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Two-phase Lattice Boltzmann modelling of streaming potentials: influence of the air–water interface on the electrokinetic coupling

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SUMMARY
The streaming potential phenomenon is an electrokinetic effect that occurs in porous media. It is characterized by an electrokinetic (EK) coefficient. The aim of this paper is to simulate the EK coefficient in unsaturated conditions using the Lattice Boltzmann method in a 2-D capillary channel. The multiphase flow is simulated with the model of Shan & Chen. The Poisson–Boltzmann equation is solved by implementing the model of Chai & Shi. The streaming potential response shows a non-monotonous behaviour due to the combination of the increase of charge density and decrease of flow velocity with decreasing water saturation. Using a ζ potential of ~20 mV at the air–water interface, an enhancement of a factor 5–30 of the EK coefficient, compared to the saturated state, can be observed due to the positive charge excess at this interface which is magnified by the fluid velocity away from the rock surface. This enhancement is correlated to the fractioning of the bubbles, and to the dynamic state of these bubbles, moving or entrapped in the crevices of the channel.

Key words: Numerical solutions; Electrical properties; Hydrogeophysics.

1 INTRODUCTION
The streaming potential (SP) phenomenon is an electrokinetic effect which arises when an electrolyte flows in a porous medium. When the surface of the solid material composing the matrix of the porous medium is electrically charged, the presence of an electrical double layer at the interface between the fluid and the solid phase creates a streaming current, counterbalanced by a conduction current, leading to a measurable electrical voltage. This electrokinetic coupling is at the origin of the self-potential and seismo-electromagnetic conversions used in earth sciences as geophysical tools for the subsurface imaging. These methods offer a non-invasive structure characterization of the near-surface in terms of fluids (water, oil, gas), and are developed for characterizing water resources, monitoring contaminated aquifers, and monitoring natural hazards which can be controlled by the role of water and ice.

The self-potential method is a passive geophysical method which consists in measuring the natural electric field on the earth surface, whereas the seismo-electromagnetic conversions are detected by measuring the electromagnetic field induced by a seismic wave propagation. These techniques have a variety of geophysical applications related to multiphase flows such as the study of the vadose zone (Thony et al. 1997; Warden et al. 2013; Jougniot et al. 2015), the estimate of the water retention parameters (Darnet & Marquis 2004), the estimate of the dispersivity (Straface & De Biase 2013), the monitoring of ground water flow (Perrier et al. 1998; Jouniaux et al. 1999; Doussan et al. 2002), the detection of deep fluid flow after stimulation of geothermal reservoir (Darnet et al. 2006), or the daily SP variations produced by capillary flow in the non-saturated zone (Perrier & Morat 2000). Groundwater flow paths and hydraulic properties of an aquifer can be inferred by SP measurements during pumping tests, especially the hydraulic conductivity, the aquifer thickness and the electrokinetic coupling (Darnet et al. 2003; Rizzo et al. 2004; Maineult et al. 2008; Straface et al. 2010; Chidichimo et al. 2015). On active volcanic areas, the upward hydrothermal flow can be characterized through SP observations usually showing positive anomalous electric signals (Hase et al. 2005; Mauri et al. 2010; Brothelande et al. 2014). These techniques are also of high interest for the hydrocarbon recovery (Saunders et al. 2006; Forté & Bentley 2013), the detection of contaminated aquifers (Naudet et al. 2004; Maineult et al. 2006; Minsley et al. 2007; Giampaolo et al. 2014), the monitoring of CO₂ storage (Zyserman et al. 2015), the prospection of ice-water interfaces (Kallay et al. 2003; Kulessa et al. 2006), and the mapping of water flow below glaciers (Kulessa et al. 2003). The knowledge of the unsaturated electrokinetic coupling is therefore essential, so that it can be included in the models for a better understanding of the observations.

The electrical double layer, which is at the origin of these phenomena, stems from the charge of the mineral when an electrolyte is in contact with the rock (Davis et al. 1978). This potential is negative for quartz at pH >3. The local electroneutrality in the immediate vicinity of the rock is satisfied thanks to an excess of positive ions adsorbed and immobile. The amount of positive charges in the electrolyte decays as getting away from the surface of the capillary, until both negative and positive species are found in equal proportion. The portion of capillary containing the positive charge excess is called the diffuse layer.
The SP phenomenon is characterized thanks to an electrokinetic (EK) coefficient, that is equal to the ratio of the potential difference $\delta V$ created by the displacement of the positive charge excess, on the pressure difference $\delta P$ that allows to generate the flow

$$C_{EK} = \frac{\delta V}{\delta P}. \quad (1)$$

The behaviour of the EK coefficient in unsaturated conditions is a debated question which is the topic of numerous studies. Wurmstich & Morgan (1994) proposed an enhancement factor of the EK coefficient with decreasing water saturation, by assuming that air forms bubbles in the medium. They assumed for this, that the bubbles decrease much less the water flow (streaming current) than they affect the conduction current through the decrease of electrical conductivity. The presence of bubbles was investigated theoretically by Sherwood (2007), Xie et al. (2010), Sherwood et al. (2013), who measured an enhancement of the output power caused by an increase of resistivity and streaming current. Perrier & Morat (2000) suggested that the EK coefficient could scale with the relative permeability and with the inverse of relative conductivity, leading to a decreasing trend with decreasing water saturation. This scaling was further developed by Linde et al. (2007) and Revil et al. (2007) who introduced a scaling of the charge density with the inverse of the saturation. Using a volume-average approach, they obtained a monotonous decreasing trend with decreasing water saturation. Laboratory measurements at various saturations (Guichet et al. 2003; Revil & Cerepi 2004; Revil et al. 2007; Vinogradov & Jackson 2011) lead to a constant or decreasing trend with decreasing water saturation. Continuous records of the EK coefficient as a function of water saturation made by Allègre et al. (2010) exhibited a non-monotonous behaviour, with a great enhancement compared to the saturated state, coherent with other data (Allègre et al. 2011). Allègre et al. (2012) modelled Richards’ equation for the hydrodynamics and Poisson’s equation for the electrical potential with a 1-D finite element method, and concluded, based on their previous experiments, that the unsaturated electrokinetic coefficient should be non-monotonous. An extension of the model of capillary tubes of Ishido & Mizutani (1981) to the case where each capillary can have a different radius was developed by Jackson (2008, 2010). This model predicts a monotonous decreasing EK coefficient with decreasing water saturation in the water-wet case and a non-monotonous and enhanced behaviour of the EK coefficient in the oil-wet case if the diffuse layer is not negligible compared to the capillary radius. Considering the same scaling of the charge density as the one used by Linde et al. (2007) and Revil et al. (2007), but using a flux-averaging approach, Jougnot et al. (2012) obtained an enhancement of three to four orders of magnitude of the steaming potential response of a rainfall event, thanks to a better computational efficiency. It is thus very well documented. As in one-phase conditions, the electrical potential is solved by implementing the model of Chai & Shi (2008). The following sections introduce the equations constituting these models and how they are used to compute the electrical field giving the EK coefficient in unsaturated conditions.

2.1 Modelling of the two-phase flow

The fundamental principle of the LB method is the use of numerical fluid particles that propagate and collide in a fixed number of directions. In a 2-D system, the number of directions needed to reproduce the behaviour of a fluid amounts to 9. The matrix of the particles velocities along these directions reads

$$c_v = c_{vp} \begin{bmatrix} 0 & 1 & 0 & -1 & 0 & 1 & -1 & 1 \ 0 & 0 & 1 & -1 & 1 & 1 & -1 & -1 \ \end{bmatrix} \quad (2)$$

where $c_v = dx_v/dt_v$ is the ratio between the space and the time steps. The time step is provided by the relationship $dt_v = \frac{dx_v}{v^{ad}}$, where $v$ is the kinematic viscosity of the fluid and $v^{ad}$ is the adimensional kinematic viscosity, fixed by the user. The space step is the distance between two lattice sites, given by $dx_v = 2R/(\eta v - 1)$ if $R$ is the radius of the channel and $\eta v$ the number sites discretizing the capillary diameter. The number of sites in the direction parallel to the flow is $nx_v$. Starting from now and until the end of this section,
all the quantities are adimensional (see Table A1 in the Appendix for a summary of the variables). Times will be expressed in time steps (ts), lengths in lattice units (lu) and masses in mass units (mu). The physical mass is obtained by multiplying the mass in mu by \( \mu_0 dx_i^3 \) where \( \mu_0 \) is a reference volumetric mass density, chosen here as the water mass density.

