential is non-zero.
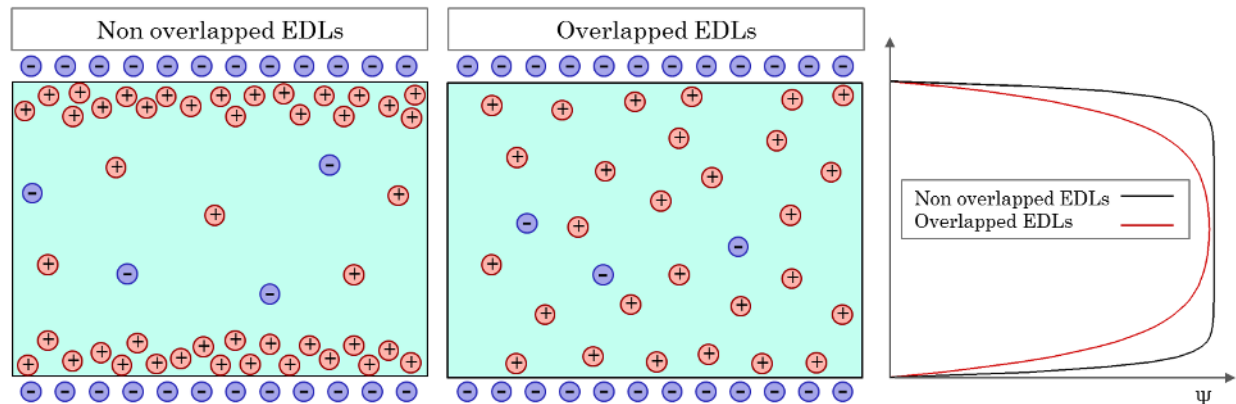

Figure 4: In non overlapped EDLs at the centre of the channel the ionic concentration is equal to the original bulk concentration and the potential falls to zero, while in overlapped EDLs the concentration of positive ions is greater than that of negative ions and the electric potential is non-zero.

The ionic sites of the solution are not enough to neutralize those of EDL, therefore under EDL overlapping conditions the electro-neutrality of the system cannot be restored (Huang and Yang, 2007). The first effect of EDL overlapping is EOF reduction (Wan, 1997).

The applicability of Poisson-Boltzmann (PB) equation was investigated by Wang and Chen (2008). The Boltzmann distribution is not suitable to describe EDL potential in case of high ionic concentration, due to molecular interactions, as confirmed by the comparison with the results determined through molecular dynamics simulation. EDL interactions can occur also at low ionic concentration if the channel is very thin: in this case EOF needs to be studied through the coupled Poisson-Nernst-Planck and Navier-Stokes equations. The comparison between this approach and the classical model highlighted that the PB model accuracy is limited to the cases in which EDL thickness is smaller than channel width, whereas it overestimates the net charge density as EDL thickness increases, confirming Hu and Chao (2007) results .

The most common boundary conditions for EO problems may be analysed under conditions of EDL overlapping: specified zeta potential, specified surface charge density, and charge regulation. During an EDL overlap, the EO contribution was found to be very low, whereas the current was mostly provided by conduction (Baldessari, 2008).

Burgreen and Nakache (1964) derived a model to describe EOF with EDL overlapping, valid only at low surface potentials. They considered a specific ion concentration in the bulk, assumed to be independent of the electric potential, and a fixed zeta potential at the shear plane.

Based on the theory proposed by Rice and Whitehead (1965) several authors derived models to study EOF overlapping. Levine et al. (1975) extended the model to higher surface potentials. Later, Wan (1997) demonstrated that EDL overlapping is significant at low range of electrokinetic radius, κa.

A detailed model for overlapped EDLs between two flat plates without using the Boltzmann equation, was

Modelling electro-osmotic flow in porous media: a review

proposed by Qu and Li (2000). They derived the equations to describe the EDL potential and the ionic concentration distributions, by considering a symmetric EDL potential distribution. The surface charge potential, and the ionic concentrations in the solution were calculated by using the site dissociation model proposed by Healy and White (1978). When the distance between the plates was higher than four times the double layer thickness, the EDL potential distribution obtained through the developed model was found to be similar to that of the classical theory. As the distance decreased, the classical theory overestimated the results. Concerning the ionic concentration distribution and the net charge density, the trends were similar: the divergence between the results of the developed model and those of the classical theory decreased as the distance between the plates increased. This model was taken up later by several authors to analyse EO micropumps (Hu and Chao, 2007) and combined electro-osmotic and pressure driven flow in a rectangular micro-channel at high zeta potential (Mondal et al., 2014). The potential across the channel increased with wall ζ potential; at centerline it tended towards the wall value at high wall ζ potential, while it decreased with the electrokinetic radius (Mondal et al., 2014).

Unlike the above mentioned works, in which a symmetric condition at the centre of the channel was assumed, Conlisk et al. (2002) considered symmetric and asymmetric flow, potential and mole fractions. The ionic concentration fields were modelled through the Nernst equation. A linear trend between flow rate and channel height was found, obtaining useful flow rate also at low applied potential. When symmetric conditions were considered, the results were comparable to those of classical theory, while in the case of asymmetric wall potentials, velocity and EDL potential were significantly different. The concentration variation in the electrolytic solution was considered also by Huang and Yang (2007), who integrated the net charge density along the channel characteristic length. The model showed the dependence of surface charge density on electrolyte concentration, only under high-salt conditions. At low-salt conditions not only the surface charge density, but also streaming conductance and potential are insensitive to the electrolyte solution.

Alternate current was found to enhance the difference in terms of concentration between anions and cations in case of EDL overlapping, with more significant effects at low ranges of frequency (Talapatra and Chakraborty, 2008).

In channels packed with charged porous media, EDLs overlapping can occur when the distance between the solid particles becomes comparable to EDL thickness. In this case the electric potential, ψ, is non-zero in a large portion of the channel, as shown in Figure 5.

2.2   Electroosmotic flow in a single pore

EOF is induced by the interaction between the EDL potential and the external applied electric field. Considering the flow as viscous and incompressible, EOF in a single pore can be modelled by using the Navier-Stokes equations. To take into account the electrokinetic effects responsible for EOF, the basic momentum conservation equation for fluid is modified by adding a source term, as follows (Patankar and Hu, 1998)

$$\rho_f \left(\frac{\partial \mathbf{U}}{\partial t} + (\mathbf{U} \cdot \nabla) \mathbf{U} \right) = -\nabla p + \mu_f \nabla^2 \mathbf{U} + \varepsilon \varepsilon_0 \kappa^2 \psi \nabla \phi \qquad (12)$$

where the linearised equation of Poisson-Boltzmann has been considered.

Von Smoluchowski (1921a) defined the EOF velocity by considering the balance between viscous and electrical forces

$$u_w = -\frac{\varepsilon \varepsilon_0 \zeta_w E}{\mu_f} \qquad (13)$$

where ζ_w is the zeta potential of the charged wall, μ_f is the viscosity of the bulk solution and E is the uniform electrical field. The fluid velocity in the pore is independent of the position in the pore and its shape.

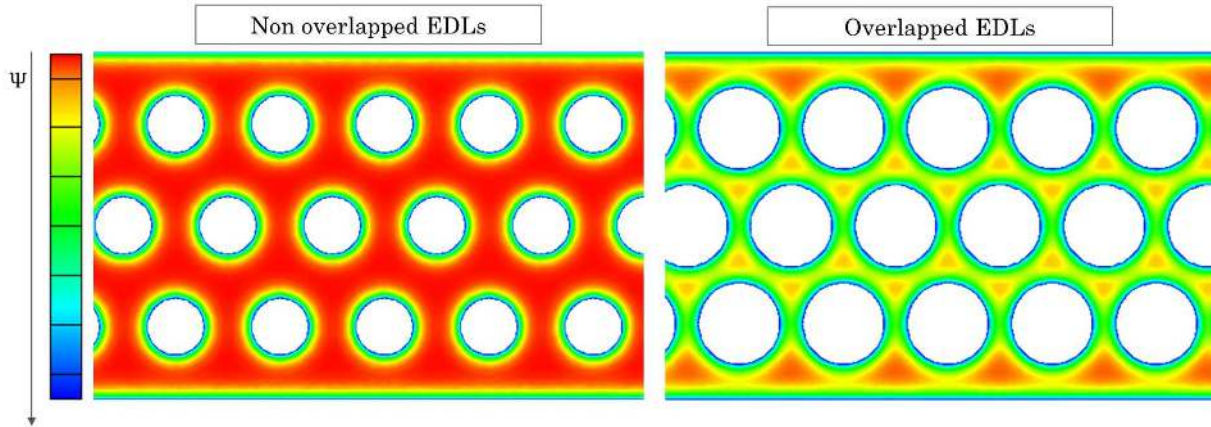Modelling electro-osmotic flow in porous media: a review

Figure 5: Channels packed with charged solid particles: when the distance between the solid particles is larger than EDL thickness, EDLs do not overlap and the potential, ψ, falls to zero at a certain distance from the particles boundaries. On the contrary, as the distance between particles decreases, EDLs overlap and the potential is non-zero.

In the classical models EOF is considered constant, neglecting the variations due to extended treatments. In soil decontamination through EO, chemical alterations should be taken into account. For this reason a predictive scheme to estimate ζ depending on pH was derived to analyse EOF variations (Eykholt and Daniel, 1994). The influence of the variation of zeta potential on EOF field along the axial position of the pore was taken into account also by other authors (Anderson and Keith Idol, 1985).

EOF involves the transport of chemical species. It was described in a tortuous capillary of a porous medium by the convective-diffusion equation (Shapiro and Probstein, 1993), as follows

$$\frac{\partial \bar{c}_i}{\partial t} = \frac{D_i}{\tau^2}\frac{\partial^2 \bar{c}_i}{\partial z^2} - \frac{\partial}{\partial z}\left[\bar{c}_i(u_{e,i}+\bar{u}_c)\right] + \bar{R}_i \tag{14}$$

where c_i is the concentration in moles per unit volume of solution of the species i, D_i is the diffusion coefficient, τ is the tortuosity (See section 3), $\bar{R}_i$ is the molar rate of production due to chemical reactions. The convection component of velocity is defined as

$$\bar{u}_c = \frac{1}{\tau^2}\frac{\varepsilon\varepsilon_0}{\mu_f}\langle\zeta\frac{\partial \bar{\phi}}{\partial z}\rangle \tag{15}$$

and the electro-migration component is given as

$$\bar{u}_{e,i} = v_i z_i F \frac{\partial \bar{\phi}}{\partial z}\frac{1}{\tau^2} \tag{16}$$

where $\langle\rangle$ denotes the volume average of the scalar product of the local ζ potential and the electric field in the z-direction, v_i is the ions mobility, F the Faraday constant.

