Temperature-gradient-induced electrokinetic flow and thermoelectricity of electrolyte solutions in a capillary

Wenyao Zhang\textsuperscript{1}, Qiuwang Wang\textsuperscript{1}, Min Zeng\textsuperscript{1} and Cunlu Zhao\textsuperscript{1}\textsuperscript{†}

\textsuperscript{1}Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China

(Received xx; revised xx; accepted xx)

A systematic theoretical study of temperature-gradient-induced electrokinetic flow and electric field of electrolyte solutions in a micro-/nanocapillary is presented. The semi-analytical model for the fluid flow and thermoelectric field are derived by solving the energy, Poisson-Nernst-Planck and Navier-Stokes equations simultaneously with the lubrication approximation. The temperature dependencies of physical properties, as well as the intrinsic Soret effect are taken into account. It is found that the thermoelectric effect has three origins: first, the difference in the Soret coefficients of cation and anion induces an electric field; second, axial gradients of ion concentrations resulting from the temperature modified Boltzmann distribution of ions produces another electric field; last, the fluid transport also causes an electric field. The first origin prevails for lower \( \zeta \) potentials or wider capillaries, while the second dominates for higher \( \zeta \) potentials and very narrow capillaries. It is shown that electrolytes affect the thermoelectric field by altering four variables relevant to cation and anion, i.e. Soret coefficient difference \( \Delta S_T \), average Soret coefficient \( S_T \), normalized difference in diffusivities \( \chi \) and intrinsic Péclet number \( \Lambda \). The thermoelectric fields due to the first two origins can cooperate with or cancel each other depending on the sign of \( \zeta \Delta S_T \). Also, non-zero \( \chi \) can enhance or reduce the induced field depending on the sign and magnitude of \( \chi \zeta \). Our model indicates that the higher the average temperature the weaker the thermoelectric field. Furthermore, the temperature-gradient-induced electrokinetic flow can be decomposed into a thermoosmotic flow caused by an osmotic pressure gradient and dielectric body force and an electroosmotic flow (EOF) due to the thermoelectric field. These two forms of flows may cooperate with or cancel each other depending on \( \zeta \) and \( \kappa_0 a \), where \( \kappa_0 a \) is the ratio of capillary radius to Debye length. It reveals that in contrast to the conventional EOF, the thermoosmotic velocity \( \propto \zeta^2 \), and the thermal induced EOF velocity \( \propto \zeta \nu \), where the value of \( \nu \) depends on \( \zeta \) and \( \kappa_0 a \).

1. Introduction

When an axial temperature gradient is exerted on a confined charged channel filled with an electrolyte solution, not only a so-called temperature-gradient-induced electrokinetic flow generates, but also an electric field is produced [Derjaguin et al. 1987; Putnam & Cahill 2005; Dietzel & Hardt 2016, 2017]. This, along with the conventional electrokinetic phenomena essentially arise from the non-uniform spatial distribution of ions near charged surfaces together with thermodynamic ‘forces’ (e.g. gradients in electric potential, pressure, concentration and temperature). In practice, most solids in contact

\textsuperscript{†} Email address for correspondence: mclzhao@xjtu.edu.cn
with electrolyte solutions in general spontaneously acquire surface charges, which are screened by the so-called electric double layer (EDL). A thermodynamic force causes electrokinetic phenomena by upsetting the mechanical equilibrium of the ion cloud in the EDL. Specially, an axial temperature gradient that exerted on an inhomogeneous charged fluid in confined systems can drive the fluid and produce an electric field. This phenomenon is relevant to diverse novel and promising applications in the realm of science and engineering, such as ζ potential measurement, low-grade waste heat recovery, charge separation, water management (Grosu & Bologa 2010; Kang et al. 2012; Wood et al. 2016; Barragán & Kjelstrup 2017; Li & Wang 2018).

Over the last couple of decades, most studies focus on the electrokinetic flow phenomena under isothermal conditions, such as electroosmotic flow (EOF) or induced-charge EOF (Huang et al. 1988; Patankar & Hu 1998; Squires & Bazant 2004) and streaming potential (Dukhin 1993; Scales et al. 1992; Yariv et al. 2011; Schnitzer et al. 2012), etc. The former has been demonstrated to be a suitable approach to drive fluid in microchannels (Kim et al. 2002; Stone et al. 2004), while the latter is usually used to measure ζ potential (Elimelech et al. 1994) or to convert mechanical energy into electric energy (Yang et al. 2003). All of these have been investigated systematically and in depth. Compared with the conventional electrokinetic flow phenomena under isothermal conditions, it becomes more complicated to obtain a theoretical description in five aspects when non-isothermal effects are brought into the electrokinetic system. First, most physical properties of electrolyte solutions or ions, such as viscosity, dielectric permittivity, electrophoretic ion mobility (i.e. ion electromobility) and ion diffusion coefficients (equally referred to as diffusivities), are temperature-dependent in nature (Knox & McCormack 1994; Rogacs & Santiago 2013; Haynes et al. 2014). Second, the energy equation with viscous dissipation (Maynes & Webb 2004; Sadeghi & Saidi 2010) and Joule heating (Zhao & Liao 2002) should be solved simultaneously to obtain the temperature distribution, which is the fundamental for accessing local material properties and analysing the thermophoretic ion motion (equally termed as intrinsic Soret effect or thermodiffusion). Third, the thermodiffusion fluxes should be brought into the phenomenological ionic species transport equation (de Groot & Mazur 1984; Guthrie et al. 1949), which is analogous to the previous works that pertain to the thermophoresis of colloidal particles in suspensions under non-isothermal conditions (Würgler 2003, 2009; Vigolo et al. 2010). Furthermore, an extra term due to inhomogeneity of the dielectric medium must be additive to the Maxwell stress tensor in the Navier-Stokes equation (Russel et al. 1989; Masliyah & Bhattacharjee 2006), i.e. the so-called dielectric body force. Last, both experimental and theoretical studies manifested that the ζ potential varies with temperature (Ishido et al. 1983; Reppert & Morgan 2003; Revil et al. 1999), because the formation processes of ζ potential, such as surface reactions (mainly, protonation-deprotonation reaction of ionisable groups) and ion absorption, are both strongly dependent on temperature (Revil et al. 1999; Behrens & Grier 2001). Accordingly, it is formidable difficult to establish an exact or even approximate analytical model of the non-isothermal electrokinetic transport phenomena due to the coupled nature of the multi-physical processes and the non-linearity.

The non-isothermal electrokinetic flow phenomena can be divided into two categories according to different origins of non-uniform temperature distribution: one is the conventional electrokinetic flow with dissipative effects (Zhao & Liao 2002; Maynes & Webb 2004; Sadeghi & Saidi 2010). The other is the electrokinetic flow caused by an externally applied temperature gradient alone, which is the focus of the present work. So far and to the best of our knowledge, most theoretical studies on the fluid transport in confined systems induced by the imposed temperature gradient are restricted to
Temperature-gradient-induced electrokinetic flow and thermoelectricity

electroneutral cases (Dariel & Kedem 1975; Ganti et al. 2017; Fu et al. 2017, 2018) or do not explicitly take into account the non-uniform ion distribution inside the charged membrane pores (Tasaka & Nagasawa 1978; Tasaka 1986). The starting point of these studies is the theory of linear non-equilibrium thermodynamics based on the Onsager reciprocal relations (Onsager 1931a, b), which connect the cross-coefficients occurring in the phenomenological equations that depicts thermodynamic fluxes and forces in irreversible transport processes. However, the electroneutral assumption does not hold for the case where the EDL gets involved. Besides, current studies on the non-isothermal electrokinetic phenomena in general focus on the thermophoresis of charged colloidal particles (Ruckenstein 1981; Anderson 1989; Würger 2008, 2010; Rasuli & Golestanian 2008).