Let \( f_i^\lambda \) be the probability of presence of a particle of the fluid component \( \lambda \) in the direction \( i \). The local adimensional density of \( \lambda \) is defined as

\[
\rho_\lambda = \sum_i f_i^\lambda
\]

and the local momentum of \( \lambda \) as

\[
\rho_\lambda u_\lambda = \sum_i c_{V_\lambda} f_i^\lambda \tag{3}
\]

Each distribution \( f_i^\lambda \) evolves following the propagation-relaxation equation

\[
f_i^\lambda(x + c_{V_\lambda} dt_i, t + dt) - f_i^\lambda(x, t) = \Omega(x, t) \tag{5}
\]

where \( \Omega(x, t) = -\delta_i (f_i^\lambda(x, t) - f_i^{\lambda, eq}(x, t)) \). This equation expresses that at each time step the distribution at \( x \) is advected to a position \( x + c_{V_\lambda} dt_i \), and interacts with the other particles to converge towards equilibrium. The left-hand side is generally called the streaming step, and the right-hand side the collision step. \( \tau_\lambda \) is a relaxation time related to the kinematic viscosity through the relationship \( \tau_\lambda = 3 \nu / 2 \) (Wolf-Gladrow 2005). \( \tau_\lambda \) controls the amount of collisions between the particles, and thus the rheology of the fluid. It must be \( >0.5 \) to have a positive viscosity, and avoid stability problems.

The equilibrium distribution function \( f_i^{\lambda, eq} \) is expressed as a function of an equilibrium velocity \( u^{eq}_i^\lambda \)

\[
f_i^{\lambda, eq} = w_i \rho_\lambda \left[ 1 + 3 \frac{c_{V_\lambda} \cdot u_i^{eq} + (c_{V_\lambda} \cdot u_i^{eq})^2}{c_{V_\lambda}} - \frac{3}{2} \frac{u_i^{eq2}}{c_{V_\lambda}} \right] \tag{6}
\]

with \( w_i = 4/9 \) for \( i = 0 \), \( w_i = 1/9 \) for \( i \in \{1,2,3,4\} \) and \( w_i = 1/36 \) for \( i \in \{5,6,7,8\} \). The equilibrium velocity \( u_i^{eq} \) is the sum of a composite macroscopic velocity of the mixture denoted \( u^{\rho} \) and an interaction force term \( F_i = F^\rho_i + F^\lambda_i \) which is the sum of the fluid–fluid and fluid–solid interaction forces:

\[
u_i^{\rho, eq} = u^\rho + \frac{\tau_\rho F_i}{\rho_\rho} \tag{7}
\]

with

\[
u^\rho = \sum_i \frac{\rho_i u_i^\rho}{\rho_\rho} \tag{8}
\]

\( F^\rho_i \) is an interparticle force allowing to introduce the cohesion of the phases. The force exercised locally by the fluid component \( \lambda \) on the fluid component \( \lambda \) is proportional to the local density of \( \lambda \) multiplied by the sum of the densities of \( \lambda \) over the 8 neighbouring sites:

\[
F^\rho_i(x, t) = -\rho_\lambda(x, t) \nabla \cdot \left( \frac{F^{\lambda, eq}_i}{\rho_\lambda} \right) \tag{9}
\]

The parameter \( G^{\rho, eq} \) controls the magnitude of the repulsion between \( \lambda \) and \( \lambda \), and thus the interfacial tension between the phases. If \( G^{\rho, eq} \) is too low, the phase separation does not occur. A high \( G^{\rho, eq} \) decreases the solubility of the fluids within each other and allows to minimize the thickness of the fluid interface. However, stability problems occur when it is too high.

The force allowing to create the fluid-solid adhesion is similar to the force creating the interparticle interaction, but instead of summing the density of the neighbouring sites, the force is computed by summing a flag variable \( s_i \) such as \( s_i = 1 \) if \( x + c_{V_\lambda} dt_i \) is solid, and \( s_i = 0 \) otherwise (Martys & Chen 1996):

\[
F^\lambda_i(x, t) = -\rho_\lambda(x, t) \nabla \cdot \left( \frac{F^{\lambda, eq}_i}{\rho_\lambda} \right) \tag{10}
\]

The difference \( G^{\lambda, eq} - G^{\rho, eq} \) allows to tune the wetting properties of the fluids. \( G^{\lambda, eq} \) is generally chosen positive for the wetting fluid and negative for the non-wetting fluid. Huang et al. (2007) proposed a straightforward translation of Young's equation using the interfacial tensions and a density factor \( (\rho_\rho - \rho_\lambda)/2 \):

\[
\cos \theta = \frac{G^{\rho, eq} - G^{\lambda, eq}}{\frac{G^{\rho, eq}}{2}} \tag{11}
\]

They found that \( G^{\rho, eq} \) and \( G^{\lambda, eq} \) can be chosen in equal magnitude, but that the correspondence between the contact angle computed from eq. (11) and the contact angle measured graphically is slightly more accurate with \( G^{\rho, eq}/2 \approx G^{\lambda, eq}/0.1 \).

Due to the diffuse nature of the interfaces modelled with the interparticle force, a fraction of each phase is present at each lattice site, even if one is always dominant far from the interfacial area. The local total density of the mixture is given by

\[
\rho = \sum_i \rho_i \tag{12}
\]

and the total velocity by

\[
u = \frac{1}{\rho} \left( \sum_i \sum_j c_{V_\lambda} f_i^\lambda + \frac{1}{2} \sum_i F_i \right) \tag{13}
\]

The physical velocity of the fluid is obtained by multiplying \( u \) with the lattice velocity \( c_{V_\lambda} \).

In the following simulations, the two fluids are given the same viscosity \( \eta = 1.002 \text{ mPa s} \) (water viscosity) and same mass density \( \mu = 10^3 \text{ kg m}^{-3} \) (water mass density). Indeed, the high density and viscosity contrasts that occur when modelling liquid-gas mixtures constitute a challenge in the LB community that is out of the scope of this paper. Both phases will be given the same viscosity, and thus, the same relaxation times \( \tau_\lambda \) (see for instance, Yang et al. 2001b; Zhang & Kwok 2005; Qian et al. 2006; Gong et al. 2010). Merely, the component representing water will be the wetting component and the phase representing air the non-wetting component.

### 2.2 Driving force

The driving force in the Shan-Chen model is classically incorporated in the equilibrium velocity with the other forces responsible for the separation of the phases. It has been argued, however, that this way to create the flow is strictly valid for \( \tau = 1 \) (e.g., Yang & Boek 2013). The flow is here generated by incorporating a term \( \Omega \) at the right-hand side of eq. (5) (see Wolf-Gladrow 2005) and also Buick & Greated (2000):

\[
\Omega_i(x, t) = \frac{dt_i c_{V_\lambda}}{12c_{V_\lambda} \mu_0} \left[ K(x, t) + K(x + c_{V_\lambda} dt_i, t + dt_i) \right] \tag{14}
\]

where \( K = \nabla P \) is the pressure gradient in physical units. \( \| \nabla P \| = \delta P/L \) where \( L \) is the channel’s length in m, and \( \delta P \) the pressure drop along the channel in Pa. \( \delta P \) determines the strength of the flow.

In this study the flow velocity is used to counteract an artefact that plagues the multiphase LB simulations. This artefact, called the
spurious currents, is the occurrence of non-physical velocities at the interface between the immiscible fluids. This phenomenon has been extensively studied in the literature (see Connington & Lee (2012) for a review). Many efforts have been made to understand it, but it is still very hard or impossible to remove completely. A possible means to decrease the impact of these spurious currents is to generate a flow that is sufficiently rapid to make the relative importance of these anomalous velocities not too big (e.g. Bao & Schaefer 2013).

In this study, the \( \delta P \) will be set to very large values so that the main current’s magnitude will minimize the contribution of the spurious currents.

### 2.3 Computation of the electrical potential

The electrical potential, denoted \( \psi \), is computed by implementing the model of Chai & Shi (2008), in a lattice of \( n_{\text{LP}} \) sites along the distance between the rock surfaces, and \( n_{\text{XP}} \) sites in the direction parallel to these surfaces. The resolution of the Poisson–Boltzmann equation is similar to the resolution of a diffusion equation, for the which the number of directions available to the particles amounts to 5. The matrix of the particle velocities along these directions is

\[
e_P = c_P \begin{pmatrix} 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & -1 \end{pmatrix}.
\]

where \( c_P = dx_P/dt_P \) is the lattice velocity, \( dt_P \) is the time step and \( dx_P = 2R/(\eta_{\text{LP}} - 1) \) the space step.

By denoting \( h_i \) the particle distributions allowing to compute the electrical potential, \( \psi \) is given by

\[
\psi(x, t) = \sum_i h_i(x, t).
\]

The particle distributions \( h_i \) follow the same propagation-relaxation equation as eq. (5)

\[
h_i(x + c_P, dt, t + dt) - h_i(x, t) = \Omega_i(x, t) + \Omega'_i(x, t).
\]

The collision operator \( \Omega_i \) defined as

\[
\Omega_i(x, t) = -\frac{1}{\tau_P}(h_i(x, t) - h_i^{eq}(x, t)),
\]

is a function of the equilibrium distributions \( h_i^{eq} \)

\[
h_i^{eq}(x, t) = \begin{cases} \frac{w_i}{1 - w_i} \sum_{i=1}^{5} h_i(x, t) & \text{if } i = 0 \\ \frac{w_i}{1 - w_i} \sum_{i=1}^{5} h_i(x, t) & \text{if } i \in \{1, 2, 3, 4\} \end{cases}
\]

where the \( w_i \) are \( w_i = 0 \) for \( i = 0 \) and \( w_i = 1/4 \) for \( i \in \{1, 2, 3, 4\} \).