3 MODELLING ELECTROOSMOTIC FLOW IN POROUS MEDIA

Porous medium is a material whose volume is partitioned into solid matrix and interconnected voids, filled by one or more fluids, as shown in Fig. 6.
The main properties which characterize a porous medium are:

8

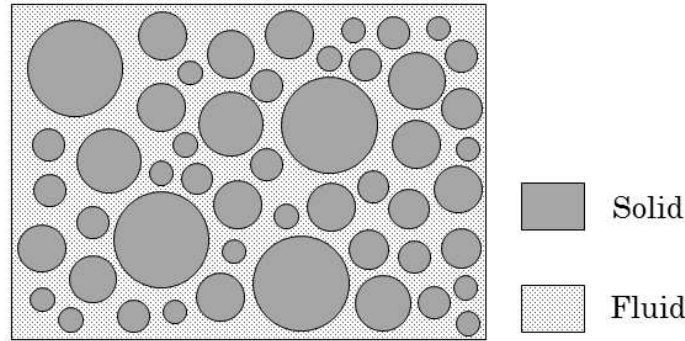Modelling electro-osmotic flow in porous media: a review

Figure 6: Schematic of a fluid-saturated porous medium.

- *porosity*, the ratio of the void space to the total volume of the medium;
- *permeability*, which describes the ability of a porous medium to transmit fluids;
- *tortuosity*, the ratio between the average length of the pore and the geometrical length of the medium.

EOF in porous media is analysed by using several methodologies and assumptions, that are described in the following sections. Generally, fluid flow and heat transfer in porous media can be investigated at the pore level or by using a macroscopic approach. In the first case, the porous medium is assimilated to an assembly of cylinders (Hlushkou et al., 2005) and the Navier-Stokes equations are assumed to govern the flow. The microscopic approach provides minute details at the particle level. Therefore its use is appropriate when the interaction mechanisms, at the internal interfaces between the materials that compose the porous medium, need to be considered (Ehlers and Bluhm, 2013). However, this approach is computationally expensive (Massarotti et al., 2003; Arpino et al., 2009) and, except for few industrial applications, porous materials present arbitrary and irregular shape (Ehlers and Bluhm, 2013), so that it is hard to clearly define their structure. If the porous medium is homogeneous, its structure can be spread over the considered domain through an appropriate averaging process (Ehlers and Bluhm, 2013). This can be done by using two approaches, statistical and spatial. The first one consists in the average over reference porous structures, assuming the statistical homogeneity. The second approach involves averaging over the so-called Representative Elementary Volume (REV) (S., 1961), whose scale, l, is larger than the pore scale, d_p, and smaller than that of the flow domain, L (Nield and Bejan, 2006), as sketched in Figure 7.

Fluid flow in saturated porous media was firstly described by using the well-known Darcy equation, which relates linearly the pressure gradient to the flow rate across the porous medium (Darcy, 1856). As porous media applications increased, some extensions to Darcy's model, known as *non-Darcy models*, were introduced. The two major additions were:

- Forchheimer's equation (Forchheimer, 1901), to take into account the drag effect on the fluid caused by the solid matrix, that can be neglected for slow moving flows;

- Brinkman extension (Brinkman, 1949), to consider macroscopic boundary effects.

The former led to the addition of a non-linear drag term to the Darcy equation, as follows

$$\nabla p = -\frac{\mu_f}{K}\mathbf{u} - \rho_f \frac{\Phi c_F}{\sqrt{K}}|\bar{\mathbf{u}}|\mathbf{u} \tag{17}$$

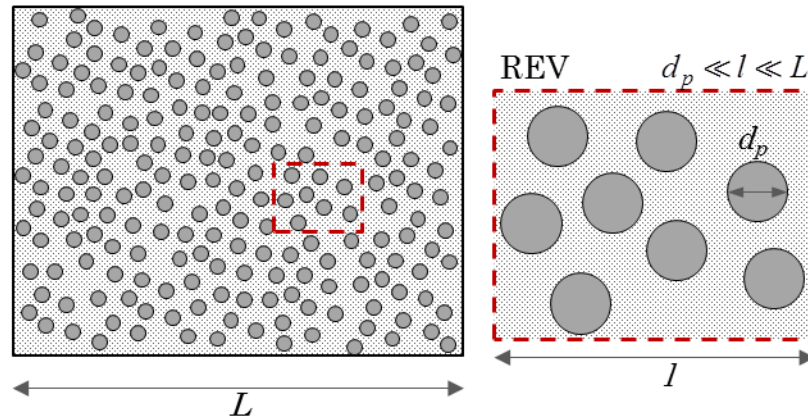Modelling electro-osmotic flow in porous media: a review

Figure 7: Representative Elementary Volume (REV) and scales in macroscopic approaches to model flow in porous media.

where K is the medium permeability, Φ is the porosity and c_F a non-dimensional form-drag constant. The Brinkman extension of Darcy model consists in the inclusion of a second order term, as follows

$$\nabla p = -\frac{\mu_f}{K}\mathbf{u} - \frac{\mu_e}{\Phi}\nabla^2\mathbf{u} \tag{18}$$

where μ_e is the effective viscosity of the porous medium, used to take into account the viscous effect that increases as porosity and permeability increase.

In order to overcome the limitations due to the use of the non-Darcy models (Massarotti et al., 2003) a generalized model that incorporates Darcy model and its extensions was introduced. The first attempt was presented by Whitaker (S., 1961), that introduced a volume averaging procedure used and followed by Vafai and Tien (1981) and Hsu and Cheng (1990). Later a control volume principle was introduced by Nithiarasu et al. (1996) to model saturated porous medium of variable porosity. The generalised model is very advantageous as it is very similar to Navier-Stokes equations, to which it approaches when the porosity approaches unity (Arpino et al., 2013, 2015). For this reason, it presents a high flexibility, since it allows the describe interface problems by using the same partial differential equations, both in the free fluid and porous domain (Arpino et al., 2011).

3.1 Macroscopic approach

The first applications of EOF in porous media concern Capillary Electro-Cromatography (CEC), where the packing surface is charged (Rathore and Horváth, 1997). In this case, EOF can be assimilated to the flow through several parallel micro-channels, whose walls present a zeta potential value equal to that of the particles. Therefore, the EOF velocity in each channel is given by Eq. (13). This relationship, proposed by von Smoluchowski (1921b), was modified by Overbeek and Wijga (1946); Overbeek (1952) for packed column. They considered:

- non-conducting particles, characterised by an uniform zeta potential, ζ_p,

- thickness of the double layer negligible compared to the pore radius.

Under these assumptions, the average EOF velocity, u_p, is given as

$$<u_p> = \frac{1}{V_c}\int_{V_{cf}} u_p dV_c = -\frac{\varepsilon\varepsilon_0\zeta_p}{\mu V_c}\int_{V_{cf}} E dV_C \tag{19}$$

Modelling electro-osmotic flow in porous media: a review

where V_c and V_{cf} are the total volume and the volume of the interstitial space, respectively. Integrating over V_c the EOF velocity generated locally at the packing surface is given by

$$u_p = -\frac{\varepsilon \varepsilon_0 \zeta_p E}{\mu} \qquad (20)$$

Considering the following relation for the current j

$$j = \sigma^* E = \frac{\sigma_b}{V_c} \int_{V_{cf}} E \, dV_c \qquad (21)$$

where σ_b and σ^* are the conductivities of the electrolyte and of the packed column, respectively, the average velocity in the porous medium is given by

$$<u_p> = -\frac{\varepsilon \varepsilon_0 \zeta_p E}{\mu} \left(\frac{\sigma^*}{\sigma_b} \right) \qquad (22)$$

To extend the theory proposed by Overbeek and Wijga to CEC, Rathore and Horváth (1997) derived the net local velocity, u_r, considering the contributions of the tube walls and the particles, characterized by different values of zeta potential, ζ_w and ζ_p, respectively:

$$u_r = u_{rw} \left(1 - \frac{\zeta_p}{\zeta_w} \right) + u_p \qquad (23)$$

where (Rice and Whitehead, 1965)

$$u_{rw} = u_w \left[\frac{I_0 (\beta r/d_p)}{I_0 (\beta a/d_p)} \right]$$

and β is a dimensionless constant, which depends on the dimensionless packing parameter, α, and the column porosity, Φ, according to the following

$$\beta = 3 \sqrt{\frac{\alpha (1 - \Phi)}{2}}$$

Using this velocity profile, the authors illustrated that the wall effect is limited to a circumscribed area close to the wall and that it increases with the particle diameter of the packing for a fixed tube diameter.

Levine and Neale (1974) proposed an analytical theory to study electrophoresis and electroosmosis in a swarm of spherical particles characterized by small surface potential, taking into account EDL overlapping. They modified von Smoluchowski velocity, Eq. (13), by using a correction factor dependent on porosity and electrokinetic radius. They found that in case of thin EDL the average velocity is not affected by the void fraction, while there is a strong dependence in case of large EDL. This analysis was extended by Kozak and Davis (1986), to examine array of ordered fibrous porous media. They underlined the importance of orientation and contact of fibres on EOF. They also developed a theory to predict particle interactions in concentrated suspensions and porous media (Kozak and Davis, 1989b). At high zeta potentials the classical theory was found to over predict EOF. The particle concentration was found to affect the mobility. In addition, they noticed similar effects on EOF when the porosity decreased or the EDL thickness increased. The model was found to be valid for $\kappa a > 20$ in case of dilute suspensions, for $\kappa a < 100$ for more concentrated suspensions (Kozak and Davis, 1989a). Effects of EDL polarization and overlap of adjacent particles were analysed also by Lee et al. (2000). For small values of κa the effect of EDL potential was more significant than that of DL polarization, while this trend is reversed for large values of κa. The EO velocity was found to increase with the surface potential and the porosity.

A very detailed study on CEC systems was presented by Liapis and Grimes (2000). They developed and

solved a mathematical model to describe electrostatic potential, pressure and EOF velocity. The simulations were carried out on charged cylindrical capillaries and capillary columns packed with charged spherical particles. The radius of interstitial channels of bulk flow was assumed to be about 25-40% of the particles radius. The motion equation and EDL potential equation for cylindrical channels were solved by using the method of orthogonal collocation on finite elements. As the particle diameter increased, velocity decreased and the size effect was most significant when the difference between the zeta potential of the walls and the particles rises. In particular, the velocity in the region close to the capillary wall was enhanced when $\zeta_w > \zeta_p$ and decreased when $\zeta_w < \zeta_p$. The enhancement obtained when $\zeta_w > \zeta_p$ was greater than the reduction found when $\zeta_w < \zeta_p$. In the first case wall and particles effects cooperated, while in the second the slower velocity due to the lower wall zeta potential negatively affected the bulk flow in the region close to the wall. The wall effect was found to influence the flow for only about one third of the capillary radius, in compliance with Rathore and Horváth (1997) results. The velocity was found to increase as the electrical field applied increased with negligible influence of particles diameter. Grimes et al. (2000) used this model together with their pore network theory to assess EOF in a capillary column packed with charged porous silica particles. As the connectivity among the intra-particle pores increased, both EO velocity and flow rate increased. EO convective flow enhanced mass transfer rate and reduced intra-particle mass transfer resistance.