In reality, studies on the flow of electrolyte solutions induced by temperature gradients can be traced to the middle of last century. The early work on this flow by Derjaguin & Sidorenkov (1941) reported an expression for the corresponding slip velocity in terms of excess enthalpy density \( \delta h \) (see Derjaguin et al. 1987), but it is inconvenient to determine \( \delta h \) occurring in their expression, which restricts its applications. Later, Kobatake & Fujita (1964) developed a (coarse) continuum description on the temperature gradient induced electrokinetic flow to analyse the experiment by Carr & Sollner (1962). However, their work is based on the Debye-Hückel (DH) approximation and neglects the temperature dependencies of local physical properties, ion concentration and electrostatic potential. As reviewed by Barragán & Kjelstrup (2017), there is still a lack of consensus on the quantitative description although a series of experiments on the temperature gradient-induced fluid transport through ion-exchange membranes have been reported. Nowadays, progress on the temperature-gradient-induced (electrokinetic) flow phenomena has been made due to diverse promising experimental techniques (Wiegand 2004; Bregulla et al. 2016), like modern optical methods, microgravity experiments, and flow channels, to name a few. Meanwhile, numerical simulation techniques for the non-isothermal electrohydrodynamics, such as finite element method (Ghonge et al. 2013; Wood et al. 2016; Benneker et al. 2017) and molecular dynamics simulation (Ganti et al. 2017; Fu et al. 2017, 2018), have been improved. Thus the temperature-gradient-induced electrokinetic flow of electrolyte solutions in micro- or nanochannels attracts growing interests recently. Ghonge et al. (2013) presented a numerical investigation on combined pressure and electroosmotic flow in slit channels with a non-isothermal wall revealed that Soret and electrothermal effects may affect the volumetric flow rate. Later, Wood et al. (2016) performed numerical simulations on electrokinetic transport in ion-selective nanochannels subject to an axial temperature difference, indicating that a temperature gradient can modify the ion-selective behaviour of the channels. Bregulla et al. (2016) reported the first microscale experimental observation of the flow field induced by an inhomogeneous temperature distribution and yielded the mechanocaloric cross-coefficient for two categories of surfaces. Although the relevant work can date back to the middle of last century, theoretical descriptions on the temperature-gradient-induced electrokinetic flow phenomena continue to be scarce and remain in infancy until Dietzel & Hardt (2017) first attempt systematically studied this flow and streaming potential of electrolyte solutions in slit channels subject to an axial temperature gradient with hydrodynamic approach. However, there exist at least four limitations in their study: first, they focused on the ion transport and solvent flow in slit channels, whereas for realistic scenarios more common structures would be circular cylindrical channels, like porous media, membrane pores and capillary tubes, to name a few. In fact, results for the porous membranes can be predicted based on those for a single capillary if the hydraulic permeability, porosity, tortuosity and membrane thickness are
known (Sasidhar & Ruckenstein 1982). Second, the assumption of identical ions diffusion coefficient, which would be abandoned in our work, was utilized in the course of their derivation. In fact, the difference in the diffusivities of cation and anion does play a role especially for higher surface (ζ-) potentials. Third, they never pointed out the synergistic condition of different thermoelectric effects. Last, they did not discussed the overall fluid transport quantitatively and in detail.

The present work aims, within the framework of hydrodynamics and linear non-equilibrium thermodynamics, at capturing a clear physical picture of the flow and induced thermoelectric field of electrolyte solutions in a capillary subject to a temperature gradient. For this purpose, we formulate a theoretical framework by taking into account a set of coupling equations, including the energy, Poisson-Nernst-Planck and Navier-Stokes equations. To obtain an analytical model for low ζ potentials and general semi-analytical model for arbitrary ζ potentials, the lubrication approximation theory is adopted to simplify above partial differential equations based on a small aspect ratio (i.e. the radius-to-length ratio of the capillary). In analogy to the work by Dietzel & Hardt (2017), in this study the temperature dependencies of viscosity and dielectric permittivity of solutions, diffusivities and electromobilities of ions are taken into account. By contrast, this work (at least) makes contributions in the following aspects: first, we consider a more practical case with a round capillary and unequal cation and anion diffusion coefficients. Second, we discuss the relative importance and synergistic condition of different thermoelectric effects for different cases in depth. Third, the influence of average temperature on the induced thermoelectric field is systematically discussed. Last, characteristics of the overall temperature-gradient-induced electrokinetic flow are analysed in detail for varying cross-sections (being measure by the ratio of capillary radius to Debye screening length), ζ potentials and electrolyte types. To the best of our knowledge, all of these have yet to be unambiguously studied.

The rest of this paper is organized as follows: in §2, we develop (semi-)analytical models for the temperature-gradient-induced electrokinetic flow and thermoelectric field of electrolyte solutions in a capillary with an axial temperature gradient. In §3, in the absence of external electric field and external pressure difference, the induced thermoelectric field is analysed for varying cross-sections and ζ potentials in depth to unveil the contributing effects under different conditions and to understand its mechanisms. Also, we analyse the effects of electrolytes and average temperature on the thermoelectric field. Next, in §4, we perform a detailed analysis of the characteristics of the temperature-gradient-induced electrokinetic flow and volumetric flow rate under different conditions to understand its origins and relative importance of each source. Finally, our findings and conclusions are summarised in §5.

2. Problem formulation

Figure 1 depicts a schematic diagram of the investigated system, which consists of a capillary subject to an axial temperature difference, ΔT, and two reservoirs at both sides (not shown). The capillary with a radius of a and a length of l contains an electrolyte solution. The capillary wall then becomes charged and the EDL in electrolyte solution near this wall forms accordingly. In this case, apart from the conventional Seebeck-type thermoelectric effect due to the difference in the Soret coefficients between cation and anion (Würger 2010), the ions redistribution along the temperature gradient in the EDL can give rise to another type thermoelectric effect as well despite the Soret coefficients of the ions being the same. This is because the temperature modified Boltzmann distribution of ions implies axial gradients of ion concentrations within the EDL, which results in
Temperature-gradient-induced electrokinetic flow and thermoelectricity

In contrast to the conventional electrokinetic phenomena, the absolute temperature $T$ in the system depicted in figure 1 is no longer constant. In the stationary state, the temperature distribution is governed by the energy equation, $\rho c_p u \cdot \nabla T = \nabla \cdot (k \nabla T) + \dot{\Phi}_\eta + \dot{\Phi}_{\text{JH}}$, where $u = (u_r, u_x)$ is the fluid velocity, $\rho$ the liquid density, $c_p$ the heat capacity at constant pressure, and $k$ the thermal conductivity. Besides, $\dot{\Phi}_\eta = 2\eta[(\partial_r u_r)^2 + (u_r/r)^2 + (\partial_x u_x)^2 + (\partial_r u_x + \partial_x u_r)^2]/2$ denotes viscous dissipation with $\eta = \eta(T)$ being the dynamic viscosity of fluid. The Joule heating is denoted by $\dot{\Phi}_{\text{JH}} \approx \sigma^* E_x^2$, where $\sigma^* = e^2 \sum_i z_i^2 \bar{D}_i n_{i,\infty}/(k_B T)$ is the bulk electric conductivity with $e$ being the elementary charge, $k_B$ the Boltzmann constant, $E_x$ the induced electric field, $z_i, n_{i,\infty}, D_i$ respectively the valence, the local bulk number concentration and the diffusion coefficient for ionic species $i$ ($i = +$ for the cation and $i = -$ for the anion). The magnitude of the induced electric field is given by $E_x = -\partial_x \phi$ with $\phi$ being the induced electric potential (we shall show that $\phi$ is only a function of $x$ coordinate). For convenience, we focus on

\[ l, \Delta T, \Delta n, \Delta p, E_x, \]

Figure 1. Schematic of a capillary of radius $a$ and length $l$, filled with an aqueous electrolyte solution. A temperature difference $\Delta T \leq T_2 - T_1$ is applied between two ends of the capillary to induce an electric field $E_x$, a salt concentration $\Delta n/l$ and a pressure $\Delta p/l$. The velocity profile $u_x$, which is the combined contributions of thermal induced electroosmotic flow and thermoosmotically driven flow, roughly resembles plug-like structure (see main text for details) with zero velocity at the shear plane, where the electrical surface charge density $q$ is constant or the electric potential is identical to the $\zeta$ potential. For the non-isothermal situation, both EDL potential $\psi$ and its thickness $\kappa^{-1}$ vary along axial direction. The net electric current $I_{\text{net}}$ vanishes in the system due to the counterbalance of advection current and conduction current.