The term \( \Omega' \) introduces the electrical source

\[
\Omega'_i(x, t) = dt_P w_i \theta(x, t) D.
\]

\( D \) is an artificial diffusion coefficient given by

\[
D = \alpha c_P \left( \frac{1}{2} - \tau \right) dt_P.
\]

with \( \alpha = \frac{1}{2} \) in this 2-D system. \( \theta \) is the right-hand side of the Poisson–Boltzmann equation:

\[
\theta(x, t) = \frac{\rho_i(x, t)}{\epsilon z_i}. \frac{\partial}{\partial t}.
\]

We calculate the value of \( \rho_i \) thanks to the local concentrations of the species denoted \( C_i(x, t) \):

\[
\rho_i(x, t) = \sum_j \rho_i(x, t) = \sum_j \epsilon z_i C_i(x, t).
\]

where \( e = 1.6021 \times 10^{-19} \) C is the fundamental charge, \( z_i \) is the valence of the species \( i \) and \( C_i \) its concentration in ions m\(^{-3}\). The species concentrations are functions of the local value of the electrical potential:

\[
C_i(x, t) = C_{\text{eq}} \exp \left( -\frac{z_i e \psi(x, t)}{k_B T} \right), \quad (24)
\]

where \( k_B = 1.3806 \times 10^{-23} \text{ J K}^{-1} \) is the Boltzmann constant, \( T \) is the temperature in K and \( C_{\text{eq}} \) is the species concentration when \( \psi = 0 \), like out of the rock sample of far from the rock surfaces.

To sum up, the medium is initialized by setting \( \rho_i(x, t) = \sum_j \epsilon z_i C_{\text{eq}} \) everywhere. The electrical potential \( \psi \) is calculated as a function of \( \rho_i \) thanks to eqs (16)–(22). The concentrations are calculated as a function of \( \psi \) using eq. (24). Then \( \rho_i \) is updated with the new values of \( C_i \) according to eq. (23). At each time step the potential evolves because some sites have a fixed potential (rock and fluid-fluid interfaces) which ‘diffuse’ to the neighbouring sites. To assign a fixed potential \( \xi \) to a particular point \( x \), the particle distributions of point \( x \) are forced to keep the value

\[
h_i(x, t) = \xi i w_i.
\]

The procedure is repeated until the electrical potential is stabilized (see next section).

It can be shown easily by combining eqs (20) and (21) that the time step \( dt_P \) simplifies with \( c_P \), so that no tuning of \( dt_P \) is needed. The space step \( dx_P \) is fixed so as to describe the diffuse phase precisely. A good precision is reached when \( d/dx_P \sim 60 \) (see Fiorentino et al. 2016). The dimensionless relaxation time is fixed at \( \tau_P = 1 \) like in the simulation tests carried out by Chai & Shi (2008). The calculation is directly made in physical units, with double precision variables.

### 2.4 Computation of the EK coefficient

In the monophasic situation, both algorithms (flow velocity and potential) were computed at the same time. The convergence of the algorithm was evaluated by calculating the relative change of \( C_{\text{EK}} \) between each 10 steps. The origin of the electrical potential was located in the rock sites, which had a fixed position. In this study, the EK coefficient is computed in the presence of two phases in three situations: (i) the phases flow in parallel, (ii) the non-wetting phase is entrapped in the crevices of the pore, and (iii) the non-wetting phase flows as one or several bubbles. The source of the potential is located not only in the rock, but also at the fluid-fluid interfaces which do not have a fixed position. The Poisson–Boltzmann equation cannot converge if the source of the potential moves at each time step. Both parts of the algorithm (velocity and potential) cannot be solved simultaneously.

In this study, the velocity field is calculated in a preliminary stage. At the initial state, the medium is immobile. Then the velocity increases until an equilibrium is reached. The convergence of the velocity is assessed using the relative change of the fluid velocity averaged over the whole medium. Once the average velocity is stabilized, a ‘snapshot’ of the interfaces locations is made. The fluid–fluid interfaces are tracked by searching the sites where \( \rho_{\text{ave}} + \rho_{\text{water}} \) is less than a threshold that varies between 1.5 and 1.8 depending on the geometry of the phases distribution.

Once the velocity field at equilibrium is calculated and once the corresponding interfaces positions are mapped, the potential is computed following the equations described in Section 2.3. The potential keeps the constant values \( \psi = \xi_M \) and \( \psi = \xi_i \) at the sites...
representing the rock matrix and the air–water interface respectively. The convergence of the potential is assessed thanks to the EK coefficient value, which is obtained by calculating the electrical field. The local electrical field is defined as

$$E(x, t) = -\frac{\rho_s(x, t)\mu(x, t)\, c_i \, \sigma_f}{\rho_i \, \sigma_f}. \quad (26)$$

where $\sigma_f$ is the fluid conductivity. A common expression for $\sigma_f$ is

$$\sigma_f = \sum_i (e_{zi})^2 b_i C_i^\infty \quad (27)$$

where $b_i = \frac{1}{\sigma_{EF,i}}$ is the mobility of the species $i$ and $R_i$ its effective ionic radius. It could be noted that the use of eq. (27) to compute eq. (26) amounts to consider that there is no variation of $\sigma_f$ within the medium. The influence of the local variations of $\sigma_f$ on the EK coefficient has been assessed in the previous study (Fiorentino et al. 2016), and is small for $|z|$ values less than $\sim 25$ mV.

The physical size of the medium must fulfill the condition $2R/d > 120$ so that the diffuse layer’s thickness can be considered as negligible compared to the channel’s diameter. The number of nodes describing the potential in the direction perpendicular to the flow is then $n_{y_f} = \frac{2R}{d} \frac{d}{dx_f} = 7200$ with $d/dx_f = 60$, which is a lot more than the number of nodes required to simulate the fluid velocity. The velocity used in eq. (26) is thus transposed from the grid used for the velocity computation to the grid used for the potential computation by bilinear interpolation. During this procedure, the position of the zero velocity must be assessed. Indeed, the bounce back condition applied on the solid sites makes the effective position of the wall, where the flow is zero, shift half way between the solid site and the first neighbouring fluid site. The position of the zero velocity is linearly interpolated with the two first neighbouring nodes of the hydraulic grid.

The macroscopic potential $\delta V$ is obtained by averaging $E$ over the whole medium. The simulated EK coefficient is obtained using the definition of eq. (1), with the $\delta\rho$ that was used to simulate the flow in the preliminary stage. This computation is considered as stabilized when the relative change between two EK coefficients is less than a value $\epsilon$ which is small (see next sections). The water saturation $S_w$ is calculated by dividing the number of sites containing water at the end of the simulation by the total number of sites constituting the pore space. The sites representing the air–water interface are excluded from the computations of $S_w$ and EK coefficient because of the non-physical value of the velocity at this place (see Section 2.2).

3 VALIDATION OF THE PROCEDURE

3.1 Validation of the Young-Laplace Law

The validation of the Young-Laplace law is checked so as to verify that the Shan-Chen model is correctly implemented. The domain is initialized with a bubble at rest. A periodic boundary condition is applied to all sides of the lattice, which means that everything that flows out through one side is re-injected at the opposite side. The pressure at the position $x$ can be determined using (Huang et al. 2007)

$$P_{ad}(x) = (\rho_s(x) + \rho_i(x))/3 + C_{coh}\rho_s(x)\rho_i(x)/3 \quad (28)$$

where $P_{ad}$ is the adimensional pressure in $\text{mu H}^{-1}\text{ts}^{-2}$ and $\rho$ is the density in $\text{mu lu}^{-1}\text{H}^{-1}$ with $H$ the out of plane thickness of the system represented by the 2-D flow. The pressure difference between inside and outside the bubble as a function of $1/r_B$ is

$$\gamma = 0.23609x + 0.0048644$$

with $r_B$ the radius of the bubble at equilibrium.

The initial size of the bubble radius must be chosen carefully due to the phenomenon of bubble shrinkage. The bubble shrinkage is a spontaneous non-physical density collapse of the droplet due to the diffusive nature of the fluid interfaces. This artefact was examined numerically and analytically by Zheng et al. (2014), who showed that there is a critical radius below which the bubble shrinks until a complete vanishing. This critical radius depends on two parameters that are the ratio of the interface thickness on the radius of the initial bubble, and the ratio of the volume of the computational domain on the volume of the initial droplet. Both of them must be small. To avoid the density shift (bubble shrinkage), the relative importance of the interface thickness compared to the bubble radius must be small, and the relative importance of the bubble volume must not be too low compared to the total volume of the domain. On the other hand, if the droplet is very large, its interface can interfere with itself through the periodic condition at the boundaries, and break the bubble geometry.