In addition to CEC systems, EOF has been analysed from a macroscopic point of view for two different applications:

- Zeng et al. (2001) proposed an analytical model, that has been used and further developed by several authors, to investigate EO pumping. This model is focused on the maximum pressure, maximum flow rate and efficiency of the pump;

- other authors applied the generalized model, described in Section 3.1, to simulate EOF in packed channels.

3.1.1   Analytical modelling

Recently, the interest in EO pumping has increased. The latest research focused on the way to increase the charged surface area, to enhance pumping efficiency (Arnold et al., 2008).

Zeng et al. (2001) extended the analysis of Rice and Whitehead (1965) on the velocity profile for the electro kinetic flow in a narrow capillary to derive the flow rate on the entire porous medium, Q, as

$$Q = -\frac{\Phi \Delta P A a^2}{8\mu L \tau} - \frac{\Phi \varepsilon \zeta V A}{\mu L \tau}\left(1 - \frac{2\kappa I_1\left(a/\kappa\right)}{a I_0\left(a/\kappa\right)}\right) \tag{24}$$

where ΔP is the pressure difference along the length of the capillary, a is the capillary radius, A is the cross-sectional area of the porous medium and I_1 is the first order modified Bessel function of the first kind. The tortuosity τ was defined as $\tau = (L_e/L)^2$, in which L_e is the average length of travel for flow along the pore path and L the physical length of the porous structure. The maximum pressure ΔP_m occurred for the condition of zero net flow rate

$$\Delta P_m = \frac{8\varepsilon\zeta V}{a^2}\left(1 - \frac{2\kappa I_1\left(a/\kappa\right)}{a I_0\left(a/\kappa\right)}\right) \tag{25}$$

while the maximum flow rate, Q_m, was found under the condition of zero counter pressure, as

$$Q_m = -\frac{\Phi\zeta}{\tau}\frac{\varepsilon V A}{\mu L}\left(1 - \frac{2\kappa I_1\left(a/\kappa\right)}{a I_0\left(a/\kappa\right)}\right) \tag{26}$$

Modelling electro-osmotic flow in porous media: a review

The thermodynamic efficiency of the pump, representing the ratio between the useful pressure work delivered by the pump over the total power consumption, was defined as

$$\eta = \frac{\Delta P Q}{V I} \tag{27}$$

where V is the applied potential and I is the total current. This analytical model has been used by several authors to investigate EO pumping. It was further developed by Yao and Santiago (2003) for a porous EO pump, operating under a pressure load. They took into account the dependence on the pressure load of the total current I, which is the sum of two contributions, advective and electromigration currents. EDL potential was described by numerically solving the Poisson–Boltzmann equation, that was confirmed to be unsuitable when EDL fields overlap, since potential associated with the wall charges is non-zero at the centre of the pore. The EDL potential was implemented into the analytical expressions, derived for the electroosmotic flow rate, current, and thermodynamic efficiency. The developed numerical model was used as design guidance to fabricate porous-structure EO pumps (Yao et al., 2003). The comparison between numerical and experimental results highlighted that the analytical model can be used for designing EO pumps, but it over-predicted the absolute flow rate, total current, and pump pressure. This was partly due to the difference between the idealized geometry of the pores used in the numerical model and the real one.

Eq.s (24)-(27) were used by Wang, Chen and Chang (2006) to investigate a high-pressure EO micro-pump made of silica-based monoliths by a sol–gel process. A good agreement was found between the numerical results and the experimental values. The maximum pressure work occurred at the middle point of the pump where $P = P_{max}/2$ and $Q = Q_{max}/2$: these values maximised the thermodynamic efficiency, representing the optimum operating condition.

Berrouche et al. (2009) modelled, designed and experimentally tested a porous EO pump (PEOP), fabricated on the base of two types of porous ceramics, sintered alumina and silica. The experimental results showed that the voltage applied to the disk is significantly lower than the one applied to PEOP (only 10.5 V were induced on the porous disk with an applied 150 V voltage at the electrode). The difference can be due to the electrical losses between the electrode and the disk surface. Comparing the two materials, alumina disk provided higher pressure drop and lower flow rate than silica, probably due to the lower pore radius of alumina disk: on one hand it increased the contact surface, on the other hand viscous losses rose. The maximum flow rate and the maximum pressure achievable were calculated by using Eq.s (25) and (26). The comparison between the numerical results and the experimental data showed that flow rate was overestimated, probably due to the difficulty in tortuosity measurement, while for the pressure a good agreement between numerical and experimental values was found.

3.1.1.1 Porous membranes

Yao et al. (2006) studied electro-osmotic pumps fabricated from porous silicon membranes. The membranes presented a hexagonal array of uniform pores, with a tortuosity that approached unity. They have been modified with a thin film deposition to provide electrical insulation, improve the surface charge density and operation and control the pore diameter. The maximum pump flow rate, maximum pump current and maximum pump pressure were measured at applied voltages of 10 to 100 V. The experimental data were compared to the numerical results obtained by using Eq. (24) for flow rate, and Eq.s (25) and (26) for maximum pressure and flow rate. As expected, the highest measured pressure was achieved by the membrane with the smallest pores, while the largest flow rate with the membrane without deposition. In contrast with results found by Berrouche et al. (2009) (See Sec. 3.1.1), the numerical model was found to accurately predict flow rate measurements, while it typically over predicted measured pressure capacity by about 60%. The thermodynamic efficiency was found to vary between 0.003% to 0.05% for the small and large pore

pumps, respectively. Finally, trying to optimize porosity, the authors found that both flow rate and pressure performance of porous silicon membrane pumps could be enhanced, by increasing pore number density and decreasing pore diameter. Cheema et al. (2013) found that EO pumping can be enhanced when layers adjacent to the solid wall of the pump present higher porosity with respect to the central region. The same result was found for packed micro-channels: under variable porosity the velocity near the walls was reported to be larger than in the case of constant porosity, therefore variation in porosity near the wall cannot be neglected (Chai et al., 2007).

3.1.2 Generalized model for porous media

The first model for describing EO and pressure driven flow in porous media was presented by Scales and Tait (2006). It was based on Navier-Stokes equations, properly scaled to simulate the average flow through a porous medium (Liu and Masliyah, 1996; Vafai and Tien, 1981; Nithiarasu et al., 1997).

$$\nabla u = 0 \tag{28}$$

$$\frac{\sqrt{\tau}}{\Phi}\frac{\partial u}{\partial t} + \frac{\sqrt{\tau}}{\Phi}u\left(\nabla\frac{u}{\Phi}\right) = -\frac{\nabla P}{\sqrt{\tau}\rho} + \frac{\mu}{\sqrt{\tau}}\nabla^2\frac{u}{\Phi} - \frac{\rho_{eff}\nabla\phi}{\sqrt{\tau}\rho} - \frac{\mu_e u}{K} - \frac{c_F u|u|}{\sqrt{K}} \tag{29}$$

The spatial derivatives were scaled by the square root of tortuosity, which relates the length scale at the pore level and the length scale at the macroscopic scale. The effective charge density, ρ_{eff}, that appears in the EO force term of Eq. (29), was defined as

$$\rho_{eff} = \frac{\varepsilon\varepsilon_o\zeta}{\sqrt{\tau}K}\left(\frac{\int\int\psi dA_p}{\psi_0 A_p} - 1\right) \tag{30}$$

in which A_p is the cross sectional area of the pore.

The flow was considered slow enough to neglect the non-linear terms in Eq. (29), and the walls containing the porous medium were assumed to be uncharged. In addition the flow was considered steady since it was demonstrated that the flow development over time can be usually neglected. Under these simplifying hypotheses and by applying the no-slip condition at the channel walls as boundary condition, several analytical solutions were derived for EOF in porous media.

EOF between two parallel plates in a porous channel of height c:

- with uncharged walls and charged porous medium

$$\bar{u}(y) = \bar{u}_d\left(1 - \frac{e^{-\lambda(c-y)} - e^{-\lambda(2c-y)} + \left(1 - e^{-\lambda c}\right)e^{-\lambda y}}{1 - e^{-\lambda 2c}}\right) \tag{31}$$

where $\bar{u}_d$ is given by Darcy's law

$$\bar{u}_d = -\frac{K}{\sqrt{\tau}\mu_e}\left(\nabla P + \rho_{eff}\nabla\phi\right) \tag{32}$$

and λ is the Brinkmann screening length defined as

$$\lambda = \sqrt{\frac{\Phi\sqrt{\tau}}{K}\frac{\mu_e}{\mu}} \tag{33}$$

Modelling electro-osmotic flow in porous media: a review

- with charged walls and uncharged porous medium

$$\bar{u}(y) = Z \left(\frac{\psi_{w1} \left(e^{-\lambda(2c-y)} - e^{-\lambda y} \right) + \psi_{w2} \left(e^{-\lambda(c+y)} - e^{-\lambda(c-y)} \right)}{1 - e^{-\lambda 2c}} \right) + Z\psi(y) \tag{34}$$

$$Z = \frac{\varepsilon\varepsilon_0 \kappa^2 \nabla\phi}{\mu(\lambda^2 - \tau\kappa^2)} \tag{35}$$

EOF in a porous cylinder:

- with uncharged walls and charged porous medium

$$\bar{u}(r) = \bar{u}_d \left(\frac{I_0(\lambda r)}{I_0(\lambda c)} - 1 \right) \tag{36}$$

- with charged walls and uncharged porous medium

$$\bar{u}(r) = Z\psi_w \left(\frac{I_0(\sqrt{\tau}\kappa r)}{I_0(\sqrt{\tau}\kappa c)} - \frac{I_0(\lambda r)}{I_0(\lambda c)} \right) \tag{37}$$

The case in which both walls and porous medium are charged can be analysed by using the superposition of the individual cases, Eq.s (31) and (34) for two parallel plates in a porous channel, and Eq.s (36) and (37) for porous cylinders.