2.1. Temperature distribution

charge separation and produces an electric field (Dietzel & Hardt 2016). Simultaneously, a thermal gradient can induce axial gradients in an osmotic pressure and a dielectric body force, both of which can drive the liquid to flow (here referred to as thermoosmotic flow (TOF)). This flow then transports the ionic charges within the EDL downstream along the capillary, leading to a streaming current and an accompanying streaming electric field. The above three forms of thermoelectric fields may partially cooperate with or counteract each other to form a net thermoelectric field, leading to a so-called thermal induced electroosmotic flow (hereafter we will refer to this part of fluid flow as thermal induced EOF to distinguish it from other origins although it is one part of the fluid motion induced by the temperature gradient in nature), which in turn weakens the induced thermoelectric field. In what follows, we shall simplify the mathematical formulation to obtain (semi-)analytical models for the thermoelectric field and flow field in a capillary subject to an axial temperature gradient.
binary symmetric $z : z$ electrolytes in the present analysis. To facilitate the analysis, several dimensionless variables for $r$-coordinate, $x$-coordinate, absolute temperature, the induced electric potential, the radial and axial velocities of fluid are introduced: $\bar{r} = r/a$, $\bar{x} = x/l$, $\theta = (T - T_0)/\Delta T$, $\varphi = \varepsilon z \varphi/(k_B T_0)$, $U_r = u_r/u_0$, and $U_z = u_z/(\beta u_0)$, where $T_0$ is the room temperature (i.e. $T_0 = 298$ K), $u_0$ the axial scaling velocity (the continuity equation suggests that the radial scaling velocity be $\beta u_0$), $\beta = a/l$ the aspect ratio (we assume that $a \ll l$). Then the dimensionless form of energy equation in two-dimensional axisymmetric coordinate can be expressed as

$$
\beta Pe_T \left( U_r \frac{\partial \theta}{\partial \bar{r}} + U_x \frac{\partial \theta}{\partial \bar{x}} \right) = \frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left( \bar{r} \frac{k}{k_0} \frac{\partial \theta}{\partial \bar{r}} \right) + \beta^2 \frac{\partial}{\partial \bar{x}} \left( \frac{k}{k_0} \frac{\partial \theta}{\partial \bar{x}} \right) + \frac{\eta u_0^2}{k_0 \Delta T} \left( 2 \beta^2 \left( \frac{\partial U_r}{\partial \bar{r}} \right)^2 + \left( \frac{\partial U_x}{\partial \bar{x}} \right)^2 + \beta^2 \left( \frac{\partial U_r}{\partial \bar{x}} \right)^2 \right) + \frac{\epsilon \kappa^2 D}{k_0 \Delta T} \left( \frac{k_B T_0}{\varepsilon z} \right)^2 \left( \frac{\partial \varphi}{\partial \bar{x}} \right)^2,
$$

(2.1)

where $Pe_T = u_0 a / \alpha$ is thermal Péclet number with $\alpha = k_0 / (\rho c_p)$ denoting the thermal diffusivity and $k_0$ being the thermal conductivity at $T_0$, $\epsilon = \varepsilon_0 \varepsilon_r$ denotes the permittivity of aqueous water with $\varepsilon_0$ and $\varepsilon_r$ respectively being the permittivity of vacuum and relative permittivity of liquid, $\kappa^{-1} = \sqrt{\varepsilon k_B T/(2e^2 z^2 n)}$ denotes the local Debye length of the EDL adjacent to solid-liquid interface for a symmetric $z : z$ electrolyte, $D = (D_+ + D_-)/2$ is the average diffusivity of cation and anion. In (2.1), the variations of the density and heat capacity of liquid with temperature are neglected, since an increase in temperature from 298 K to 323 K merely gives rise to a 0.9% change in density and $\sim O(10^{-2})$% in heat capacity [Haynes et al. 2014], respectively. For a symmetric $1 : 1$ electrolyte solution with a widely used concentration ranging from 0.01 mM to 0.1 M [Levine et al. 1975; Baldessari 2008], the typical values of physical properties are approximately equal to those of water: $k_0 \approx 0.6 \text{ W m}^{-1} \text{ K}^{-1}$, $D_i \approx 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\eta \approx 0.89 \times 10^{-3} \text{ Pas}$ and $\epsilon \approx 6.95 \times 10^{-10} \text{ F m}^{-1}$, $\rho = 997 \text{ kg m}^{-3}$, $\alpha \approx 1.47 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. For $\Delta T = 10$ K and the above values, we can calculate that $\epsilon \kappa^2 D k_B^2 T_0^2/(k_0 \Delta T e^2 z^2) \lesssim O(10^{-3})$. Noting that $\partial_\bar{x} \varphi \lesssim O(1)$, the Joule heating is negligibly small. Next, to illustrate that the contributions of the viscous dissipation and the advective effect can be neglected as well, we estimate the order of magnitude of the flow velocity. In the following, we choose conventional Helmholtz-Smoluchowski (HS) velocity for the thermal voltage $V_0 = k_B T_0/(\varepsilon z)$ under the reference electric field $E_0 = k_B T_0/(\varepsilon z l)$, $u_0 = \epsilon_0 V_0 E_0 / \eta_0$, as characteristic velocity to estimate the order of magnitude of these terms. As will be demonstrated later, at least within the range we focus on there should be $u_x \lesssim O(u_0)$. Thus for the previous parameter values, the last term on the right-hand side of (2.1) can be evaluated as $u_0^2/(k_0 \Delta T) \lesssim O(10^{-4}) \beta^2$, which indicates the viscous dissipation is vanishing small. With the analogous approach, one finds that $Pe_T / \beta \lesssim O(10^{-3})$, illustrating that the advective term is also negligibly small. Neglecting all terms of $O(\beta^2)$ and higher, using the symmetric condition along the central axis (i.e. $r = 0$), one finds that $\partial_\theta T \approx 0$, demonstrating the radial variations of temperature can be neglected. Then consider the $O(\beta^2)$ terms, one has $\partial_x (k \partial_x T) = 0$ (since the above order-of-magnitude analysis indicates that the advective term, viscous dissipation and Joule heating should be much smaller than $O(\beta^2)$). Note that thermal conductivity $k$ can be assumed as constant since $k$ has a change less than 4% as temperature increases from 293 K to 313 K [Haynes et al. 2014]. Thus a linear temperature distribution along $x$ coordinate can be derived straightforwardly, i.e. $T \approx T_1 + x \Delta T/l$ (here $T_1$ is the cold end temperature), which implies $\partial_x T \approx \Delta T/l$. 


2.2. Ion concentration and double layer potential

To obtain the double layer potential distribution, we should determine the ion concentration distribution firstly. In the steady state and in the absence of chemical reactions, the transport of ionic species \( i \) is in general described by the stationary Nernst-Planck (NP) equation, \( \nabla \cdot \mathbf{j}_i = 0 \), where \( \mathbf{j}_i = (j_{i,r}, j_{i,z}) \) denotes the overall ionic fluxes. For a dilute electrolyte solution (therefore the finite size of ions and interionic correlations can be neglected), sufficiently small the electric fields and thermal gradients (to meet the postulate of the linear non-equilibrium thermodynamics), \( \mathbf{j}_i \) is a linear superimposition of advection \((n_i \mathbf{u})\), diffusion \((-D_i \nabla n_i)\), thermodiffusion \((-n_i D_{T,i} \nabla T)\) and electromigration \((-n_i \mu_i^* \nabla \phi)\) fluxes, and then can be written as

\[
\mathbf{j}_i = n_i \mathbf{u} - D_i \nabla n_i - n_i D_{T,i} \nabla T - n_i \mu_i^* \nabla \phi,
\]