Fig. 1 shows the pressure difference between inside and outside the bubble as a function of $1/r_B$. The domain is a square lattice of side $1.16 \times 10^{-4}$ m discretized with $nx_f = ny_f = 50$. The medium is initialized such as $\rho_s = \rho_0$ and $\rho_i = 0$ inside the bubble and $\rho_s = 0$ and $\rho_i = \rho_0$ outside. The thickness of the interface is fixed by the parameter $G_{coh}$ which controls the surface tension. Huang et al. (2007) report that a good compromise between stability and interface thickness is found for $1.6 \leq \rho_0 G_{coh} \leq 2.0$. The interparticle force is set such as $G_{coh} = 2$ with $\rho_0 = 2$. The tested bubble sizes range from the critical radius described above until the radius at which the bubble starts to interact through the boundaries. According to Sukop & Thorne Jr (2006), the low resolution of the domain increases the interface thickness and complicates the question of where to measure the densities of each fluid in the vicinity of the interface. This problem yields a non-zero plot intercept of the order of 0.005, which remains acceptable compared to value of 0.001 they obtain for a $200 \times 200$ domain. The linear trend confirms the ability of the code to reproduce the Young-Laplace law.
In these simulations, the two fluids have the same density and the same viscosity fixed by \( \tau = 1 \). The surface tension is measured to be \( \gamma = 0.236 \) mu H \( \cdot \) m \(^{-1} \) \( \cdot \) s\(^{-2} \), which corresponds to a physical value of \( 0.360 \) N m\(^{-1} \) using \( H = \Delta x \). This value is greater than the real air–water surface tension of \( 0.072 \) N m\(^{-1} \) and is barely tunable, because it is not possible, with the Shan-Chen method, to adjust the surface tension independently from the density and viscosity ratios (Ahrenholz et al. 2008). The consequences of a surface tension that is different from the air–water one is discussed later in Section 4.3.

### 3.2 Flows in parallel

The procedure is validated by calculating an analytical solution when both phases flow in parallel. Air occupies a corridor at the centre of the capillary and water flows on either side between the air and the rock walls.

#### 3.2.1 Analytical solution

The geometry of parallel flows is sufficiently simple to compute an analytical expression of the EK coefficient as a function of the water saturation \( I \). It is given by eq. (23). The species concentrations obey a Boltzmann distribution given by eq. (24). With the assumption that the fluids have the same dynamic viscosities, the velocity of the electrolyte should follow a Poiseuille profile

\[
v(\chi) = \frac{1}{2\eta L} \frac{\delta P}{\chi(2R - \chi)}
\]

with \( \chi \) the distance from the rock surface. The potential gradient along the capillary is expressed as

\[
\frac{\delta V}{L} = -\langle E \rangle = -\frac{\delta \rho_w}{\sigma_f}
\]

where \( \sigma_f \) is the electrolyte conductivity defined by eq. (27). This gives, with the definition of \( C_{\text{EK}} \) and using eqs (23) and (30):

\[
C_{\text{EK}} = \frac{\delta V}{\delta P} = \frac{e^2 C_{\infty}}{\eta \kappa B T \sigma_f}
\]

where

\[
\mathcal{I} = \frac{1}{2R} \int_0^{2R} \chi(2R - \chi) \psi(\chi) d\chi.
\]

The Debye-Hückel approximation (Pride 1994) allows to express the potential as

\[
\psi(\chi) = \zeta e^{-\frac{d}{\delta}}
\]

where \( d \) is a characteristic lengthscale termed the Debye length which measures the thickness of the diffuse layer:

\[
\frac{1}{d^2} = \sum_j \left( \frac{\epsilon_j e^2 C_{\infty}}{\epsilon_0 \kappa B T} \right)
\]

with \( \epsilon_0 = 8.8531 \times 10^{-12} \) F m\(^{-1} \) the vacuum permittivity and \( \epsilon_r \) the relative permittivity of water, equal to 80.1 at 20 °C for a salinity \(<0.1\) mol L\(^{-1} \). Using eq. (34), \( \mathcal{I} \) can be split into two contributions, the contribution from the potential of the capillary walls denoted \( T_{\text{rock}} \)

\[
T_{\text{rock}} = \frac{\zeta_w}{2R} \int_0^{2R} \chi(2R - \chi) \left( e^{-\frac{d}{\delta}} + e^{-\frac{(2R-\chi)}{\delta}} \right) d\chi
\]

and the contribution from the potential of the fluid–fluid interfaces denoted \( T_{\text{flow}} \)

\[
T_{\text{flow}} = \frac{\zeta_l}{2R} \int_0^{h_1} \chi(2R - \chi) \left( e^{-\frac{(h_1-\chi)}{\delta}} + e^{-\frac{(h_1+\chi)}{\delta}} \right) d\chi + \frac{\zeta_l}{2R} \int_{h_1}^{h_2} \chi(2R - \chi) \left( e^{-\frac{(h_2-\chi)}{\delta}} + e^{-\frac{(h_2+\chi)}{\delta}} \right) d\chi
\]

where \( h_1 \) and \( h_2 \) are the positions of the fluid–fluid interfaces. With the assumption that these interfaces are symmetrical with respect to the central axis parallel to the flow, they can be rewritten as a function of the water saturation \( S_w \) like

\[
h_1 = R S_w \quad \text{and} \quad h_2 = 2R(1 - S_w/2)
\]

where \( S_w \) varies between 0 (no water) and 1 (no air). By remarking that the potential is non-zero only in the very close vicinity of the interface and that the velocity in this area can be approximated to the velocity of the interface, eq. (37) simplifies to

\[
T_{\text{flow}} = \alpha \zeta = \frac{\zeta}{2R} \frac{d R^2}{2} S_w (2 - S_w)
\]

with \( \alpha = 4 \). By remarking that the velocity of the fluid-fluid interface is much more important than the velocity near the rock, the contribution \( T_{\text{rock}} \) can be neglected and \( C_{\text{EK}} \) can be approximated to

\[
C_{\text{EK}} = \frac{e^2 C_{\infty} \zeta}{2\eta B T \sigma_f} d R S_w (2 - S_w).
\]

#### 3.2.2 Simulations

The medium is initialized by setting the air pressure at the centre of the capillary and the water phase on either side of the corridor formed by the air. Starting from now and until the end of this paper, the density is initialized such as \( \rho_{\text{air}} = \rho_0 \) and \( \rho_{\text{wat}} = 0 \) in the phase representing air, \( \rho_{\text{air}} = 0 \) and \( \rho_{\text{wat}} = \rho_0 \) in the phase representing the water, and \( \rho_{\text{air}} = \rho_{\text{wat}} = \rho_0/2 \) at the sites representing the rock, meaning that the total density is initialized to \( \rho_{\text{air}} + \rho_{\text{wat}} = \rho_0 \) in the whole medium. \( C_{\text{ob}} \) is fixed such as \( C_{\text{ob}} \rho_0 = 2 \) with \( \rho_0 = 2 \). A periodic condition is applied at the boundaries perpendicular to the flow, and a bounce back condition is applied at the boundaries parallel to flow, meaning that all the particles that reach these boundaries are sent back in the opposite direction.

The velocity is computed until the relative change between 100 computations is less than \( 10^{-9} \). The convergence is reached after \( \sim 100 \) 000 ts. The concentration of the electrolyte is fixed at \( 10^{-3} \) mol L\(^{-1} \), and the channel’s diameter is 1.16 \( \times \) 10\(^{-6} \) m so that the criterion \( 2R/d > 120 \) is verified. Both phases have the viscosity \( \nu_{\text{mol}} = 0.1666 \) giving the same relaxation time \( \tau = 1 \). The size of the velocity grid is \( n_x = 100, n_y = 10 \). The lattice speed is \( c_v = 514 \) m s\(^{-1} \). The \( dx_p \) of the potential grid must fulfill the condition \( dx_p \sim 60 \), giving \( n_y = 7200 \) and \( n_x = 655 \). The computation of the potential stops when the relative change between 10 computations of \( C_{\text{EK}} \) is less than \( 10^{-8} \). The convergence of the potential is achieved after \( \sim 130000 \) iterations, which takes 2 hr, parallelized on a 16 cores computer. The imposed pressure difference \( \delta P \) is \( 6.7 \times 10^4 \) Pa. The potentials of the air–water and fluid-rock interfaces \( \zeta \) and \( \zeta_M \) are both set to \( -20 \) mV.

In Fig. 2(a), the simulated velocity is compared to the theoretical Poiseuille profile. The peaks located at the interfaces positions \( h_1 \) and \( h_2 \) are barely tunable, giving the same relaxation time \( \tau = 1 \).
and \( h_2 \) are the so-called spurious currents, whose magnitude can be obtained by subtracting the Poiseuille velocity to the simulations. This magnitude varies between 0.009 \( \text{lu} \, \text{ts}^{-1} \) and 0.027 \( \text{lu} \, \text{ts}^{-1} \) from the lowest to the highest tested \( S_w \). This is below the value of 0.059 \( \text{lu} \, \text{ts}^{-1} \) obtained by Hou \textit{et al.} (1997) for a rounded bubble.