AC driven EO systems in closed-end micro-channels densely packed with uniform charged spherical micro-particles were analysed by Kang et al. (2004a) by using the Carman–Kozeny theory (Probstein, 2005). They determined the backpressure, generated in presence of a fixed excitation frequency, by analytically solving the modified Brinkman momentum equation. The electro kinetic effects were implemented by introducing the EDL potential derived through the analytical solution of Poisson-Boltzmann equation. The hydraulic diameter or effective pore diameter, defined as

$$d_{pore} = \frac{4\Phi}{A_0(1-\Phi)} \tag{38}$$

was used as reference length. For a fixed pore size, the backpressure was found to decrease with increasing excitation frequency when the excitation frequency was lower than the system characteristic frequency. The opposite trend was obtained when the excitation frequency was higher than the system characteristic frequency. This model was validated against experimental results and used to investigate the influence of several parameters on EOF (Kang et al., 2007). It was found that wall effect cannot be neglected when the ratio between the capillary diameter and the particle diameter is small. EOF velocity was shown to be significantly affected by the ionic concentration and the type of electrolyte, since they influence the zeta potential magnitude, while the effect of the capillary length was negligible. The model was further developed (Kang et al., 2004b) by considering separately the contribution from the charged capillary wall with neutral packing and that from charged particles, as in Eq. (23) (Rathore and Horváth, 1997). The modified Brinkman momentum equation was used to model the macroscopic EOF in the porous channel with neutral packing particles: the electro-kinetic effect was taken into account by introducing the EDL potential, determined by analytically solving the Poisson-Boltzmann equation with channel width used as reference length; no pressure gradient was considered and, due to low Reynolds number, the macroscopic inertial force was neglected. The macroscopic velocity in charged microspheres was determined by considering tortuosity and porosity, as

$$u_p = -\frac{\varepsilon\varepsilon_0}{\mu} E_0 \zeta_p \frac{\Phi}{\tau} \frac{2}{\zeta_p R_{pore}^2} \int_0^{R_{pore}} r\psi_i(r)dr \tag{39}$$

Modelling electro-osmotic flow in porous media: a review

The model was used to demonstrate that EOF is affected by the properties of the working fluid and the porous medium, the size and the charge condition of the capillary and packing particles (Kang et al., 2005). The electro-kinetic wall effect appeared to be more significant when the size of the particles is comparable to that of the micro-capillary; the effect of the difference between the charge of the wall and the particles was found to be similar to those found by Liapis and Grimes (2000).

The Carman-Kozeny model was also used by Chai et al. (2007), who analysed EOF in porous media through the generalized porous medium equations solved by using LBM. Fluid flow in porous media was analysed through the model proposed by Nithiarasu et al. (1997), and the EO effect was implemented into the source term by the net charge density, ρ_e, and the effective charge density, ρ_{eff}. Internal potential was estimated through the linearized Poisson-Boltzmann equation. The authors performed a parametric analysis of EOF through a micro-channel filled with a solid medium with varying porosity. It was found that larger particle diameters cause larger velocity, probably due to the consequent porosity increase. An important result was that the viscous transfer of momentum from the channel walls to the centre of the channel is prevented by the drag action induced by the porous medium: this effect was more significant at high particle diameters. Velocity increased with porosity. The zeta potential considered for both the channel and the solid particles was comparable to that used in capillary electro-chromatography. Higher values of wall zeta potential caused larger velocity near the channel wall, but had negligible influence on the velocity in the central region. The velocity increased also with increasing applied electric field. Considering tortuosity, the velocity decreased as it rose, due to the reduction of permeability. Finally, in all the cases analysed it was found that under variable porosity the velocity near the walls was much larger with respect to constant porosity, therefore near wall porosity variation cannot be neglected.

3.2.2.1 Non-Newtonian flow

Many practical EO driven systems are based on the use of non-Newtonian fluids, such as bio-fluids. In these cases the rheological behaviour of the fluid must be taken into account (Cho et al., 2015).

Electro-osmotically driven non-Newtonian flow in a porous medium was studied by Tang et al. (2010) through a LBM based on the REV scale. To simulate the fluid flow in porous media they adopted the generalised model proposed by Nithiarasu et al. (1997): they implemented two source terms, one to take into account the flow resistance for Non Newtonian fluids flowing in porous media (Herschel and Bulkley, 1926; Al-Fariss and Pinder, 1987), and the other to consider the electro-osmotic effect. For the non-Newtonian fluid the Herschel-Bulkey model (Herschel and Bulkley, 1926) was used to determine the yield stress value, τ, as

$$\tau = \eta_0 \dot{\gamma}^n + \tau_0, \qquad \tau > \tau_0 \tag{40}$$

where η_0 is the dynamic viscosity, n is the power law exponent, τ_0 is the fluid yield stress and γ is the local shear rate. Concerning the EO effect, the charge of both solid porous material and channel walls was taken into account. For solid particles, the effective charge (See Eq. (30)) was used in order to remove the charge density's dependence on the position at pore level. The particle zeta potential was assumed to be small enough to be linearised and analytically solved through the Poisson–Boltzmann equation as follows

$$\rho_{eff} = \frac{\Phi \varepsilon \varepsilon_0}{K} \left(\frac{2I_1(\kappa R_p)}{\kappa R_p I_0(\kappa R_p)} - 1 \right) \tag{41}$$

where I_n is a modified Bessel function of the first type of order n, and R_p is the hydraulic radius. Since the charged solid particles may affect the electric potential distribution between the parallel channel, a modified zeta potential was implemented as boundary condition, given as follows

$$\zeta_w' = \zeta_p \left(1 - \frac{2I_1(\kappa R_p)}{\kappa R_p I_0(\kappa R_p)} \right) + \zeta_w - \zeta_p \tag{42}$$

Modelling electro-osmotic flow in porous media: a review

By using this model, the velocity was found to increase as the power law exponent and the yield stress, see Eq. (2), decrease, and as the solid particle diameter and the porosity increase. The zeta potential of solid particles significantly affected velocity in centre region of the channel, while the influence of the channel wall zeta potential was high close the wall.

3.2 *Microscopic approach*

The first attempts to simulate electroosmosis in a porous medium constructed using ordered arrays of spheres were carried out by O'Brien (1986) and Mehta and Morse (1975). The first derived an analytical formula for the flow rate when the double layer is much thinner than the particle radius. Mehta and Morse simulated flow in porous membranes by a cell model composed of the generalized Nernst-Planck flux equations, the Navier-Stokes equation, and the Poisson-Boltzmann equation. Inhomogeneous porous membranes were analysed by Jin and Sharma (1991), who extended the capillary tube model to a network model to take into account complexity and inhomogeneity of porous media. The membranes were approximated using tubes in series or in parallel. In general they demonstrated that pore size distribution and connectivity affect the streaming potential. The contribution to macroscopic streaming potential was larger for the tubes in series when the pores were small, while for the parallel ones when the pores size increase.

Porous media subjected to electroosmosis were approximated using periodic hollow circular capillaries also by Coelho et al. (1996), who derived two coupling coefficients. The comparison with experimental results showed a good agreement also with other porous structures. In order to fit the data the average pore size, chosen as reference length, should be appropriately determined. This reference length was used by Marino et al. (2001) to determine the coupling tensors between external electric field, pressure gradient, and concentration gradient acting on a dilute electrolyte flowing through a charged porous medium or a charged fracture. These tensors were computed for several configurations of porous media, with known permeability and the conductivity. The model developed by Coelho et al. (1996) was extended to high zeta potential by Gupta et al. (2008), that investigated several configurations of porous media, i.e. simple cubic packing of spheres and simple cubic packing of ellipsoids, random packing of monodisperse spheres.

Dufrêche et al. (2005) studied EO in hydrated montmorillonite clays, by comparing mesoscopic theories to microscopic models. The methods were found to agree for large interlayer distance, due to the negligible interactions between the particles and the surface in the PB model.

Packed channels, similar to the columns used in electro-chromatography, can be used to pump fluid through porous media (Paul et al., 1998). Li, Zhou, Yan and Tian (2013) examined, experimentally and numerically, the combined effect of gravitational force and electro-osmosis on flow rate in micro-porous media, for filtering applications, demonstrating the effectiveness of electro-osmosis pumping at micro-scale (less than $1 \cdot 10^{-4}$ mm). Experimental results showed that electro-osmosis effect is responsible for around 15-20% of the total flow rate. The experiments were simulated by using a modified LBM with porous micro-channel assumed as a compact spherical packing model, that was found to be appropriate to model this kind of problems. Indeed, LBM has been widely used to model EOF in porous media. Wang, Wang, Chen and Pan (2006) used Lattice Poisson Boltzmann Method (LPBM) to model and analyse EO pumping in structured charged porous media packed in a micro-channel. The effect of particle surface potential on the electric potential distribution has been taken into account by solving the nonlinear Poisson–Boltzmann equation in the whole domain. The authors considered nanoparticles, whose size was of the same order of magnitude as or even smaller than the EDL thickness. They found that the influence of particle surface charge is significant and the addition of porous media improves EO pumps performance considerably, with higher pumping pressures and lower flow rates. The highest maximum pumping was obtained by using smaller particles: in nano-scale, contrary to macro-scale, particles size affects the bulk potential distribution, and therefore the driving force. Particle size also influences the maximum value of electric potential and its distribution,

and as a consequence the flow rate, that under zero pressure drop increases faster for smaller particles. Finally, the results indicated that the main driving force comes from the charged porous media rather than the channel walls. The model was also used to simulate EOF in charged anisotropic porous media (Wang et al., 2007): the porous medium was defined by arrays of ellipses, whose axis lengths and angles are used to estimate the effect of anisotropy. The flow rate increased as the axis length along the external electric field direction increased, and decreased when the angle between the semimajor axis and the flow direction was smaller than $\pi/2$. The authors introduced some factors to describe the anisotropy of the medium and found that it decreased EOF permeability. EOF permeability was also studied (Wang and Chen, 2007) in three-dimensional homogeneously charged micro- and nano-scale random porous media, whose structure was reproduced through the random generation-growth method. The results, compared with existing experimental data, showed that EO permeability monotonically increases with porosity, average characteristic length of solid particles and with bulk ionic concentration. As the porosity increased, the increasing rate of EO permeability rose, while increase in ionic concentration decreased EO permeability. Zeta potential on solid surfaces of porous media was found to directly affect EO permeability with a proportional linear relationship for very small values. The model was also used to investigate the influence of porous media structure (granular, fibrous, or network) on EOF (Wang, 2012). The network configuration showed the highest surface–volume ratio, that increased EOF permeability at low porosity. On the contrary, as the porosity increased, the granular structure was the most efficient due to its low resistance to flow. A similar approach was used to investigate the influence of the structure of porous media on electro-osmotic permeability in shear-thinning, shear-thickening and Newtonian fluids (Chen et al., 2014), finding that electro-osmotic permeability grows monotonically with increasing porosity. Furthermore, the relation between permeability and external electric field resulted in almost linear relationship for both shear-thinning and shear-thickening fluids, and constant for the Newtonian fluid. For low values of zeta potential or bulk concentration, the shear-thickening fluid was found to be the highest permeable, while for a high zeta potential or bulk ion concentration the shear-thinning fluid was shown the highest electro-osmotic permeability. Other factors influencing electro-osmotic permeability in topographically complicated porous media, composed by two constituents, characterized by different values of ζ potential, were porous medium morphology, solid fraction and ratio between the two solid constituents (Bandopadhyay et al., 2013).