where \( D_{T,i} \) and \( \mu_i^* \) denote the thermophoretic mobility (i.e. thermodiffusion coefficient) and electrophoretic mobility (defined as velocity per unit applied field) of ionic species \( i \), respectively. The Nernst-Einstein relationship suggests that \( \mu_i^* = e z_i D_i/(k_B T) \). The overall electric potential \( \phi \), which is assumed as a linear superposition of the EDL potential \( \psi(r, x) \) and the induced electric potential \( \varphi \), is governed by the Poisson equation \( \nabla \cdot (\varepsilon \nabla \phi) = -\rho_e \), where \( \rho_e \) is the charge density evaluated as \( \rho_e = e \sum_i z_i n_i \). In the present analysis, we assumed that the charge density only contributes to the EDL potential. Then the induced electric potential satisfies the Laplace equation from which we show that the induced potential \( \varphi \) as well as the corresponding induced field \( E_x \) is only a function of \( x \)-coordinate. By introducing \( \tilde{n}_i = n_i/n_0 \), \( \tilde{z}_i = z_i/z \), \( \tilde{\phi} = e z \phi/(k_B T_0) \) and \( \tilde{\psi} = e z \psi/(k_B T_0) \), as well as using the continuity equation and other nondimensional variables defined in \( \{2.1\} \) the NP equation can be transformed into the following non-dimensional form as

\[
\beta^2 \left\{ \frac{P_e}{r} \frac{\partial n_i}{\partial r} + U_x \frac{\partial \tilde{n}_i}{\partial x} \right\} - \frac{1}{D^*} \left[ \frac{D_i}{D^*} \left( \frac{\partial n_i}{\partial x} + \tilde{n}_i S_{T,i} \Delta T \frac{\partial \theta}{\partial x} + \frac{\tilde{z}_i \tilde{n}_i}{1 + \theta \Delta T/T_0} \frac{\partial \tilde{\phi}}{\partial x} \right) \right] = 0,
\]

where \( S_{T,i} = D_{T,i}/D_i \approx Q_i/(k_B T^2) \) stands for the (intrinsic) Soret coefficients in units of \( K^{-1} \) with \( Q_i \) representing heat of transport of the ionic species \( i \) (see Appendix B), and \( P_e = u_0 l/D^* \) denotes ionic Péclet number with \( D^* = 10^{-9} \text{ m}^2 \text{ s}^{-1} \) being reference diffusivity. With the expression for \( u_0 \) and the parameter values given in the previous section, one finds that \( P_e \approx 0.5 \) and thus the advection term (i.e. the term on the left-hand side of \( \{2.3\} \)) can be safely eliminated. Neglecting all terms of \( O(\beta^2) \) and higher, using symmetric boundary conditions along the central axis (i.e. \( r = 0 \)), and replacing the non-dimensional parameters by the corresponding dimensional counterparts, one finds

\[
n_i = n_{i,\infty}(x) \exp \left( -\frac{e z_i \psi}{k_B T} \right),
\]

with \( n_{i,\infty} \) being the local bulk concentration of ionic species \( i \) at \( \psi = 0 \) (i.e. electroneutral region in general found far from the charged wall). Specially, for a binary symmetric electrolyte, we have \( n_{i,\infty} \equiv n \) for each ionic species due to the electroneutrality. Next, to obtain an explicit expression for \( n(x) \), we consider \( O(\beta^2) \) terms of \( \{2.3\} \) alone (here we neglect the advective term, and the case of \( Pe > 1 \) can be left for future studies) and
notice that the electroneutrality, one shows that the bulk salt concentration satisfies
\[
\frac{\partial \ln n}{\partial x} = -S_T \frac{\partial T}{\partial x}, \tag{2.5}
\]
where \( S_T = (Q_+ + Q_-)/(2k_B T^2) \) is the average Soret coefficient of cations and anions. This relation is the so-called Soret equilibrium \cite{Wurger2010}, which suggests that the bulk ion concentration be affected by the ion thermodiffusion alone. Further, we assume that \( S_T \) takes a constant value of room temperature and infinite dilution, and then obtain from (2.5) the solution of the bulk ion concentration as
\[
n = n_0 \exp[-S_T(T - T_0)], \tag{2.6}
\]
which exactly recovers the expression utilized in the literature \cite{Braun2002, Jiang2009}. After substituting (2.5) into (2.4), one can find the solution of ion distribution.

To obtain the solution of double layer potential, we transform the Poisson equation in nondimensional form as
\[
\beta^2 \left( \frac{\partial^2 \tilde{\phi}}{\partial \tilde{x}^2} + \gamma \Delta T \frac{\partial \tilde{\phi}}{\partial \tilde{x}} \frac{\partial \theta}{\partial \tilde{x}} \right) + \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{\psi}}{\partial \tilde{r}} \right) + \gamma \Delta T \frac{\partial \tilde{\psi}}{\partial \tilde{r}} \frac{\partial \theta}{\partial \tilde{r}} = -\frac{(\kappa_0 a)^2}{2} \frac{\epsilon_0}{\epsilon} (\tilde{n}_+ - \tilde{n}_-), \tag{2.7}
\]
where \( \kappa_0^{-1} = \sqrt{\epsilon_0 k_B T_0/(2e^2 z^2 n_0)} \) is defined as the Debye screening length under the room temperature \( T_0 \). It should be noted that the temperature dependence of permittivity can be nicely described by the ‘exponential formula’ according to the tabulated data in \cite{Haynes2014}. Such dependence suggests that \( \epsilon = \epsilon_0 e^{-(T - T_0)/T^*} \) with \( T^* = 216.9 \) K, which results in \( \gamma = \partial_T \epsilon/\epsilon = -1/T^* \). Neglecting terms of \( O(\beta^2) \) and higher and noting \( \partial_T \theta \approx 0 \), simultaneously substituting the solutions of ion distribution into (2.7), one obtains the governing equation of double layer potential as
\[
\frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{\psi}}{\partial \tilde{r}} \right) \approx \kappa^2 \sinh \left( \frac{e \tilde{\psi}}{k_B T} \right), \tag{2.8}
\]
which is subject to a symmetric boundary condition along the central axis of the capillary (i.e. \( \tilde{r} = 0 \)) and a constant potential (\( \tilde{\zeta} \)) or constant charge density (\( \tilde{q} \)) boundary at the capillary wall (i.e. \( \tilde{r} = a \)). For wide capillaries without EDL overlap, the Gouy-Chapman model suggests that a constant \( \tilde{\zeta} \) potential boundary is equivalent to a constant surface charge boundary, while under the condition of EDL overlap, the constant \( \tilde{\zeta} \) boundary deviates from the constant charge density boundary due to charge regulation effect. The realistic boundary under the condition of EDL overlap is expected to fall in between constant potential and constant charge boundaries \cite{Israelachvili2011, Ruiz-Cabello2014, Zhao2015}. The formulation of such boundary requires the detailed knowledge of surface chemistries of capillary and thus is beyond the scope of our present work. In addition, the present work neglects the temperature dependence of \( \tilde{\zeta} \) or of \( \tilde{q} \) are neglected since \cite{Dietzel2016} have shown that for silicate walls in contact with an aqueous electrolyte \( q \) appears to be merely a weak function of temperature. Equation (2.8) resembles the conventional Poisson-Boltzmann (PB) equation under the isothermal condition, and then one can use the methodology of solving isothermal PB equation to solve (2.8). For the case of \( |e \tilde{\psi}/(k_B T)| \ll 1 \), using the Debye-Hückel (DH) linearization and the constant potential boundary condition, one obtains the analytical solution of (2.8), which reads \( \tilde{\psi}(\tilde{r}) = I_0(\kappa_0 \tilde{r})/I_0(\kappa_0 a) \), here \( I_\nu \) is the \( \nu \)th order modified Bessel function of the first kind. For higher \( \tilde{\zeta} \) potentials, we use the numerical method which is detailed in Appendix B.
been defined in \(2.3\). It is noted that this parameter varies along the axial direction, and hence the EDL potential is a function of \(x\) coordinate. For further calculation, the local Debye parameter \(\kappa a\) can be evaluated from the room temperature Debye parameter \(\kappa_0 a\) by using the following relationship:

\[
\frac{\kappa a}{\kappa_0 a} = \frac{\exp[-(\gamma + S_T)T_0\vartheta/2]}{\sqrt{1 + \vartheta}}, \tag{2.9}
\]

where \(\vartheta = (T - T_0)/T_0\). For sufficiently small \(\vartheta\), \(2.9\) can be linearised by using Taylor series as \(\kappa a = \kappa_0 a\{1 - \frac{1}{2}[1 + (\gamma + S_T)T_0] \vartheta + O(\vartheta^2)\}\), which helps us understand the influence of temperature on the EDL in a straightforward way. It is obvious that a temperature increment may expand or shrink the EDL depending on the sign of \(1 + (\gamma + S_T)T_0\). Notably, the modification of the local double layer thickness is of no importance if \((\gamma + S_T)T_0 = -1\) despite a non-uniform temperature distribution.