Two EK coefficients are calculated: an EK coefficient denoted \( C_{w,EK}^{\text{all}} \) which excludes the sites belonging to the air phase, at the centre of the capillary. Only the second one has a physical meaning, since the first one would be the result for conductive air. The sites containing air are caught by tracking the sites where \( \rho_{aw} > 1 \). As mentioned in Section 2.4, the lattice sites located at the interface are excluded from the computation of the EK coefficient so as to remove, at least partly, the artefact caused by the spurious velocities.

### 3.2.3 Comparison

Fig. 2(b) shows the comparison between eq. (32) and the simulated EK coefficient. Fig. 2(c) shows a crossplot of the simulations versus the analytical solution. The algorithm provides reliable results, as shown by the unitary slope. The small difference observable in Fig. 2(b) is attributed to the presence of the spurious velocities. These spurious currents slightly increase the EK coefficient, but do not modify its behaviour. The increasing trend of \( C_{w,EK} \) with increasing \( S_w \) is triggered by the positive charge excess associated to the fluid-fluid interfaces. This positive charge excess is magnified by the flow velocity. The higher \( S_w \), the closer to the channel’s centre the positive charge excess, the higher the velocity, and the higher the enhancement. The EK coefficient is here a continuous, increasing function of \( S_w \), until the medium is completely filled with water. When \( S_w = 1 \), the fluid-fluid interfaces do not exist anymore, and the EK coefficient collapses to the value determined by the Helmholtz–Smoluchowski (HS) equation which gives the EK coefficient at full water saturation:

\[
C_{w,EK} = \frac{\varepsilon_0 \varepsilon \zeta M}{\eta \sigma_f}.
\]

As it could be expected, the values of \( C_{w,EK}^{\text{all}} \) represent the half of the values of \( C_{w,EK}^{\text{all}} \). This relies on the fact that the contribution of the charge density near the fluid-fluid interface completely overwhelms the contribution of the capillary walls, due to the increase of the velocity approaching the centre of the channel. Removing the inner part of the corridor is like removing one half of the profile close to the interface, where the potential is not negligible; the rest does not contribute to the electrokinetic coupling. Starting from now, the EK coefficient will refer to \( C_{w,EK}^{\text{all}} \) which corresponds to an air-water system, the air phase being an electrical insulator that does not support any conduction current. The good agreement between eqs (32) and (40) plotted in dashed line in Fig. 2 validates again that the contribution of the fluid-fluid interface overwhelms the contribution of the fluid-rock area, since it is one of the hypothesis used in the derivation of eq. (40).

It should be noted that the example of parallel flows could not really occur at very high \( S_w \) due to the Rayleigh Plateau instability. It is essentially a useful configuration for comparison with an analytical solution and validation of the code. In reality, a thin corridor of air would be split into a multiple bubbles configuration, which will be analysed later in this paper.

### 3.3 Choice of the \( \zeta \) potential

For an NaCl electrolyte at pH = 7, the literature reports potential values of the air–water interface comprised between \(-20 \) and \(-40 \) mV (Yang \textit{et al.} 2001a; Takahashi 2005; Creux \textit{et al.} 2007; Leroy \textit{et al.} 2012). The \( \zeta \) potential of the fluid-rock interface is generally described as a decreasing function of the electrolyte concentration (e.g. Kirby & Hasselbrink 2004). Some studies suggest it...
can be constant of about −20 mV on sands and sandstones (Jouniaux & Ishido 2012) or suggest that this salinity-dependence might be blurred considering complex porous networks as encountered in realistic rocks (Lorne et al. 1999b; Fiorentino et al. 2016).

Fig. 3(a) shows eq. (32) computed for \( \zeta_I = -20 \) mV and \( \zeta_M = \{-20,-40,-60,-80\} \) mV. The dots represent the HS equation. We can observe an increase of the EK coefficient with increasing \( \zeta_M \), but this increase remains low compared to the general increase observed from full to partial water saturation. A contrario, when \( \zeta_M \) is fixed, the variations of \( \zeta_I \) impact the EK coefficient in a quasi-proportional manner (Fig. 3b). This illustrates again that the SP response is dominated by the contribution of the gas-water interface, whose associated charge density is magnified by the local velocity of the fluid. The value of \( \zeta_I \) appears to be a key parameter controlling the magnitude of the EK coefficient. The potential of the fluid-rock interface can thus be set arbitrarily, considering the weak impact of its impact. For the rest of this study, both \( \zeta_I \) and \( \zeta_M \) will keep the value of −20 mV.

4 RESULTS

The behaviour of the EK coefficient is now examined when the non-wetting phase is discontinuous at the scale of the capillary. We recall that the simulations of this work are 2-D simulations. For a monophasic electrolyte, the correspondence between these simulations and a 3-D analytical solution assuming an axisymmetric geometry was shown to be valid (Fiorentino et al. 2016). This question is a bit more complex in biphasic conditions, where the distribution of the non-wetting phase has more degrees of freedom in 3-D than in 2-D. This probably induces a certain variability of the EK coefficient, but we do not think that this modifies the overall process presented in the following study.

4.1 Entrapped bubbles

In this section, we focus on the behaviour of the EK coefficient when bubbles are entrapped in anfractuosities. Different configurations are simulated so as to compute the EK coefficient at several saturations. The resulting systems are presented in Fig. 4. The wetting properties are fixed with \( G_{\text{water}}^{\text{ads}} = 0.3 \) and \( G_{\text{water}}^{\text{ads}} = -0.2 \) (\( \cos \theta = -0.5 \)). The velocity grid is \( n_{V} = 100 \), \( n_{V} = 150 \). The channel’s diameter is a bit wider than in Section 3.2.2 so that the narrowest distance between the channel’s walls is still >120d. The asperities have a 10 lu width, so that 80 lu represent 1.16 × 10^{-4} m. This gives a channel diameter \( 2R = 1.45 \times 10^{-4} \) m. With the criterion \( d/dx \sim 60 \), the potential grid is \( n_{P} = 9024 \), \( n_{x} = 13582 \). The viscosity of the fluids is \( \nu = 0.1666 \), giving the lattice velocity \( c_{V} = 411 \) m s^{-1}.

The pressure drop along the capillary is \( 6.29 \times 10^{7} \) Pa, giving the pressure gradient \( \nabla P = 2.9 \times 10^{-4} \) Pa m^{-1} with \( L = 3 \). This value is not representative of pressure gradients that can be found in realistic geologic media, and is made strong for numerical purposes only. A strong velocity makes the spurious currents less observable, and decreases the shrinkage of the small bubbles. It should be noted however that keeping the same ratio \( 2R/d \), these simulations could represent an electrolyte with a smaller concentration flowing in a wider channel, giving a lower pressure gradient, and thus a smaller velocity. According to eq. (35), a decrease of the concentration such as \( C_{2} = (1/\lambda)C_{1} \) with \( \lambda > 0 \) would yield an increase of the Debye length \( d_{2} = \sqrt{\lambda d_{1}} \), equivalent to an increase of the channel’s radius \( R_{2} = \sqrt{\lambda} R_{1} \), giving a velocity increase \( v_{2} = \lambda v_{1} \) according to eq. (30).

The velocity fields show oscillations that do not completely fade away, so the convergence is assessed over a long period, typically when the relative change between 10 000 computations of the average velocity is less than \( 10^{-4} \), which can take up to 65 800 ts. The convergence of the potential is reached when the relative change between 10 EK computations is less than \( 10^{-6} \). This is achieved after \( \sim 72 \) 000 ts, which takes between 24 and 28 hr on a 16 cores parallel computer. At the end of the simulation, all the sites belonging to the air phase are zeroed so as to take into account the water phase only, and the electrical field is averaged over the whole space, giving the simulated EK coefficient.

The charge density is averaged over the number of sites belonging to the water phase, and is compared in Fig. 5(a) to the interface area, i.e. the number of lattice sites constituting the gas-water frontier. Both of them are decreasing functions of \( S_{w} \). The velocity averaged over the whole medium (excluding the sites constituting the interface that are non-physical) is an increasing function of \( S_{w} \) (Fig. 5b). This is consistent with the analysis of Sherwood (2007); Sherwood et al. (2013) who showed that for a given pressure gradient, the injection of bubbles modifies the relationship between the total flow rate and the pressure drop. This behaviour corresponds to the decrease of relative permeability with increasing air saturation invoked by the models of Perrier & Morat (2000), Linde et al. (2007), Revil et al. (2007), Jackson (2008, 2010), Jougnot et al. (2012). The EK coefficient (Fig. 5c) exhibits a non-monotonous trend, that results
Two-phase LB modelling of streaming potentials

Figure 4. Bubbles trapped in asperities for several saturations. Rock in grey, air in black, water in white.