Kang et al. (2004a) studied ac-driven electroosmotic flow in open-end and closed-end micro-channels densely packed with uniform charged spherical microparticles. For open-end channels they used the so-called capillary flow model and solved the motion equation employing the Green function method. The Poisson–Boltzmann equation governing the EDL potential field was analytically solved by considering the hydraulic diameter (Kaviany, 2012) as reference length. It was found that both the pore size and the excitation frequency affected the oscillating Darcy velocity profile. EOF decreased as the frequency increased for a fixed pore size, while as the pore size increased velocity rose in the low frequency domain, and got lower in the high frequency domain.

Hlushkou et al. (2005) derived a numerical model used to simulate EOF through dense regular and random arrays of hard spheres. Volumetric EOF was not significantly affected by the particle size distribution, while velocity fields were enhanced, in terms of homogeneity, if the particles distribution was heterogeneous, due to the better filling of void space. In another work they proposed a numerical approach for EOF in an array of hard spheres representing colloidal particles (Hlushkou et al., 2006). The model coupled Nernst-Planck, Navier-Stokes, and Poisson equations, solved by using Lattice Boltzmann and finite-difference methods. With respect to the previous papers, some simplifying hypotheses were removed, such as Debye-Hückel and thin EDL. EO velocity showed a nonlinear dependence on ζ potential at small values of the aspect ratio of sphere diameter to EDL thickness. This trend was more significant when EDLs overlapped. On the contrary the relation between EOF and the external applied electric field was found to be linear in the whole range of aspect ratio.

Li, Zhou, Yan, Han and Ren (2013) simulated EO pumping in molecular sieve adsorbent of zeolite through

Modelling electro-osmotic flow in porous media: a review

LBM, by assuming the sieve as an assembly of uniformed spherical nano-particles. Only the zeta potential of solid particles was taken into account neglecting that of the container walls. The porosity effect on EOF was analysed by varying the distance between the particles from $0.6\kappa^{-1}$ to $9\kappa^{-1}$; this range corresponds to the ideal porosity from 5% to 60%. For a distance between 0.6λ and 2λ, the Stern layer and the Gouy-Chapman layer overlap. As a consequence of the dense screening charge cloud and the presence of less active free ions, the flow inside the nano-pores decreases. Beyond this range of 0.6λ - 2λ, EOF increases up to a maximum and of 5λ where EOF contributes the entire driving forces in the channel. Beyond this value EOF contribution decreases because as the distance between the particles increase the superpositional zeta potentials on each particle is negligible. The resistance of viscous liquid was found to exert dominant shear stress to block the flow in the porous media.

A fractal model was used also by Liang et al. (2015) to examine EOF in a system constituted by two vessels connected by a porous medium. They derived an analytical expression to investigate the height difference of electrolyte between the two vessels. This expression was defined as a function of physical properties of the electrolyte solution, micro-structural parameters, zeta potential on the solid surface and Debye thickness. They found that the maximum height difference increases monotonously as the applied voltage increases, while decreases when the diameter of the particles and porosity increase. The numerical results were compared with experimental data and a good agreement was found.

The influence of charged solid particles on EOF was investigated by considering an effective porosity in the equation governing internal potential by Di Fraia et al. (2017). The results demonstrated that, under the analysed conditions, introducing charged solid particles into channels wider than $100~\mu m$ enhances the flow rate induced by electroosmosis.

3.2.1 Non-Newtonian flow

Non-Newtonian EO and pressure driven flow in microporous structures was studied by Tang (2011) by using Lattice Boltzmann method. The results on viscosity distribution agreed with fluid rheological properties, which resulted in significantly affecting electro-viscous effect on the flow. For Newtonian and shear thickening fluids, the electro-viscous effect showed a low contribution to the flow, whereas it acted as a resistance in case of non Newtonian fluid. This resistant effect increased with surface zeta potential.

Power-law fluids were analysed also by Zhu et al. (2015), who developed an analytical model to take into account the effect of EDL on permeability in porous fibers by using the fractal technique of pore distribution. They found that the resistant effects of EDL were significantly affected by the flow behaviour index and effective permeability increased as the porosity and the pore radius increased. Effective permeability was derived by using a mean velocity, determined by introducing the EDL potential as a source term in the motion equation and using the approximation for velocity distribution of power-law fluids proposed by Zhao and Yang (2009). The porous fibrous media were regarded as an assembly of yarns with EDL small enough to linearize the Poisson–Boltzmann equation. The velocity increased as the solid particle diameter and the porosity increased, in compliance with the results reported by Tang et al. (2010).

4   CONCLUDING REMARKS

Electro-osmotic flow driven systems have been largely studied and their application is constantly growing. Main uses of such systems are pumping, mixing, capillary electro-chromatography and drying. Due to small scale of these systems, numerical modelling is particularly appropriate for their investigation. Fluid systems have been widely analysed both numerically and experimentally. For this reason, there are well defined numerical approaches and in the majority of the cases they are validated against experimental data. On the

Modelling electro-osmotic flow in porous media: a review

contrary, the scientific literature concerning numerical modelling of electro-osmotic flow in porous media is quite heterogeneous and only few experimental results are available for validation. In addition, many simplifying hypotheses are adopted, such as:

- linearisation of Poisson-Boltzmann equation to describe Electric Double Layer (EDL) distribution;
- low surface potential or considerable difference between EDL thickness and channel diameter, to avoid EDL overlapping;
- neglecting of charge of wall or solid particles.

Based on the model for electro-osmotic flow in a single capillary, several approaches have been developed. It is apparent that two main categories of flow modelling in porous media can be identified, macro- and microscopic approaches. Macroscopic models are more computationally-efficient and allow to investigate a wider range of porous structures, while a microscopic approach provides more accurate details of the quantities of interest. Within the first group, two different branches have been developed:

- analytical models to simulate electroosmotic pumping focusing on thermodynamic efficiency of the pumps; the results of these models were compared to experimental data, with contradicting conclusions. Some authors found a good agreement, whereas others experienced an overestimation of flow rate and/or pressure gradient;
- the use of a generalised model for porous media to investigate electro-osmosis in micro-channels packed with charged spherical micro-particles. Some analytical solutions were provided for these models, with several simplifying hypotheses. Some authors applied Lattice Boltzmann method, but the results were not validated against experimental values.

In the works analysed, the influence of several parameters and different operating conditions has been considered. EOF increases with applied electric field. The ionic concentration and its influence on ζ potential, can affect the electro-osmotic velocity. The majority of authors agree that as particle size and porosity increase electro-osmotic flow is enhanced, even though there are some studies that report no influence of the particle size on the flow. Some papers highlight that the effect of porosity can be connected to particle morphology. Some studies consider characteristic properties of porous media, such as tortuosity. It is clear that as it increases, electro-osmotic velocity decreases.

The analysis of literature has highlighted the absence of an universal model to analyse electro-osmosis in porous media, without simplifying assumptions. The heterogeneity of properties of materials considered and the operating conditions used, makes it more difficult to compare available data. For this reason, more work needs to be done to identify precise models for electro-osmosis in porous media and validate them extensively.

References

Ai, Y., Yalcin, S. E., Gu, D., Baysal, O., Baumgart, H., Qian, S. and Beskok, A. (2010), 'A low-voltage nano-porous electroosmotic pump', *Journal of colloid and interface science* **350**(2), 465–470.

Al-Fariss, T. and Pinder, K. (1987), 'Flow through porous media of a shear-thinning liquid with yield stress', *The Canadian Journal of Chemical Engineering* **65**(3), 391–405.

Anderson, J. L. and Keith Idol, W. (1985), 'Electroosmosis through pores with nonuniformly charged walls', *Chemical Engineering Communications* **38**(3-6), 93–106.

Arnold, A., Nithiarasu, P. and Tucker, P. (2008), 'Finite element modelling of electro-osmotic flows on unstructured meshes', *International Journal of Numerical Methods for Heat & Fluid Flow* **18**(1), 67–82.

Modelling electro-osmotic flow in porous media: a review

Arpino, F., Carotenuto, A., Massarotti, N. and Mauro, A. (2013), 'New solutions for axial flow convection in porous and partly porous cylindrical domains', *International Journal of Heat and Mass Transfer* **57**(1), 155–170.

Arpino, F., Cortellessa, G. and Mauro, A. (2015), 'Transient thermal analysis of natural convection in porous and partially porous cavities', *Numerical Heat Transfer, Part A: Applications* **67**(6), 605–631.

Arpino, F., Massarotti, N. and Mauro, A. (2011), 'Efficient three-dimensional FEM based algorithm for the solution of convection in partly porous domains', *International Journal of Heat and Mass Transfer* **54**(21), 4495–4506.

Arpino, F., Massarotti, N., Mauro, A. and Nithiarasu, P. (2009), 'Artificial compressibility-based cbs scheme for the solution of the generalized porous medium model', *Numerical Heat Transfer, Part B: Fundamentals* **55**(3), 196–218.

Asadi, A., Huat, B. B., Nahazanan, H. and Keykhah, H. A. (2013), 'Theory of electroosmosis in soil', *International Journal of Electrochemical Science* **8**(1), 1016–1025.

Baldessari, F. (2008), 'Electrokinetics in nanochannels: Part i. electric double layer overlap and channel-to-well equilibrium', *Journal of colloid and interface science* **325**(2), 526–538.

Bandopadhyay, A., DasGupta, D., Mitra, S. K. and Chakraborty, S. (2013), 'Electro-osmotic flows through topographically complicated porous media: Role of electropermeability tensor', *Physical Review E* **87**(3), 033006.

Bennacer, R., Carcadea, E., Ene, H., Ingham, D., Lazar, R., Ma, L., Pourkashanian, M. and Stefanescu, I. (2007), 'A computational fluid dynamics analysis of a pem fuel cell system for power generation', *International Journal of Numerical Methods for Heat & Fluid Flow* **17**(3), 302–312.

Berrouche, Y., Avenas, Y., Schaeffer, C., Chang, H.-C. and Wang, P. (2009), 'Design of a porous electroosmotic pump used in power electronic cooling', *Industry Applications, IEEE Transactions on* **45**(6), 2073–2079.

Brinkman, H. (1949), 'A calculation of the viscous force exerted by a flowing fluid on a dense swarm of particles', *Applied Scientific Research* **1**(1), 27–34.

Burgreen, D. and Nakache, F. (1964), 'Electrokinetic flow in ultrafine capillary slits1', *The Journal of Physical Chemistry* **68**(5), 1084–1091.