### 2.3. Liquid flow

An fluid motion through a charged capillary subject to an axial temperature gradient originates from diverse physical mechanisms. In brief, this fluid flow is the combination of an electrosmotic flow (EOF) induced by thermoelectric field and a thermoosmotic flow (TOF). The latter primarily originates from two mechanisms: first, a gradient in temperature induces an axial gradient of the osmotic pressure to drive the solvent flow. Second, a temperate dependence of the permittivity gives rise to a dielectric body force to drive the fluid. In the following, we present a detailed analysis of these flows. For the steady-state incompressible Newtonian fluid flow, the velocity field is governed by the continuity equation, \(\nabla \cdot \mathbf{u} = 0\), together with the (modified) Navier-Stokes equation

\[
\rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot \eta [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] - \rho \eta \nabla \phi - \frac{1}{2} (\nabla \phi)^2 \nabla \epsilon, \tag{2.10}
\]

where \(p\) denotes pressure. In \(2.10\), the last two terms on the right hand side represent the Korteweg-Helmholtz electric body force \([\text{Russel et al. 1989}; \text{Masliyah & Bhattacharjee 2006}](\text{2.10})\), which comprises a Coulomb (or electrostatic body force), \(\rho \eta \nabla \phi\), and a dielectric body force, \(-(\nabla \phi)^2 \nabla \epsilon/2\). For the sake of lubrication analysis, the axial and radial components of \(2.10\) are respectively nondimensionalised as

\[
\beta \text{Re} \left( U_r \frac{\partial U_x}{\partial r} + U_x \frac{\partial U_r}{\partial x} \right) - \beta^2 \left( \eta^2 \frac{\partial^2 U_x}{\partial x^2} + 2 \frac{\partial U_x}{\partial x} \frac{\partial \eta}{\partial x} + \frac{\partial U_r}{\partial x} \frac{\partial \eta}{\partial x} \right) \]

\[
- \frac{\beta^3 \epsilon}{\epsilon_0} \left[ \frac{\partial^2 \Phi}{\partial x^2} \frac{\partial \Phi}{\partial x} \frac{\partial \theta}{\partial x} \frac{\partial \theta}{\partial x} \right] + \frac{\beta^2 \epsilon}{\epsilon_0} \left( \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{v}}{\partial \tilde{r}} \right) \frac{\partial \Phi}{\partial x} + \frac{\beta^2 \epsilon}{\epsilon_0} \left( \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{v}}{\partial \tilde{r}} \right) \frac{\partial \theta}{\partial x} \right) \right) \]; \tag{2.11}

and

\[
\beta^3 \text{Re} \left( U_r \frac{\partial U_r}{\partial r} + U_x \frac{\partial U_r}{\partial x} \right) - \beta^2 \left( \eta \frac{\partial}{\partial r} \left( \frac{\partial \Phi}{\partial r} \right) - \frac{\eta U_r}{r^2} + 2 \frac{\partial U_r}{\partial r} \frac{\partial \eta}{\partial r} + \frac{\partial U_x}{\partial x} \frac{\partial \eta}{\partial x} \right) \]

\[
+ \beta^2 \frac{\partial}{\partial x} \left( \tilde{\eta} \frac{\partial U_r}{\partial x} \right) \right) - \beta^2 \frac{\epsilon}{\epsilon_0} \left( \frac{\partial^2 \Phi}{\partial x^2} \frac{\partial \Phi}{\partial x} \frac{\partial \theta}{\partial x} \frac{\partial \theta}{\partial x} \right] + \frac{\beta^2 \epsilon}{\epsilon_0} \left( \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{v}}{\partial \tilde{r}} \right) \frac{\partial \Phi}{\partial x} \right) \]
\[ \begin{align*}
\frac{1}{r} \frac{\partial}{\partial r} \left( \eta \frac{\partial u_x}{\partial r} \right) &= \frac{\partial p}{\partial x} - \frac{\partial}{\partial r} \left( \frac{r \partial \psi}{\partial r} \right) \frac{\partial \psi}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) E_x + \frac{\gamma \epsilon}{2} \left( \frac{\partial \psi}{\partial r} \right)^2 \frac{\partial T}{\partial x},
\end{align*} \] (2.14)

Substituting the leading-term of (2.3) and (2.7) into (2.13), then integrating along radial coordinate \( r \), one deduces \( p = p_0 + \Pi \) (see Appendix A), here \( p_0 \) denotes the externally applied pressure whose derivative with respect to \( x \) is zero when the externally imposed pressure difference is absent, and \( \Pi = k_B T \sum_i (n_i - n_{i,\infty}) \) is the excess osmotic pressure (see [Masliyah & Bhattacharjee 2006; W"urger 2008, 2010; Israelachvili 2011]).

In the absence of the external pressure difference, the first term on the right-hand side of (2.14) is the contribution to the fluid flow due to the gradient of the excess osmotic pressure \( \partial_x \Pi \). The second term is caused by the excess ion concentration (one should bear in mind that \( (\epsilon/r) \partial_t (r \partial_r \psi) \approx -\epsilon z (n_+ - n_-) \)) together with a gradient in the EDL potential \( \partial_x \psi \). As detailed in Appendix A, the second term is found to be cancelled by part of the first term. Moreover, the third term refers to the electroosmotically driven flow due to the induced electric field, while the last term stands for the contribution of the dielectric body force. Furthermore, (2.14) fulfills the symmetry boundary condition at \( r = 0 \) and satisfies the no-slip condition on the solid-liquid surface, namely

\[ \frac{\partial u_x}{\partial r} \bigg|_{r=0} = 0, \quad u_x \big|_{x=a} = 0. \] (2.15a, b)

Then the solution of (2.14) with the boundary conditions in (2.15) gives rise to the axial velocity of the solvent flow (see Appendix A for details), which is expressed as

\[ u_x = -\frac{a^2 - r^2}{4\eta} \frac{\partial p_0}{\partial x} - \frac{\epsilon E_x}{\eta} (\zeta - \psi) - \frac{2nk_B T}{\eta} \frac{\partial T}{\partial x} \left\{ \frac{1}{T} \int_a^r \frac{1}{r} \int_0^r r \Psi \sinh(\Psi) dr dr - \left( \frac{1}{T} + \frac{\partial_T n}{n} \right) \int_a^r \frac{1}{r} \int_0^r r[\cosh(\Psi) - 1] dr dr \right\} - \frac{\gamma \epsilon}{2} \frac{\partial T}{\partial x} \int_a^r \frac{1}{r} \int_0^r \left( \frac{\partial \psi}{\partial r} \right)^2 dr dr, \] (2.16)

with \( \Psi = \epsilon z \psi/(k_B T) \).