Figure 5. Trapped bubbles configuration (see Fig. 4). (a) Charge density averaged over the number of water sites, and interface area versus $S_w$. (b) Velocity of the electrolyte averaged over the whole pore space versus $S_w$. (c) EK coefficient versus $S_w$. The solid circle is the Helmholtz–Smoluchowski reference, the star is the configuration $S_w = 0.84$ with the bubbles replaced with rock.

from the combination of the decrease of velocity with the increase of total volumic charge density at decreasing $S_w$.

For any saturation, the EK coefficient is stronger than the value at full saturation given by the HS equation. An increase by a factor four to five can be observed compared to the saturated state. This enhancement is explained by the presence of an excess charge at the gas-water interface, which increases the average charge density. Another reason for that is the fact that when the walls of the capillary harbour bubbles, the velocity of the electrolyte approaching the capillary surface is non-zero, due to the continuity of the tangential component of the velocity at the fluid-fluid interface. The velocity in the bubble being non-zero, the velocity at the frontier between air and water is greater than the velocity if the bubble area were made of solid rock. This phenomenon is illustrated by Fig. 6 which shows the velocity field of the configuration $S_w = 0.84$, and the velocity field computed by replacing the air phase with rock. In the presence of bubbles, the average velocity is $24 \text{ m s}^{-1}$, against $21 \text{ m s}^{-1}$ in the monophasic situation. The resulting EK coefficient is $-9.61 \times 10^{-7} \text{ V Pa}^{-1}$ in the single-phase case (denoted by a star in Fig. 5c), and increases to $-4.62 \times 10^{-6} \text{ V Pa}^{-1}$ in the two-phase situation, for the same average charge density of $3 \text{ kC m}^{-3}$.

As side remark, we can notice that the EK coefficient computed at full water saturation is $-7.71 \times 10^{-7} \text{ V Pa}^{-1}$, which is lower than the HS forecast of $-1.08 \times 10^{-6} \text{ V Pa}^{-1}$. This shows again (Fiorentino et al. (2016), appendix) that the presence of anfractuosities, which breach the smooth capillary assumption on which the HS equation is based, results in a decrease of the magnitude of the EK coefficient.

Figure 6. (a) Velocity field in the configuration $S_w = 0.84$ (trapped bubbles, Fig. 4). (b) Velocity field obtained by replacing the bubbles with rock.
4.2 Flowing bubbles

An air injection is simulated by imposing \( \rho_{\text{air}} = \rho_0 \) and \( \rho_{\text{wat}} = 0 \) on a portion of sites, in the centre of the channel for several steps at the beginning of the simulation (e.g. Parmigiani et al. 2011). The quantity of air injected in the system is tuned by varying the duration, the position and the period of injection. The injection is made between \( t = 5000 \) ts and \( t = 6200 \) ts for the highest \( S_w \), and \( t = 25000 \) ts for the lowest \( S_w \). The resulting systems are presented in Fig. 7. The associated contour line plots of the velocity field are shown in Fig. A1 (see the Appendix). The fact that the bubbles are not created with the same injection time, before the establishment of the steady state explains why the bubbles have different sizes. The configuration ‘bis’ at \( S_w = 0.82 \), and later denoted \( S_{w2} \), has an interface area 75 per cent greater than the two-bubble configuration at the same saturation. It allows to assess the impact of the fractioning of the non-wetting phase.

The wetting properties are set using \( G^{\text{abh}}_{\text{wat}} = 0.5 \) and \( G^{\text{abh}}_{\text{air}} = -0.4 \) \((\cos \theta = -0.9)\), so that there is a strong repulsion between the phase representing air and the capillary walls. The channel’s diameter is \( 1.16 \times 10^{-6} \text{ m} \). The dimensions of the velocity grid are \( n_{xV} = 100 \), \( n_{yV} = 150 \). The convergence of the flow is reached when the relative change of the mean velocity is less than \( 10^{-3} \) over 100 ts, which can take up to 50 600 ts. The dimensions of the potential grid are \( n_{xP} = 6200 \), \( n_{yP} = 10836 \). Both fluids have the viscosity \( \nu_{\text{air}} = 0.4 \). The lattice velocity \( c_V \) is \( 214 \text{ m s}^{-1} \). The convergence of the potential is achieved when the relative change between 10 \( C_{\text{EK}} \) computations is less than \( 10^{-6} \). The simulations stop after \( \sim 72000 \) ts, which represents between 15 and 19 hr of calculation on a 16 cores parallel computer. The same pressure gradient as the trapped bubbles configuration is applied, which yields a pressure drop of \( 5.03 \times 10^7 \text{ Pa} \) along the capillary using \( L = 3R \).

The assumption that the charge density scales with the inverse of \( S_w \) implies that there is no positive charge excess associated to the gas-water interface. For comparison, the corresponding situation is simulated by setting \( \zeta_f = 0 \text{ V} \) in the computation of the potential and using the same flow configurations. The resulting average charge density is plotted together with the average charge density of the simulations with \( \zeta_f = -20 \text{ mV} \) in Fig. 8(a). A significant divergence can be observed with decreasing \( S_w \), with a factor close to 2 at the lowest tested saturation. The interface area shows a good correlation with the average charge density computed with a non-zero \( \zeta_f \); it increases with decreasing \( S_w \) and drops when the bubbles merge.

Similarly to what was observed in the entrapped bubbles case, the average velocity of the flow decreases with decreasing \( S_w \) (Fig. 8b). The EK coefficient shows a non-monotonous behaviour, with an enhancement up to a factor 30 compared to the saturated state (Fig. 8c, circles). The EK coefficients computed with \( \zeta_f = 0 \text{ V} \) (crosses) are shown for comparison: in that case, the EK coefficient is constant or slightly decreasing with decreasing \( S_w \).

The configuration \( S_{w2} \) yields a charge density increase of 41 per cent and a velocity decrease of 7 per cent compared to the two-bubbles configuration at the same saturation. The corresponding EK coefficient is represented by a star in Fig. 8(c) and amounts to \(-3.72 \times 10^{-5} \text{ V Pa}^{-1}\) against \(-2.38 \times 10^{-5} \text{ V Pa}^{-1}\) for the two-bubbles case, which is a significant difference. For a given saturation, increasing the fractioning of the gas phase results in an increase of the EK coefficient, which illustrates again the correlation between charge density and interface area.

4.3 Influence of the pressure gradient

The expression used to validate the simulations in a situation where the phases flow in parallel (eq. 32), is independent of the pressure gradient. However, it could be expected that when the non-wetting phase forms discontinuous bubbles, the pressure gradient is able to influence the EK coefficient.

The configuration \( S_w = 0.91 \) in Fig. 7 is computed with a pressure gradient \( \|\nabla P\| = 1.2 \times 10^{12} \text{ Pa m}^{-1} \), which is 4 times larger than the pressure gradient \( \|\nabla P\| = 2.9 \times 10^{11} \text{ Pa m}^{-1} \) that was used in Section 4.2. The simulated EK coefficients are \(-2.58 \times 10^{-5} \text{ V Pa}^{-1}\) in the first case and \(-2.60 \times 10^{-5} \text{ V Pa}^{-1}\) in the latter. The slight discrepancy (less than 1 per cent) can be attributed to the difference in the bubbles spreading, and appears negligible.

In the trapped bubbles configuration \( S_w = 0.66 \) presented in Section 4.1, the EK coefficient amounts to \(-4.69 \times 10^{-6} \text{ V Pa}^{-1}\) using the pressure gradient \( \|\nabla P\| = 2.9 \times 10^{11} \text{ Pa m}^{-1} \). By imposing a higher gradient such as \( 6.0 \times 10^{11} \text{ Pa m}^{-1} \), it is possible to observe...
the release of the entrapped bubbles. The opposite bubbles join the main flow, merge and switch to a flowing configuration (see Fig. 9). Once the equilibrium state is reached, the EK coefficient jumps to $2.63 \times 10^{11}$ Pa $m^{-1}$, which is an increase of a factor 6.

The difference between the EK coefficient value obtained after the merging of the bubbles and the EK coefficient obtained with $\|\nabla P\| = 2.9 \times 10^{11}$ Pa $m^{-1}$ in Section 4.2 at a similar saturation (Fig. 7, $S_w = 0.65$) is of the order of 2 per cent.

These results mean that increasing the pressure gradient allows to observe a discontinuity between the two regimes (entrapped and flowing bubbles), but for a given situation, the value of the pressure gradient is one of the reasons why the switching from one regime to the other has such spectacular effects.