Cameselle, C. (2015), 'Enhancement of electro-osmotic flow during the electrokinetic treatment of a contaminated soil', *Electrochimica Acta* **181**, 31–38.

Chai, Z., Guo, Z. and Shi, B. (2007), 'Study of electro-osmotic flows in microchannels packed with variable porosity media via Lattice Boltzmann method', *Journal of applied physics* **101**(10), 104913.

Chapman, D. L. (1913), 'A contribution to the theory of electrocapillarity', *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **25**(148), 475–481.

Cheema, T., Kim, K., Kwak, M., Lee, C., Kim, G. and Park, C. (2013), Numerical investigation on electroosmotic flow in a porous channel, *in* 'The 1st IEEE/IIAE International Conference on Intelligent Systems and Image Processing 2013 (ICISIP2013)'.

Chen, S., He, X., Bertola, V. and Wang, M. (2014), 'Electro-osmosis of non-newtonian fluids in porous media using Lattice Poisson–Boltzmann method', *Journal of colloid and interface science* **436**, 186–193.

Chen, Y.-F., Li, M.-C., Hu, Y.-H., Chang, W.-J. and Wang, C.-C. (2008), 'Low-voltage electroosmotic pumping using porous anodic alumina membranes', *Microfluidics and Nanofluidics* **5**(2), 235–244.

Cho, C.-C., Chen, C.-K. and Yau, H.-T. (2015), 'Mixing of electrokinetically-driven power-law fluids in zigzag microchannels', *International Journal of Numerical Methods for Heat & Fluid Flow* **25**(2), 391–399.

Coelho, D., Shapiro, M., Thovert, J. and Adler, P. (1996), 'Electroosmotic phenomena in porous media', *Journal of colloid and interface science* **181**(1), 169–190.

Conlisk, A., McFerran, J., Zheng, Z. and Hansford, D. (2002), 'Mass transfer and flow in electrically charged micro-and nanochannels', *Analytical Chemistry* **74**(9), 2139–2150.

Darcy, H. (1856), *Les fontaines publiques de la ville de Dijon: exposition et application...*, Victor Dalmont.

Di Fraia, S., Massarotti, N. and Nithiarasu, P. (2017), 'Effectiveness of flow obstructions in enhancing electroosmotic flow', *accepted for publication in Microfluidics and Nanofluidics* .

Dufrêche, J.-F., Marry, V., Malikova, N. and Turq, P. (2005), 'Molecular hydrodynamics for electro-osmosis in clays: from kubo to smoluchowski', *Journal of molecular liquids* **118**(1), 145–153.

Ehlers, W. and Bluhm, J. (2013), *Porous media: theory, experiments and numerical applications*, Springer Science & Business Media.

Eykholt, G. R. and Daniel, D. E. (1994), 'Impact of system chemistry on electroosmosis in contaminated soil', *Journal of geotechnical engineering* **120**(5), 797–815.

Flatt, R. J. and Bowen, P. (2003), 'Electrostatic repulsion between particles in cement suspensions: Domain of validity of linearized poisson–boltzmann equation for nonideal electrolytes', *Cement and concrete Research* **33**(6), 781–791.

Forchheimer, P. (1901), 'Wasserbewegung durch boden', *Z. Ver. Deutsch. Ing* **45**(1782), 1788.

Gouy, M. (1910), 'Sur la constitution de la charge electrique a la surface d'un electrolyte', *J. Phys. Theor. Appl.* **9**(1), 457–468.

Grimes, B., Meyers, J. and Liapis, A. (2000), 'Determination of the intraparticle electroosmotic volumetric flow-rate, velocity and peclet number in capillary electrochromatography from pore network theory', *Journal of Chromatography A* **890**(1), 61–72.

Gupta, A., Coelho, D. and Adler, P. (2008), 'Universal electro-osmosis formulae for porous media', *Journal of colloid and interface science* **319**(2), 549–554.

Healy, T. W. and White, L. R. (1978), 'Ionizable surface group models of aqueous interfaces', *Advances in Colloid and Interface Science* **9**(4), 303–345.

Herschel, W. H. and Bulkley, R. (1926), 'Consistency measurements of rubber-benzol solutions', *Colloid & Polymer Science* **39**(4), 291–300.

Hlushkou, D., Apanasovich, V., Seidel-Morgenstern, A. and Tallarek, U. (2006), 'Numerical simulation of electrokinetic microfluidics in colloidal systems', *Chemical Engineering Communications* **193**(7), 826–839.

Hlushkou, D., Seidel-Morgenstern, A. and Tallarek, U. (2005), 'Numerical analysis of electroosmotic flow in dense regular and random arrays of impermeable, nonconducting spheres', *Langmuir* **21**(13), 6097–6112.

Modelling electro-osmotic flow in porous media: a review

Hsu, C. and Cheng, P. (1990), 'Thermal dispersion in a porous medium', *International Journal of Heat and Mass Transfer* **33**(8), 1587–1597.

Hu, J. and Chao, C. Y. (2007), 'Numerical study of electroosmotic (eo) flow in microfabricated eo pump with overlapped electrical double layer (edl)', *International journal of refrigeration* **30**(2), 290–298.

Hu, L., Harrison, J. D. and Masliyah, J. H. (1999), 'Numerical model of electrokinetic flow for capillary electrophoresis', *Journal of colloid and interface science* **215**(2), 300–312.

Huang, A., Liu, H.-M., Lee, C.-W., Tang, C.-Y. and Tsang, Y.-M. (2009), 'On conside 3d simple point characterizations: a marching cubes paradigm', *IEEE Transaction on Medical Imaging* **28**, 43–51.

Huang, K.-D. and Yang, R.-J. (2007), 'Electrokinetic behaviour of overlapped electric double layers in nanofluidic channels', *Nanotechnology* **18**(11), 115701.

Jin, M. and Sharma, M. M. (1991), 'A model for electrochemical and electrokinetic coupling in inhomogeneous porous media', *Journal of colloid and interface science* **142**(1), 61–73.

Kang, Y., Tan, S. C., Yang, C. and Huang, X. (2007), 'Electrokinetic pumping using packed microcapillary', *Sensors and Actuators A: Physical* **133**(2), 375–382.

Kang, Y., Yang, C. and Huang, X. (2004*a*), 'AC electroosmosis in microchannels packed with a porous medium', *Journal of Micromechanics and Microengineering* **14**(8), 1249.

Kang, Y., Yang, C. and Huang, X. (2004*b*), 'Analysis of the electroosmotic flow in a microchannel packed with homogeneous microspheres under electrokinetic wall effect', *International journal of engineering science* **42**(19), 2011–2027.

Kang, Y., Yang, C. and Huang, X. (2005), 'Analysis of electroosmotic flow in a microchannel packed with microspheres', *Microfluidics and Nanofluidics* **1**(2), 168–176.

Kaviany, M. (2012), *Principles of heat transfer in porous media*, Springer Science & Business Media.

Kozak, M. W. and Davis, E. J. (1986), 'Electrokinetic phenomena in fibrous porous media', *Journal of colloid and interface science* **112**(2), 403–411.

Kozak, M. W. and Davis, E. J. (1989*a*), 'Electrokinetics of concentrated suspensions and porous media: 2. moderately thick electrical double layers', *Journal of colloid and interface science* **129**(1), 166–174.

Kozak, M. W. and Davis, E. J. (1989*b*), 'Electrokinetics of concentrated suspensions and porous media: I. thin electrical double layers', *Journal of colloid and interface science* **127**(2), 497–510.

Kwon, K., Park, C.-W. and Kim, D. (2012), 'High-flowrate, compact electroosmotic pumps with porous polymer track-etch membranes', *Sensors and Actuators A: Physical* **175**, 108–115.

Lee, E., Lee, Y.-S., Yen, F.-Y. and Hsu, J.-P. (2000), 'Electroosmotic flow of a general electrolyte solution through a fibrous medium', *Journal of colloid and interface science* **223**(2), 223–228.

Levine, S., Marriott, J., Neale, G. and Epstein, N. (1975), 'Theory of electrokinetic flow in fine cylindrical capillaries at high zeta-potentials', *Journal of Colloid and Interface Science* **52**(1), 136–149.

Levine, S. and Neale, G. H. (1974), 'The prediction of electrokinetic phenomena within multiparticle systems. I. electrophoresis and electroosmosis', *Journal of Colloid and Interface Science* **47**(2), 520–529.

Lewis, R. and Garner, R. (1972), 'A finite element solution of coupled electrokinetic and hydrodynamic flow in porous media', *International Journal for Numerical Methods in Engineering* **5**(1), 41–55.

Lewis, R. W. and Humpheson, C. (1973), 'Numerical analysis of electro-osmotic flow in soils', *Journal of Soil Mechanics & Foundations Div* **99**(Proc Paper).

Li, B., Zhou, W., Yan, Y., Han, Z. and Ren, L. (2013), 'Numerical modelling of electroosmotic driven flow in nanoporous media by Lattice Boltzmann method', *Journal of Bionic Engineering* **10**(1), 90–99.

Li, B., Zhou, W., Yan, Y. and Tian, C. (2013), 'Evaluation of electro-osmotic pumping effect on microporous media flow', *Applied Thermal Engineering* **60**(1), 449–455.

Li, D. and Remcho, V. T. (1997), 'Perfusive electroosmotic transport in packed capillary electrochromatography: Mechanism and utility', *Journal of Microcolumn Separations* **9**(5), 389–397.

Liang, M., Yang, S., Miao, T. and Yu, B. (2015), 'Analysis of electroosmotic characters in fractal porous media', *Chemical Engineering Science* **127**, 202–209.

Liapis, A. I. and Grimes, B. A. (2000), 'Modeling the velocity field of the electroosmotic flow in charged capillaries and in capillary columns packed with charged particles: interstitial and intraparticle velocities in capillary electrochromatography systems', *Journal of Chromatography A* **877**(1), 181–215.

Liu, S. and Masliyah, J. H. (1996), 'Single fluid flow in porous media', *Chemical Engineering Communications* **148**(1), 653–732.

Mahmud Hasan, A., Wahab, M. and Guo, S. (2011), 'Cfd analysis of a pem fuel cell for liquid dispersion at the interface of gdl-gfc', *International Journal of Numerical Methods for Heat & Fluid Flow* **21**(7), 810–821.

Marino, S., Shapiro, M. and Adler, P. (2001), 'Coupled transports in heterogeneous media', *Journal of Colloid and Interface Science* **243**(2), 391–419.

Massarotti, N., Nithiarasu, P. and Carotenuto, A. (2003), 'Microscopic and macroscopic approach for natural convection in enclosures filled with fluid saturated porous medium', *International Journal of Numerical Methods for Heat & Fluid Flow* **13**(7), 862–886.