Under the DH approximation (|\( \Psi \)\| \ll 1), i.e. \( \sinh(\Psi) \approx \Psi \) and \( \cosh(\Psi) - 1 \approx \Psi^2/2 \), one obtains the explicit expression of (2.16) as

\[ u_x^{(\text{DH})} = -\frac{a^2 - r^2}{4\eta} \frac{\partial p_0}{\partial x} - \frac{\epsilon E_x}{\eta} \left[ \frac{I_0(kr)}{I_0(ka)} - 1 \right] + \frac{\epsilon \zeta}{4\eta} \frac{\partial T}{\partial x} \left\{ \left( \frac{1}{T} - \frac{\partial_T n}{n} \right) \times \left[ \frac{g_1(ka) - g_1(kr)}{I_0^2(ka)} \right] + \gamma \left[ \frac{g_2(ka) - g_2(kr)}{I_0^2(ka)} \right] \right\}, \] (2.17)
in which
\[ g_1(\xi) = \xi^2 I_2^2(\xi) - \xi I_0(\xi) I_1(\xi) - \xi^2 I_1^2(\xi), \quad g_2 = g_1(\xi) - I_0^2(\xi). \] (2.18a, b)

For arbitrary \( \zeta \) potential, the overall volumetric flow rate (VFR) can be evaluated by integrating (2.16) over the cross section, i.e. \( \dot{Q} = 2\pi \int_0^a u_x r dr \). Following the work by Peters et al. (2016), we see that the triple integrals in \( \dot{Q} \) can be reduced to single integrals, thus
\[
\frac{\dot{Q}}{\pi a^2} = -\frac{\partial p_0}{\partial x} \frac{a^2}{8\eta} + \frac{2\varepsilon E_x}{\eta} \int_0^1 \hat{r} \left( \frac{\psi}{\zeta} - 1 \right) + \frac{\partial T}{\partial x} \frac{\varepsilon (\kappa a)^2}{4\eta} \left( \frac{k_B T}{\varepsilon z} \right)^2 \\
\times \left\{ \frac{1}{T} \int_0^1 \hat{r}(1 - \hat{r}^2) [\Psi \sinh(\Psi) - \cosh(\Psi)] + 1 d\hat{r} - \frac{\partial T}{\partial n} \int_0^1 \hat{r}(1 - \hat{r}^2) [\cosh(\Psi) - 1] d\hat{r} \\
- \frac{1}{2(\kappa a)^2} \frac{\partial T}{\epsilon} \int_0^1 \hat{r}(1 - \hat{r}^2) \left( \frac{\partial \Psi}{\partial r} \right)^2 d\hat{r} \right\}.
\] (2.19)

Under the Debye-Hückel approximation, \( \dot{Q} \) can be explicitly written as
\[
\frac{\dot{Q}^{(DH)}}{\pi a^2} = -\frac{a^2 \partial p_0}{8\eta \partial x} - \frac{\epsilon \varepsilon E_x}{\eta} \left( 1 - \frac{2A}{\kappa a} \right) + \frac{\epsilon \varepsilon^2}{4\eta} \frac{\partial T}{\partial x} \left[ \frac{1}{3} \left( \frac{1}{T} - \frac{\partial T}{\epsilon} - \frac{\partial T}{n} \right) F_\alpha - \gamma A^2 \right],
\] (2.20)
in which
\[ F_\alpha = (\kappa a)^2 - \kappa a A - [(\kappa a)^2 - 1] A^2, \] (2.21)
where \( A = I_1(\kappa a)/I_0(\kappa a) \).

It is evident that (2.17) and (2.20) can respectively reduce to the corresponding velocity and VFR of the conventional pressure and electroosmotically driven flow (see Masliyah & Bhattacharjee, 2006) when the axial temperature gradient vanishes.

### 2.4. Induced electric field

So far, the induced electric field, \( E_x \), is yet to be determined for calculating the fluid velocity field. For this purpose, we utilize the condition of the zero net current, \( I_{\text{net}} = 2\pi \varepsilon \int_0^a \sum_i z_i j_i x r dr = 0 \), which can be expanded as
\[
-2\pi \varepsilon \int_0^a \sum_i z_i D_i \left[ \frac{\partial n_i}{\partial x} + n_i S_{T,i} \frac{\partial T}{\partial x} + \frac{e z_i n_i}{k_B T} \left( \frac{\partial \psi}{\partial x} - E_x \right) \right] r dr \\
+ 2\pi \varepsilon \int_0^a \sum_i z_i n_i u_x r dr = 0.
\] (2.22)

The first term on the left-hand side of (2.22) stands for the conduction current, \( I_c \), while the second term represents the advection current (i.e. convection current in the literature), \( I_a \). With help of (2.4), the conduction current, \( I_c \) can be rewritten as
\[
I_c = \frac{2\pi e^2 E_x}{k_B T} \int_0^a \sum_i z_i^2 n_i D_i r dr - \frac{2\pi e^2}{k_B T^2} \frac{\partial T}{\partial x} \int_0^a \sum_i z_i^2 n_i D_i r dr \\
- 2\pi \varepsilon \frac{\partial T}{\partial x} \int_0^a \sum_i z_i n_i D_{S_{T,i}} r dr - 2\pi \varepsilon \frac{\partial \ln n}{\partial T} \frac{\partial T}{\partial x} \int_0^a \sum_i z_i n_i D_i r dr.
\] (2.23)
For binary symmetric $z:z$ electrolytes, substituting the solution of ion distribution obtained from (2.4) and (2.6) into (2.23), one obtains

$$I_c = -L_{c,E}E_x + L_{c,T} \frac{\partial T}{\partial x}$$  \hspace{1cm} (2.24)$$

with

$$L_{c,E} = -\frac{4\pi e^2 z^2 n D}{k_B T} \int_0^a [\cosh(\Psi) - \chi \sinh(\Psi)] r dr,$$  \hspace{1cm} (2.25)$$

$$L_{c,T} = -\frac{4\pi e z n D}{T} \left\{ \int_0^a \Psi [\cosh(\Psi) - \chi \sinh(\Psi)] r dr \\
+ \frac{\Delta S_T T}{2} \int_0^a [\cosh(\Psi) - \chi \sinh(\Psi)] r dr \right\},$$  \hspace{1cm} (2.26)$$

where $\Delta S_T = S_{T,+} - S_{T,-}$ denotes the difference in Soret coefficients between cation and anion, and $\chi = (D_+ - D_-)/(D_+ + D_-)$ measures the difference in the diffusion coefficients between cation and cation. Making use of the Einstein-Stokes relationship, we find that $\chi$ is a temperature-independent constant for a given solute. In addition, in the course of derivation of (2.26), we make use of $\partial T \ln n = -S_T$. Within the DH approximation, (2.23) can be evaluated as

$$I_c^{(DH)} = \pi a^2 \kappa^2 D E_x \left[ 1 + \frac{\hat{\zeta}^2}{2} (1 - A^2) - 2\chi \frac{\hat{A}}{\kappa a} \right] - \pi a^2 \kappa^2 D \frac{\partial T}{\partial x} \left\{ \frac{\hat{\zeta} T}{\kappa a} \right\},$$  \hspace{1cm} (2.27)$$

where $\hat{\zeta} = ez\zeta/(k_B T)$.

Returning our attention to the second term of (2.22), i.e. advection current $I_a$. Noticing that the charge density is denoted by $\rho_e = \sum_i e z_i n_i$, one finds $I_a = 2\pi \int_0^a \rho_e u_x r dr$. Taking the leading-order terms of (2.7) into account alone, in dimensional form, one obtains $\rho_e \approx -\epsilon r^{-1} \partial_r (r \partial_r \psi)$, integrating by parts and combining the corresponding boundary conditions, one obtains

$$I_a \approx 2\pi \epsilon \int_0^a r \frac{\partial u_x}{\partial r} \frac{\partial \psi}{\partial r} dr.$$  \hspace{1cm} (2.28)$$

Substitution of the axial velocity (2.16) into (2.28), we find that

$$I_a = L_{a,p} \frac{\partial p_0}{\partial x} - L_{a,E} E_x + L_{a,T} \frac{\partial T}{\partial x},$$  \hspace{1cm} (2.29)$$

with

$$L_{a,p} = \frac{2\pi \epsilon}{\eta} \int_0^a r (\zeta - \psi) dr,$$  \hspace{1cm} (2.30)$$

$$L_{a,E} = -\frac{2\pi \epsilon^2}{\eta} \int_0^a r \left( \frac{\partial \psi}{\partial r} \right)^2 dr,$$  \hspace{1cm} (2.31)$$

$$L_{a,T} = \frac{2\pi \epsilon^2 \kappa^2}{\eta} \left\{ \left( \frac{k_B T}{ez} \right)^2 \left( 1 + \frac{\partial_T n}{n} \right) \int_0^a \frac{\partial \psi}{\partial r} \int_r^a r [\cosh(\Psi) - 1] dr dr \right\}.$$
Temperature-gradient-induced electrokinetic flow and thermoelectricity

\[ -\frac{k_B T}{e z} \int_0^a \frac{\partial \psi}{\partial r} \int_0^r r \psi \sinh(\psi) dr dr + \frac{\gamma}{2 \kappa^2} \int_0^a \frac{\partial \psi}{\partial r} \int_0^r r \left( \frac{\partial \psi}{\partial r} \right)^2 dr dr \}. \tag{2.32} \]