By balancing the pressure gradient exercised along the entrapped bubble to the capillary pressure, we can express the critical pressure gradient $\|\nabla P\|_c$ needed to overcome the surface force which maintains the bubble on the rock capillary as

$$\|\nabla P\|_c = \frac{\gamma}{r_B^2}.$$  \hfill (42)

With $r_B = 35 \mu m$, $dx_f = 1.46 \times 10^{-8}$ m and the $\gamma$ value estimated in Section 3.1, the calculation gives $\|\nabla P\|_c = 1.37 \times 10^{12}$ Pa $m^{-1}$. This remains consistent with the $\|\nabla P\|_c$ observed in the simulations, comprised in the range $3-6 \times 10^{11}$ Pa $m^{-1}$, since eq. (42) does not take into account the geometry of the asperity and the contact angle properties. For the present case, the repulsion between the air phase and the solid phase contributes to the decrease of $\|\nabla P\|_c$. In this model, the value of $\|\nabla P\|_c$ is the only way the surface tension between the two fluids influences the general mechanism.

Another question related to the pressure gradient is whether the flow is still in the laminar regime despite the strong imposed pressure drop. This feature is quantified thanks to the Reynold’s number defined as

$$Re = \frac{UL}{v}$$  \hfill (43)

where $U$ is a characteristic velocity chosen here as the maximum velocity, and where $L$ is a characteristic length of the medium, typically the pore diameter. This question matters since according to the study of Watanabe & Katagishi (2006), the EK coefficient begins to deviate from the HS equation at Reynold’s number $>3$. The Reynold’s numbers of the present simulations are much higher. However, the mechanism proposed by Watanabe & Katagishi (2006) to explain this deviation, based on the work of Lorne et al. (1999a), is the occurrence of counter-flows in the crevices of the irregularly shaped...
channel, leading to a decrease of the EK coefficient when the flow is fast. Most of the present simulations take place in a smooth capillary which is not prone to generate such counter-flows. When the channel is irregularly shaped we can observe some fluctuations of the velocity directions in the anfractuosities (see Fig. 10a). However, these fluctuations correspond to very small velocity amplitudes (less than 1 m s$^{-1}$, see Fig. 10b) which can be safely neglected compared to the velocity of the main flow (maximum velocity $U = 131$ m s$^{-1}$). If they were not, they would mask a further increase of the EK coefficient.

5 DISCUSSION

In this paper, the influence of a non-zero potential at the gas-water interface has been investigated. The results show that this contribution is a key component of the EK response in unsaturated conditions. The fluid–gas interfaces generate an enhancement of the EK coefficient not only because they increase the charge density, but also because they are placed away from the rock surface, where the related positive charge excess is multiplied by a large velocity. The distribution of the air phase greatly affects the magnitude of the streaming potential enhancement. It can be observed in Fig. 11 that the configuration of parallel flows is a kind of maximum envelope of the EK coefficient in unsaturated conditions, because in this case, the interface is located in the area that maximizes the velocity multiplying its associated charge density. When the air takes the form of bubbles, the flow velocity is slowed, which results, combined with the increase of charge density with increasing air saturation, in a non-monotonous behaviour of the EK coefficient. At high $S_w$, $C_{EK}$ increases compared to the saturated state because of the apparition of the polarized air–water interfaces. When $S_w$ decreases, the related positive charge excess increases, and so does the EK coefficient. At high $S_w$, the velocity decrease remains low and does not prevent $C_{EK}$ from increasing. Below a critical $S_w$, the velocity decrease overcomes the charge density increase, leading to a constant (Fig. 5c) or decreasing (Fig. 8c) EK coefficient. The velocity decrease reflects the decrease of relative permeability at low $S_w$. When the air is entrapped in the crevices of the porous network, the enhancement is lower, because the interface is placed in areas where the fluid velocity is lower.

A weakness of this model could be the use of a unitary viscosity contrast between the air and the water phase. We think nonetheless that it does not change the main conclusions of this work. In the case of the bubbles flowing, the deformation of the bubbles at $S_w < 0.5$ (see Fig. 7) is quite similar to what can be observed for real air bubbles propagating at high speed. The velocity profile inside the bubble is roughly homogeneous (see Fig. 12), meaning that the viscosity of the phase representing air is not a sensitive parameter. Considering the trapped bubble case, we know from Fig. 6 that the convection movement described by the air phase in the bubble accelerates the water flow compared to the solid case. This convection cell turns slowly than if it were real air, because real air is less viscous than the viscosity used in these simulations. Consequently, a real air bubble would even more increase the velocity of the electrolyte, which would further increase the EK coefficient value, and thus reinforce these results.

The mechanisms creating the negative potential of the air–water interface being not thoroughly understood, an assumption that is implicitly made in this paper is that the negative charges causing the $\zeta_I$ potential are placed in the air. In monophasic conditions, the negative potential of the rock matrix creates a positive charge excess that creates an electrical current when these positive ions are dragged with the flow; this current is counterbalanced by the conduction current, but is not counteracted by the negative charges causing $\zeta_M$, because these charges stand still at the rock surface. In multiphase conditions, we made the hypothesis that the negative charges are placed in the air phase and do not contribute to the calculation of $C_{EK}$, since the potential difference $\Delta V$ is measured in the water. However, if these negative charges were in the water, they should be taken into account in the calculation of the local electric charge density. This would not impact the configuration of trapped bubbles, because in that case the air–water interface does not move, and the negative charges adsorbed at this interface would not create any current. In contrast, the flowing bubbles configuration would be very impacted, because in that case the interface is flowing, and the negative charges moving with the interface would create a countercurrent balancing the current associated to the positive charge excess. The contribution of the air-water interface to $\Delta V$ would only come from the velocity difference between the negative
charges creating $\zeta_1$ and the positive charges screening $\zeta_2$, which is small. In that case, the enhancement caused by the bubbles should be close to zero, and the system should be described with $\zeta_1 \approx 0$. In other words, if the negative charges causing $\zeta_1$ were in the water, the enhancement of $C_{\text{EK}}$ compared to the saturated state would be non-zero, as long as the air–water interface would remain fixed. The dynamic aspect of the EK response would then induce a maximum enhancement with fixed bubbles, and no enhancement obtained with flowing bubbles. This is not the case in this article, where we made the assumption that the negative charges remain in the air, leading to an EK coefficient which is more increased for flowing bubbles than for fixed bubbles.

Let us now compare this work to the other models predicting an enhancement of the EK coefficient. These simulations have allowed to investigate the contribution of the fluid-gas interface when the gas phase is distributed in a single capillary. This is a very different approach from the bundle of capillary tubes model which considers several capillaries occupied by a single phase. By developing such model to the case where each capillary can have a different radius, Jackson (2008, 2010) shows that the excess charge density transported by the flow depends on the capillary size distribution, the wettability and the relative importance of the electrical double layer compared to the capillary radius. In the water-wet case, the EK coefficient is shown to be a decreasing function of the air saturation, because the irreducible water in the smaller capillaries contributes to the electrical conductivity without contributing to the streaming current. In the oil-wet case, when the diffuse layer is not negligible compared to the capillary radius, the electrical conductivity is more impacted by the increasing occupancy of oil than the streaming current. In that case, the EK coefficient can be enhanced up to a factor 2 depending on the capillary size distribution, before decreasing to zero at the irreducible saturation. Under certain conditions, by expressing the EK coefficient as

$$C_{\text{EK}} = \frac{Q_1 k}{\sigma_1 \eta}$$

(44)

where $Q_1$ is the electric charge density and $k$ the rock permeability, and by using Archie’s law $\sigma_1 = S_w^n$ to express the rock electrical conductivity, Jackson (2010) obtains an enhancement of the EK coefficient in the water-wet case, but specifies that this approach is consistent only if the saturation exponent is $n = 1$, and that it does not apply to all geologic porous media.

Jougnot et al. (2012) also obtain an enhancement of the EK coefficient with a non-monotonous behaviour. Using eq. (44) extended at partial saturation to calculate the EK coefficient, they express the charge density as a flux-averaged quantity, which is defined using the charge density at water saturation, the velocity of the electrolyte and a capillary size distribution. The capillary size distribution is inferred from soil properties using either capillary pressure-saturation relationships or relative permeability functions. Depending on the soil characteristics (porosity, permeability, irreducible saturation), they can obtain a decreasing $C_{\text{EK}}$ with decreasing $S_w$ or a non-monotonous trend with an enhancement compared to the saturated state up to a factor 5, consistent with experimental and field measurements. The enhancement of the EK coefficient is there again related to the rock texture.

These works allow to capture petrophysical features which are not possible to study with the present simulations, such as the effect of irreducible saturation and capillary size distribution. They do not consider a non-zero $\zeta_1$ potential at the air–water interface.

Another element, which deserves to be studied if the fluid-gas interface contribution is considered as significant, is the behaviour of the interfacial area. In the topology of real porous media, the interconnected pores of the rock networks offer more possibilities to the air phase to spread, merge, and be trapped. It has been reported (Allègre et al. 2015) according to both experimental and numerical studies (Culligan et al. 2004; Porter et al. 2009) that the air–water interfacial area during drainage experiments is a non-monotonous function of $S_w$. Such behaviour could reinforce the decrease of $C_{\text{EK}}$ at low $S_w$, which is weak in these single capillary model simulations, where the interfacial area increases with decreasing $S_w$ or remains roughly constant.