McLaughlin, S. and Mathias, R. T. (1985), 'Electro-osmosis and the reabsorption of fluid in renal proximal tubules.', *The Journal of general physiology* **85**(5), 699–728.

Mehta, G. D. and Morse, T. (1975), 'Flow through charged membranes', *The Journal of Chemical Physics* **63**(5), 1878–1889.

Mondal, M., Misra, R. P. and De, S. (2014), 'Combined electroosmotic and pressure driven flow in a microchannel at high zeta potential and overlapping electrical double layer', *International Journal of Thermal Sciences* **86**, 48–59.

Nicholson, P. G. (2014), *Soil improvement and ground modification methods*, Butterworth-Heinemann.

Nield, D. A. and Bejan, A. (2006), *Convection in porous media*, Springer Science & Business Media.

Nithiarasu, P., Seetharamu, K. and Sundararajan, T. (1996), 'Double-diffusive natural convection in an enclosure filled with fluid-saturated porous medium: A generalized Non-Darcy approach', *Numerical Heat Transfer, Part A - Applications* **30**, 413–426.

Nithiarasu, P., Seetharamu, K. and Sundararajan, T. (1997), 'Natural convective heat transfer in a fluid saturated variable porosity medium', *International Journal of Heat and Mass Transfer* **40**(16), 3955–3967.

Modelling electro-osmotic flow in porous media: a review

O'Brien, R. (1986), 'Electroosmosis in porous materials', *Journal of colloid and interface science* **110**(2), 477–487.

Overbeek, J. T. G. (1952), Electrochemistry of the double layer, *in* H.R.Kruyt, ed., 'Colloid Science, Irreversible Systems', Vol. 1, Elsevier.

Overbeek, J. T. G. and Wijga, P. (1946), 'On electro-osmosis and streaming-potentials in diaphragms', *Recueil des Travaux Chimiques des Pays-Bas* **65**(8), 556–563.

Patankar, N. A. and Hu, H. H. (1998), 'Numerical simulation of electroosmotic flow', *Analytical Chemistry* **70**(9), 1870–1881.

Paul, P. H., Arnold, D. W. and Rakestraw, D. J. (1998), Electrokinetic generation of high pressures using porous microstructures, *in* 'Micro Total Analysis Systems' 98', Springer, pp. 49–52.

Probstein, R. F. (2005), *Physicochemical hydrodynamics: an introduction*, John Wiley & Sons.

Qu, W. and Li, D. (2000), 'A model for overlapped edl fields', *Journal of Colloid and Interface Science* **224**(2), 397–407.

Rathore, A. and Horváth, C. (1997), 'Capillary electrochromatography: theories on electroosmotic flow in porous media', *Journal of Chromatography A* **781**(1), 185–195.

Rice, C. and Whitehead, R. (1965), 'Electrokinetic flow in a narrow cylindrical capillary', *The Journal of Physical Chemistry* **69**(11), 4017–4024.

S., W. (1961), 'Diffusion and dispersion in porous media', *Americal Institute of Chemical Engineering Journal* **13**, 420–427.

Scales, N. and Tait, R. N. (2006), 'Modeling electroosmotic and pressure-driven flows in porous microfluidic devices: Zeta potential and porosity changes near the channel walls', *The Journal of chemical physics* **125**(9), 094714.

Shapiro, A. P. and Probstein, R. F. (1993), 'Removal of contaminants from saturated clay by electroosmosis', *Environmental Science & Technology* **27**(2), 283–291.

Sheu, T. W., Kuo, S. and Lin, R. (2012), 'Prediction of a temperature-dependent electroosmotically driven microchannel flow with the joule heating effect', *International Journal of Numerical Methods for Heat & Fluid Flow* **22**(5), 554–575.

Stojek, Z. (2010), The electrical double layer and its structure, *in* 'Electroanalytical Methods', Springer, pp. 3–9.

Talapatra, S. and Chakraborty, S. (2008), 'Double layer overlap in ac electroosmosis', *European Journal of Mechanics-B/Fluids* **27**(3), 297–308.

Tallarek, U., Rapp, E., Seidel-Morgenstern, A. and Van As, H. (2002), 'Electroosmotic flow phenomena in packed capillaries: from the interstitial velocities to intraparticle and boundary layer mass transfer', *The Journal of Physical Chemistry B* **106**(49), 12709–12721.

Tang, G. (2011), 'Non-newtonian flow in microporous structures under the electroviscous effect', *Journal of Non-Newtonian Fluid Mechanics* **166**(14), 875–881.

Tang, G., Ye, P. and Tao, W. (2010), 'Pressure-driven and electroosmotic non-Newtonian flows through microporous media via Lattice Boltzmann method', *Journal of Non-Newtonian Fluid Mechanics* **165**(21), 1536–1542.

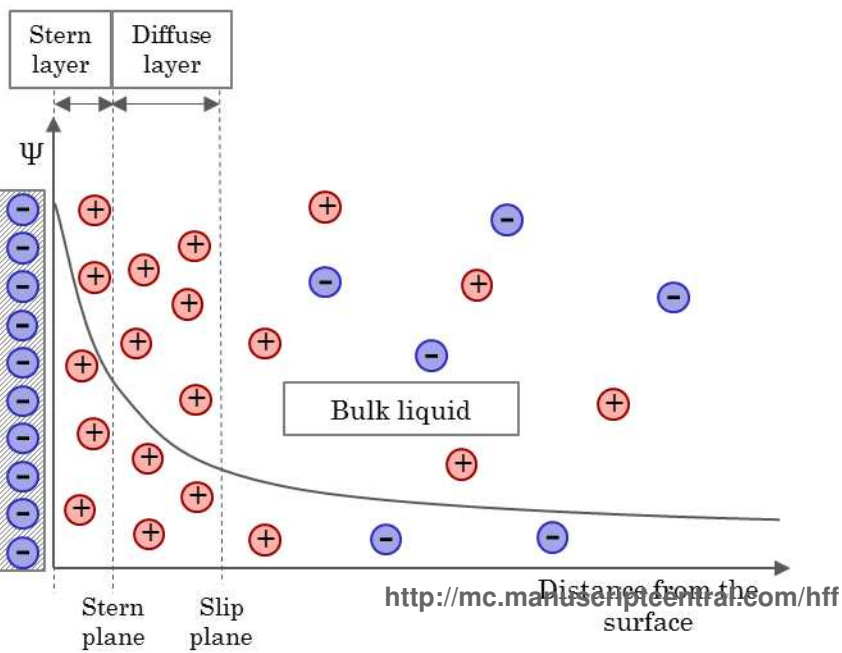Tripp, J. A., Svec, F., Fréchet, J. M., Zeng, S., Mikkelsen, J. C. and Santiago, J. G. (2004), 'High-pressure electroosmotic pumps based on porous polymer monoliths', *Sensors and Actuators B: Chemical* **99**(1), 66–73.

Vafai, K. and Tien, C. (1981), 'Boundary and inertia effects on flow and heat transfer in porous media', *International Journal of Heat Mass Transfer* **24**, 195–203.

Verwey, E. J. W. and Overbeek, J. T. G. (1948), 'Theory of stability of lyophobic solids'.

Von Helmholtz, H. (1879), 'Studies of electric boundary layers', *Wied. Ann* **7**, 337–382.

Von Smoluchowski, M. (1921*a*), 'Handbuch der elektrizität und des magnetismus', *Barth, Leipzig* p. 366.

von Smoluchowski, M. (1921*b*), *Handbuch der Elektrizität und des Magnetismus*, Second edn, Barth, Leipzig.

Wan, Q.-H. (1997), 'Capillary electrochromatography: effect of electrolyte concentration on electroosmotic flow and column efficiency', *Journal of Chromatography A* **782**(2), 181–189.

Wang, M. (2012), 'Structure effects on electro-osmosis in microporous media', *Journal of Heat Transfer* **134**(5), 051020.

Wang, M. and Chen, S. (2007), 'Electroosmosis in homogeneously charged micro-and nanoscale random porous media', *Journal of Colloid and Interface Science* **314**(1), 264–273.

Wang, M. and Chen, S. (2008), 'On applicability of poisson-boltzmann equation for micro-and nanoscale electroosmotic flows', *Commun. Comput. Phys* **3**(5), 1087–1099.

Wang, M., Pan, N., Wang, J. and Chen, S. (2007), 'Lattice poisson-boltzmann simulations of electroosmotic flows in charged anisotropic porous media', *Communications in Computational Physics* **2**(6), 1055–1070.

Wang, M., Wang, J., Chen, S. and Pan, N. (2006), 'Electrokinetic pumping effects of charged porous media in microchannels using the Lattice Poisson–Boltzmann method', *Journal of colloid and interface science* **304**(1), 246–253.

Wang, P., Chen, Z. and Chang, H.-C. (2006), 'A new electro-osmotic pump based on silica monoliths', *Sensors and Actuators B: Chemical* **113**(1), 500–509.

Wu, R. C. and Papadopoulos, K. D. (2000), 'Electroosmotic flow through porous media: Cylindrical and annular models', *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **161**(3), 469–476.

Yao, S., Hertzog, D. E., Zeng, S., Mikkelsen, J. C. and Santiago, J. G. (2003), 'Porous glass electroosmotic pumps: design and experiments', *Journal of Colloid and Interface Science* **268**(1), 143–153.

Yao, S., Myers, A. M., Posner, J. D., Rose, K. A. and Santiago, J. G. (2006), 'Electroosmotic pumps fabricated from porous silicon membranes', *Microelectromechanical Systems, Journal of* **15**(3), 717–728.

Yao, S. and Santiago, J. G. (2003), 'Porous glass electroosmotic pumps: theory', *Journal of Colloid and Interface Science* **268**(1), 133–142.

Zeng, S., Chen, C.-H., Mikkelsen, J. C. and Santiago, J. G. (2001), 'Fabrication and characterization of electroosmotic micropumps', *Sensors and Actuators B: Chemical* **79**(2), 107–114.