Under the DH approximation, the explicit expression for the advection current can be derived as

\[ I_a^{(DH)} = -\frac{\epsilon \zeta}{\eta} \frac{\partial \rho_0}{\partial x} \left( 1 - \frac{2A}{\kappa a} \right) + \frac{\pi \epsilon^2 \zeta^2 (\kappa a)^2 E_x}{\eta} \left( \frac{2A}{\kappa a} + A^2 - 1 \right) \]

\[ -\frac{\pi \epsilon^2 \zeta^3 (\kappa a)^2 \partial T}{2\eta} \left[ \left( \frac{1}{T} - \frac{\partial_T n}{n} \right) B_1 + \gamma B_2 \right], \tag{2.33} \]

in which

\[ B_1 = \frac{1}{\kappa a I_0^1(\kappa a)} \int_0^1 I_1(\kappa a \hat{r}) h_1(\kappa a \hat{r}) d\hat{r}, \tag{2.34} \]

\[ B_2 = \frac{1}{\kappa a I_0^3(\kappa a)} \int_0^1 I_1(\kappa a \hat{r}) h_2(\kappa a \hat{r}) d\hat{r}, \tag{2.35} \]

with

\[ h_1(\xi) = \xi^2 \left[ I_0^2(\xi) - I_1^2(\xi) \right], \quad h_2(\xi) = \xi^2 \left[ I_0^2(\xi) - I_1^2(\xi) \right] - 2\xi I_0^1(\xi) I_1(\xi). \tag{2.36a, b} \]

Using the result of conduction current in (2.24) and of advection current in (2.29), and noticing that there is no external pressure gradient, we determine the local induced field to be (see Appendix B for explicit and reduced expressions)

\[ E_x = \frac{L_{c,T} + L_{a,T} \partial T}{L_{c,E} + L_{a,E} \partial x}. \tag{2.37} \]

Under the DH approximation, (2.37) can reduce to

\[ \left( \frac{E_x}{\partial x T} \right)^{(DH)} = \left( F_{cc} + \frac{\zeta^2 \epsilon}{\eta D} F_1 \right)^{-1} \left\{ \frac{\zeta^3}{2} \frac{\epsilon}{\eta D} \left( \frac{1}{T} - \frac{\partial_T n}{n} \right) B_1 + \frac{\zeta^3}{2} \frac{\epsilon \gamma}{\eta D} B_2 \right. \]

\[ + \frac{\zeta}{T} \left[ \frac{2A}{\kappa a} + \zeta^2 B_3 - \chi \zeta (1 - A^2) \right] + \frac{\Delta S_T k_B T}{e z} F_{cc} \right\}, \tag{2.38} \]

with

\[ F_{cc} = 2 \int_0^1 \left[ \cosh(\psi) - \chi \sinh(\psi) \right] \hat{r} d\hat{r} \approx 1 + \frac{\hat{r}^2}{2} \left( 1 - A^2 \right) - 2\chi \zeta \frac{A}{\kappa a}, \tag{2.39} \]

\[ F_1 = \frac{2A}{\kappa a} + A^2 - 1, \tag{2.40} \]

\[ B_3 = \frac{1}{I_0^3(\kappa a)} \int_0^1 \hat{r} \hat{r}^3(\kappa a \hat{r}) d\hat{r}. \tag{2.41} \]

where \( F_{cc} \) is a factor which reflects the deviation of the conductivity from its bulk value due to the presence of the charged capillary wall, and the second term in the first round bracket of (2.38) (proportional to \( F_1 \)) measures an increase in the electrical conductivity due to the thermal induced EOF. Since temperature makes a less impact on the Einstein radii (i.e. hydrodynamic radii) of simple ions like Na\(^+\), K\(^+\) and Cl\(^-\) for a small \( \Delta T \).
The Stokes-Einstein relationship suggests that \( \eta D/T = \eta D_0/T_0 \) should be a constant for a given solute. After some algebraic operations, we obtain

\[
\left( \frac{E_x}{T} \right)_{(DH)} = \left( F_{cc} + \zeta^2 \frac{A}{\epsilon_0} \frac{\epsilon_0 T_0}{T} F_1 \right)^{-1} \left\{ \frac{\zeta^2 A}{T} \frac{\epsilon_0 T_0}{2 \epsilon_0} B_1 + \frac{\zeta^2 A}{T} \frac{\epsilon_0 S T_0 B_1}{2 \epsilon_0} \right. \\
+ \frac{\zeta^2 A}{T} \frac{\epsilon_0}{2} \gamma T_0 B_2 + \frac{\zeta}{T} \left[ \frac{2 A}{\kappa a} + \zeta B_3 - \chi \zeta (1 - A^2) \right] \left. + \frac{\Delta S_T k_B T}{2 \epsilon_0} F_{cc} \right\}, 
\]

with

\[
\Lambda = \frac{\epsilon_0}{\eta_0 D_0} \left( \frac{k_B T_0}{\epsilon_0} \right)^2 = \frac{2 n_0 k_B T_0}{\kappa_0^2 \eta_0 D_0} \tag{2.43}
\]

being the intrinsic Péclet number (see Saville 1977; Yariv et al. 2011), where \( D_0 \) is the average diffusivity of cation and anion calculated at \( T_0 \) and \( \tilde{\zeta} = e \zeta / (k_B T_0) \).

The contributions to the induced electric field due to the TOF are given by the first three terms in the curly bracket of (2.42). The fourth term is caused by the axial gradients of ion concentrations due to the temperature modified Boltzmann distribution of ions in the presence of the EDL (Dietzel & Hardt 2016). The last term is induced by the Seebeck-type effect due to the difference in the Soret coefficients of cations and anions. From (2.42), one finds neither the temperature dependence of the viscosity nor that of the ion diffusivity has an effect on the induced electric field, whereas variations of the dielectric permittivity with temperature play a role. Under non-isothermal conditions, the induced electric field \( E_x \) is a (weak) function of \( x \)-coordinate since \( E_x \) is expressed in terms of a series of temperature-dependent variables, such as \( \kappa a, \epsilon, S_T \) and \( \tilde{\zeta} \). Therefore, an induced electric potential, \( \Delta \varphi = -\int_t^l dx E_x = -\int_{T_1}^{T_2} dT E_x / \partial_x T \), which can be evaluated by means of numerical integration, is discussed in the following instead of \( E_x \).

3. Analysis of induced thermoelectric field

Obviously, in the absence of externally applied temperature gradient, the expression for the net induced current derived in this paper, i.e. the sum of (2.27) and (2.33) (here \( \chi = 0 \)), exactly reduces to the net electric current under isothermal conditions in the literature (Masliyah & Bhattacharjee 2006). In addition, for an uncharged capillary subject to an axial temperature gradient, one has

\[
E_x^{(DH)} \bigg|_{\zeta \rightarrow 0} = \frac{\Delta S_T k_B T}{2 \epsilon_0} \frac{\partial T}{\partial x} \simeq \frac{1}{T_0} \frac{\Delta Q}{2 \epsilon_0} \frac{\partial T}{\partial x}, 
\]

which is essentially the thermoelectric field due to the Soret equilibrium for a symmetric electrolyte (we refer to the corresponding induced thermoelectric potential as the bulk Soret voltage, see Würger 2010). In (3.1), \( \Delta Q \) is the difference in the heats of transport between cation and anion, i.e. \( \Delta Q = Q_+ - Q_- \). Furthermore, the results (3.1) can be recovered from the general solution in the limit of \( \kappa a \) approaching infinity (thus \( \kappa a \rightarrow \infty \) as well), since this situation is equivalent to the case where the EDL disappears.