The pressure gradient does not appear to affect the SP response per se, but high flow velocities generated by high pressure drops are able to release entrapped bubbles, and thus modify the EK coefficient enhancement. The value of pressure drop allowing the release of bubbles is determined by the pore size, bubbles sizes and surface tension between the fluids (see Section 4.3). In a realistic rock and for a given pressure drop, the fraction of pores below a critical radius should be in the trapped bubble configurations, while the fraction of pores above the critical radius should be in the flowing bubble configuration, meaning that the impact of the global flow rate on the SP response may be another element determined by the pore size distribution. This opens a new perspective to explain the
change of magnitude in EK coefficient observed in the experiments of Allègre et al. (2010), where the lower the dipole, the stronger the SP response. Considering the analysis of the pressures recorded in these experiments, a change of the interface mobilities going down in the column corresponding to a transition of bubble configuration could yield an increase of the SP response. Future work on experimental measurements of the saturation and bubble state during such experiments is needed to confirm this interpretation.

6 CONCLUSIONS

The simulations of this work show that the electrical charge density associated to the gas-water interfaces is a key element of the EK response. These interfaces yield an increase of the EK coefficient compared to the saturated state. With the assumption that the negative charges causing the $\zeta$ potential are in the air, this increase is more important for flowing bubbles than entrapped bubbles.

The EK coefficient enhancement generated by fluid-gas interfaces should improve the performance of the SP-based geophysical techniques in unsaturated conditions. This enhancement should affect the estimate of water flux and unsaturated soil hydraulic parameters inferred from SP measurements, whose magnitude is determined by the electrokinetic coupling (Sailhac et al. 2004). Some SP observations related to pumping tests and showing an unexplained enhancement of 25 per cent just above the water table may find an explanation in the enhancement of the EK coefficient in unsaturated conditions, rather than assuming a decaying exponential behaviour as a function of the decreasing water saturation (Malama 2014). The transmissivity and storativity inferred from SP observations may thus be better constrained even for a confined heterogeneous aquifer. When using the SP to deduce the hydrothermal zones on volcanoes, the air–water interface should be taken into account since air convection can also be present if the porous medium is sufficiently permeable (Antoine et al. 2009). Finally, these results should be accounted for the monitoring of the water alternate gas injections in reservoirs, where the interfaces between injected water and injected gas could explain the peak of the SP signal associated to the water front (Anuar et al. 2014).

ACKNOWLEDGEMENTS

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REFERENCES


**APPENDIX**

Figure A1. Contour line plots (m s$^{-1}$) of the velocity fields corresponding to the bubbles shown in Fig. 7.
Table A1. Notation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{E K}$</td>
<td>Electrokinetic coefficient</td>
<td>V Pa(^{-1})</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Local concentration of species $i$</td>
<td>ions m(^{-3})</td>
</tr>
<tr>
<td>$C_i^{\infty}$</td>
<td>Concentration of species $i$ in the middle of the channel or out of the sample</td>
<td>ions m(^{-3})</td>
</tr>
<tr>
<td>$x$</td>
<td>Local coordinate measuring the distance to the rock surface</td>
<td>m</td>
</tr>
<tr>
<td>$d$</td>
<td>Debye length</td>
<td>m</td>
</tr>
<tr>
<td>$\delta V$</td>
<td>Macroscopic potential difference</td>
<td>V</td>
</tr>
<tr>
<td>$\delta P$</td>
<td>Macroscopic pressure difference</td>
<td>Pa</td>
</tr>
<tr>
<td>$E$</td>
<td>Local electrical field</td>
<td>V m(^{-1})</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Fluid relative permittivity</td>
<td>-</td>
</tr>
<tr>
<td>$k$</td>
<td>Rock permeability</td>
<td>m(^2)</td>
</tr>
<tr>
<td>$l$</td>
<td>Flow characteristic length</td>
<td>m</td>
</tr>
<tr>
<td>$L$</td>
<td>Capillary length</td>
<td>m</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Fluid volumetric mass</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>$n$</td>
<td>Saturation exponent in Archie’s law</td>
<td>-</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Fluid kinetic viscosity</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Local electrical potential</td>
<td>V</td>
</tr>
<tr>
<td>$Q_e$</td>
<td>Electrical charge density</td>
<td>C m(^{-3})</td>
</tr>
<tr>
<td>$R$</td>
<td>Capillary radius</td>
<td>m</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynold’s number</td>
<td>-</td>
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<tr>
<td>$S_w$</td>
<td>Water saturation</td>
<td>-</td>
</tr>
<tr>
<td>$\sigma_r$</td>
<td>Rock electrical conductivity</td>
<td>S m(^{-1})</td>
</tr>
<tr>
<td>$\sigma_f$</td>
<td>Fluid electrical conductivity</td>
<td>S m(^{-1})</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
<td>-</td>
</tr>
<tr>
<td>$v$</td>
<td>Local velocity</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>$U$</td>
<td>Flow characteristic velocity</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Valence of species $i$</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Fluid kinetic viscosity</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>$\zeta_M$</td>
<td>Potential of the fluid-rock interface</td>
<td>V</td>
</tr>
<tr>
<td>$\zeta_I$</td>
<td>Potential of the fluid-fluid interface</td>
<td>V</td>
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</table>

**Modelling variables**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$c$</td>
<td>Lattice velocity</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>$dx$</td>
<td>Lattice space step</td>
<td>m</td>
</tr>
<tr>
<td>$dt$</td>
<td>Lattice time step</td>
<td>s</td>
</tr>
<tr>
<td>$D$</td>
<td>Artificial diffusion coefficient</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>$f^\lambda_i$</td>
<td>Local particle distribution function of phase $\lambda$ in direction $i$ for the velocity calculation</td>
<td>mu lu(^{-2}) H(^{-1})</td>
</tr>
<tr>
<td>$F_{\lambda}$</td>
<td>Interaction force term exercised on component $\lambda$</td>
<td>mu lu(^{-1}) H(^{-1}) ts(^{-2})</td>
</tr>
<tr>
<td>$F_{\lambda}^{\text{adh}}$</td>
<td>Fluid-solid interaction term in $F_{\lambda}$</td>
<td>mu lu(^{-1}) H(^{-1}) ts(^{-2})</td>
</tr>
<tr>
<td>$F_{\lambda}^{\text{coh}}$</td>
<td>Fluid-fluid interaction term in $F_{\lambda}$</td>
<td>mu lu(^{-1}) H(^{-1}) ts(^{-2})</td>
</tr>
<tr>
<td>$G_{\lambda}^{\text{adh}}$</td>
<td>Parameter allowing to tune the contact angle</td>
<td>ts(^{-1})</td>
</tr>
<tr>
<td>$G_{\lambda}^{\text{coh}}$</td>
<td>Parameter controlling the magnitude of the surface tension</td>
<td>lu(^2) H mu lu(^{-1}) ts(^{-1})</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface tension</td>
<td>mu lu H(^{-1}) ts(^{-2})</td>
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<tr>
<td>$h_i$</td>
<td>Local particle distribution function in direction $i$ for the potential calculation</td>
<td>-</td>
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<tr>
<td>$\mu_{ad}$</td>
<td>Adimensional kinematic viscosity</td>
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<tr>
<td>$p_{ad}$</td>
<td>Local adimensional fluid pressure</td>
<td>-</td>
</tr>
<tr>
<td>$r_B$</td>
<td>Bubble radius at equilibrium</td>
<td>-</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Local total density</td>
<td>mu lu(^{-2}) H(^{-1})</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>Initial total density</td>
<td>mu lu(^{-2}) H(^{-1})</td>
</tr>
<tr>
<td>$\rho_\lambda$</td>
<td>Local density of component $\lambda$</td>
<td>mu lu(^{-2}) H(^{-1})</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>Local electrical density</td>
<td>C m(^{-3})</td>
</tr>
<tr>
<td>$\tau_{\lambda}$</td>
<td>Relaxation time of component $\lambda$</td>
<td>ts</td>
</tr>
<tr>
<td>$u_{\lambda}$</td>
<td>Local velocity of component $\lambda$</td>
<td>lu ts(^{-1})</td>
</tr>
<tr>
<td>$u_{\lambda}^{\text{eq}}$</td>
<td>Local velocity used in the equilibrium distribution</td>
<td>lu ts(^{-1})</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Local composite velocity of the mixture</td>
<td>lu ts(^{-1})</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Local total velocity</td>
<td>lu ts(^{-1})</td>
</tr>
<tr>
<td>$s_i$</td>
<td>Flag variable of the lattice site $i$</td>
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<tr>
<td>$w_{ij}$</td>
<td>Weights of the equilibrium distribution</td>
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**Physical constants**

<table>
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<th>Symbol</th>
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<tbody>
<tr>
<td>$e$</td>
<td>Fundamental charge</td>
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<td>Vacuum permittivity</td>
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<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>J K(^{-1})</td>
</tr>
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</table>