Zhao, C. and Yang, C. (2009), 'Analysis of power-law fluid flow in a microchannel with electrokinetic effects', *International Journal of Emerging Multidisciplinary Fluid Sciences* **1**(1), 37–52.
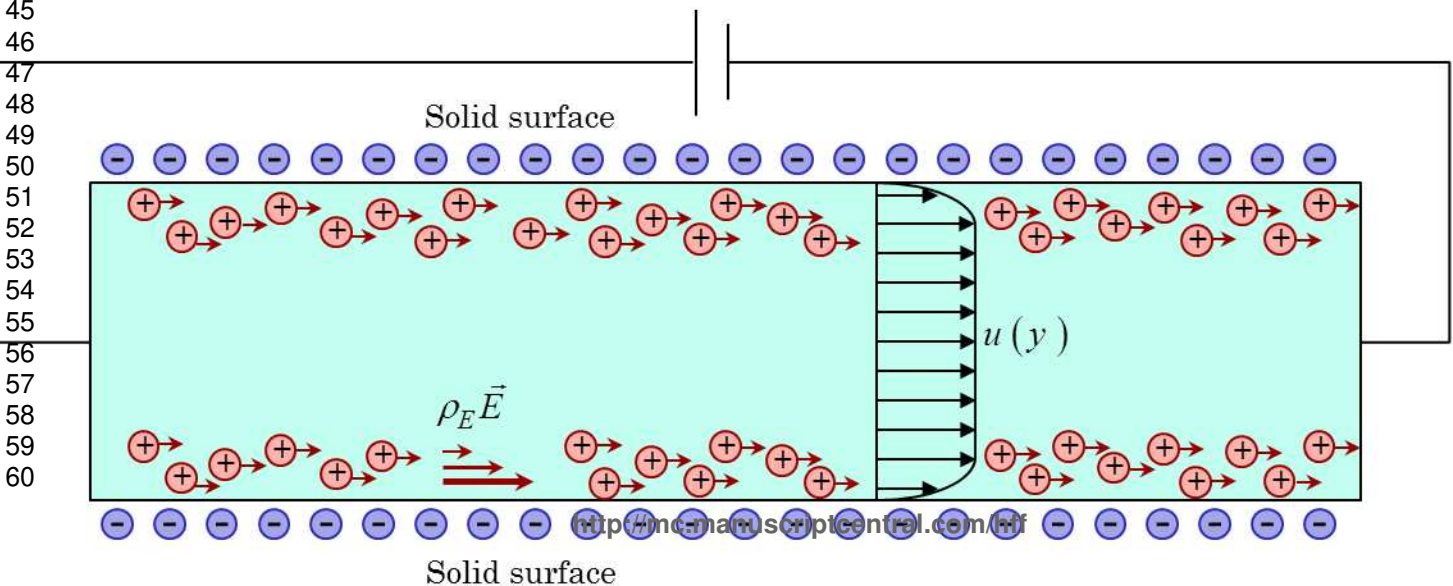
Modelling electro-osmotic flow in porous media: a review

Zhu, Q., Zhuang, Y. and Yu, H. (2015), 'An analytical permeability model for power-law fluids in porous fibrous media with consideration of electric double layer', *International Journal of Heat and Mass Transfer* **91**, 255–263.
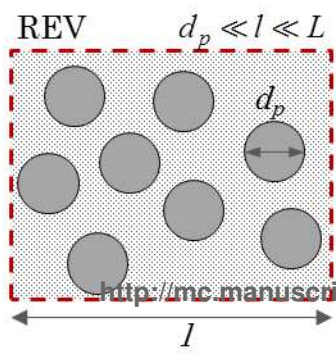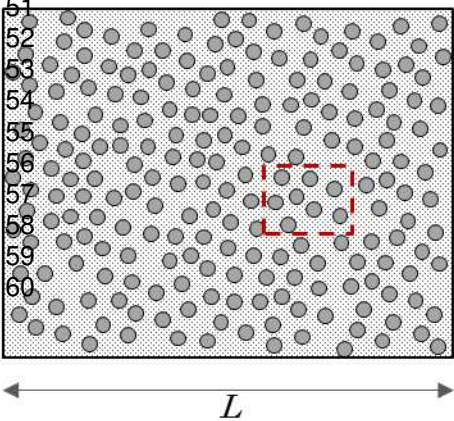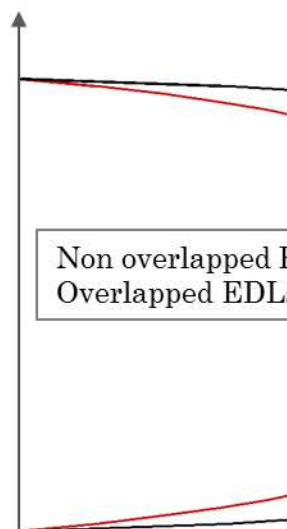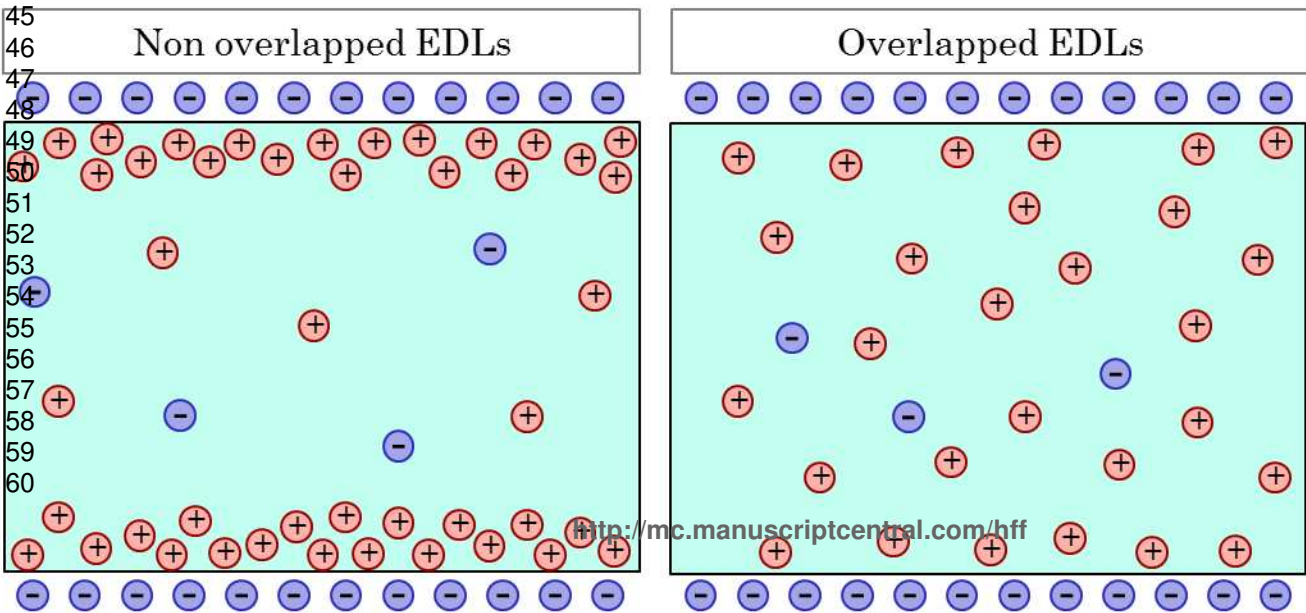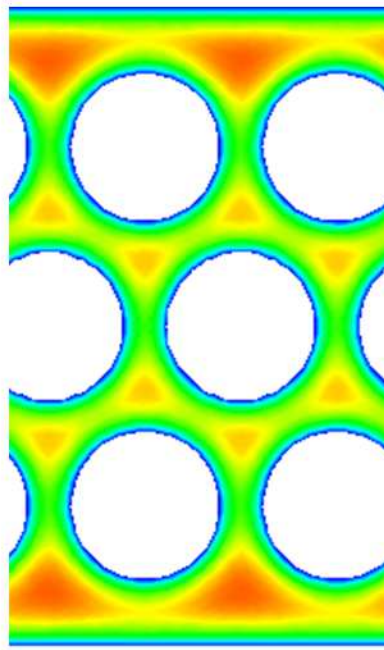
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Stern
layer

Diffuse
layer

Ψ

Charged
surface

Bulk liquid

Stern
plane

Slip
plane

Distance from the
surface

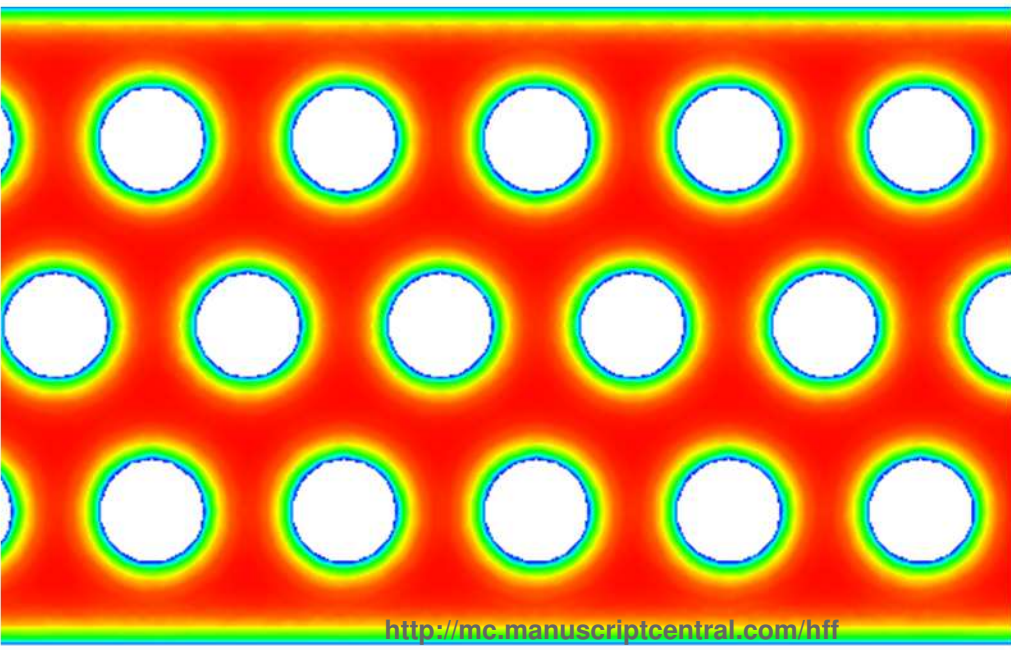Solid surface

$u(y)$

$\rho_E \vec{E}$

Solid surface

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

REV $d_p \ll l \ll L$

d_p

L

l

Non overlapped EDLs

Overlapped EDLs

Non overlapped E
Overlapped EDL

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
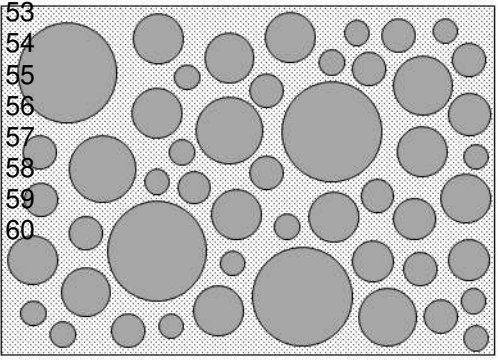47
48
49
50
51
52
53
54
55
56
57
58
59
60

Ψ

Non overlapped EDLs

Ov

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Solid

Fluid

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

y / a

Increasing
κa

$\dfrac{e\psi}{k_B T}$