3.1. Contributions of different mechanisms

In this section, we present a detailed analysis of the thermoelectric field for an aqueous solution of sodium chloride (NaCl, see Appendix B for material properties) induced by an axial temperature gradient to understand its various mechanisms and also clarify the relative importance of each mechanism. To this end, the induced thermoelectric potential
per temperature difference $\Delta \varphi/\Delta T$ normalized by $k_B/(e\Delta T)$ is evaluated by integrating (2.37) (which is valid for arbitrary values of $\zeta$ and is termed as PB solution) or (2.42) (which is only valid for small $\zeta$ values and is referred to as DH solution) numerically across the capillary (see Appendix B for details). The temperature difference and the cold side temperature are set to $\Delta T = 25$ K and $T_1 = 298$ K, respectively.

In figure 2(a), $e\Delta \varphi/(k_B \Delta T)$ is plotted as a function of $\kappa_0 a$ for varying $\zeta$ potentials. Expectedly, for low $\zeta$ potentials, the difference between the DH and PB solutions is undistinguished, indicating an excellent agreement. Nevertheless, as $\zeta$ potential is beyond $-75$ mV, the DH solutions start to deviate from the PB solutions. As shown in figure 2(a) for small values of $\zeta$ potential (e.g., $\zeta = -15$ mV), the induced thermoelectric potential $\Delta \varphi$ is negative, namely, the induced thermoelectric field is directed toward the hot end, and
the magnitude of $\Delta \varphi / \Delta T$ increases with increasing $\kappa_0 a$. As $\kappa_0 a \to \infty$, $\Delta \varphi$ approaches the Soret voltage in the bulk electrolyte. By contrast, for higher $\zeta$ potentials, $\Delta \varphi / \Delta T$ becomes a positive value under the extreme confinement (i.e. $\kappa_0 a \to 0$) and drops to zero as $\kappa_0 a$ is increased to a critical value $(\kappa_0 a)_{cr}$ (for instance, $(\kappa_0 a)_{cr} \approx 2.54$ if $\zeta = -25 \text{ mV}$, see figure 2(a)). When $\kappa_0 a$ exceeds the critical value, the sign of $\Delta \varphi / \Delta T$ switches from positive to negative, i.e. the direction of the induced thermoelectric field is reversed. If one continues to increase $\kappa_0 a$, the magnitude of $\Delta \varphi$ is expected to increase until reaching the bulk Soret voltage. The reason for this behaviour mainly lies in the two counteracting thermoelectric effects: (i) the difference in the Soret coefficients between cation and anion gives rise to charge separation and thus produces a thermoelectric field (here referred to as Seebeck-type effect); and (ii) the temperature modified Boltzmann distribution implies additional axial gradients of ion concentrations (which will be detailed later), leading to charge separation and an electric field.

Figure 2(b) illustrates the effect of the fluid flow on the thermoelectric field. Solutions excluding the flow effect are compared with the complete solutions depicted in figure 2(a). It is clear from this plot that for lower $\zeta$ potentials, the fluid flow has a negligible effect on the induced thermoelectric field, while for large values of $\zeta$, the fluid flow contributes substantially to the induced thermoelectric field in a certain range of $\kappa_0 a$ (which varies with varying $\zeta$, e.g. for $\zeta = -75 \text{ mV}$ and $10 \leq \kappa_0 a \leq 50$ the induced thermoelectric potential excluding the effect of fluid flow deviates from the complete solution by more than 10%). The higher the $\zeta$ potential is, the more significant the fluid flow contributes to the induced thermoelectric field. Besides, the contribution of the fluid flow disappears if $\kappa_0 a \to 0$ (see figure 2b) or $\kappa_0 a \to \infty$ (not shown) regardless of the values of $\zeta$. In general, for higher $\zeta$ potentials and in the absence of the flow effect, the induced thermoelectric potential (without sign) would be underpredicted if $\kappa_0 a < (\kappa_0 a)_{cr}$, while be overpredicted if $\kappa_0 a > (\kappa_0 a)_{cr}$. Note that the TOF always drives the fluid to the warmer side under the (sufficient and unnecessary) condition of $S_T > 0$ (see (2.17)). Thus in the case of $\kappa_0 a < (\kappa_0 a)_{cr}$, the direction of the thermoelectric field due to the TOF is consistent with that due to the overall non-advective effect, leading to an increase in the value of induced thermoelectric potential. However, in the case of $\kappa_0 a > (\kappa_0 a)_{cr}$ the thermoelectric field due to the TOF and due to the non-advective effect act in opposite directions, which reduces the (unsigned) thermoelectric potential.

To analyse the significance of the flow effect with respect to the induced thermoelectric potential more clearly, in figure 2(c) the induced thermoelectric potential due to the TOF alone is plotted as a function of $\kappa_0 a$ for the same parameters used in (a). It is evident from this plot that the TOF-induced thermoelectric potential increases with increasing $|\zeta|$. The thermoelectric potential in this case shares the same mechanism to the conventional streaming potential due to the pressure driven flow, both being caused by the charge separation due to the flow-induced streaming current. Nevertheless, in contrast to the conventional streaming potential which arrives at the maximum as $\kappa_0 a \gg 1$, the TOF-induced thermoelectric potential reaches its maximum at $\kappa_0 a \approx 2.5$, and asymptotically goes to zero for $\kappa_0 a \to 0$ or $\kappa_0 a \to \infty$. This can be explained as follows: in the limit of $\kappa_0 a \to 0$, as will be discussed later, there is no TOF and therefore no TOF-induced thermoelectric potential; in the limit of $\kappa_0 a \to \infty$, the electrolyte solution in the whole capillary is electroneutral, and thus there is no streaming current to induce electric field. In quantitative, for $\zeta = -125 \text{ mV}$ the maximum value of the TOF-induced thermoelectric potential is equal to ca. $1.1k_B/(\varepsilon z)$, which amounts to ca. 27% of the maximum value of the overall induced thermoelectric potential.

Next, we focus on the third thermoelectric mechanism apart from the flow and Seebeck-type effects. Figure 2(d) displays $\Delta \varphi / \Delta T$ as a function of $\kappa_0 a$ for the hypothetical case
where the flow and Seebeck-type effects are absent. For comparison purpose, the complete solutions in (a) are also included in this plot. Clearly, the induced thermoelectric potential excluding the flow and Seebeck-type effects is quite substantial. It is found that this thermoelectric effect is due to the temperature modified Boltzmann distribution of ions, which gives rise to axial gradients of $n_{\pm}$ in the EDL, $\pm n_{\pm} \Psi \partial_x \ln T$. These induced ion concentration gradients move cations and anions in different directions and result in a current. This leads to charge separation and sets up an electric field such that a current flows in the opposite direction. When reaching the steady state, this effect gives rise to an induced thermoelectric field expressed by the fourth term in the curly bracket of (2.42). As been demonstrated by Dietzel & Hardt (2016), this thermoelectric field is enhanced by confinement, i.e. it attains the maximum $-\zeta/T$ as $\kappa_0 a \to 0$ and vanishes when $\kappa_0 a \to \infty$.

Figure 2(d) reveals that the difference between the thermoelectric potential without the consideration of the flow and Seebeck-type effects and the complete solution becomes more significant as $\zeta$ potential decreases. This new thermoelectric mechanism proposed by Dietzel & Hardt (2016) indeed plays a key role for high $\zeta$ potentials and small $\kappa_0 a$ values. However, we find that in the present case even for $\zeta = -125$ mV and under extreme confinement, the induced thermoelectric potential due to this mechanism deviates from the complete solution by ca. 15%, let alone for lower $\zeta$ potentials and wider capillaries. Thus it is to some extent questionable to omit the thermoelectric effects resulting from other mechanisms, especially for lower $\zeta$ potentials or wider capillaries.

Finally, from figures 2(b, d), one finds that for lower $\zeta$ potentials or sufficiently large $\kappa_0 a$ the Seebeck-type effect dominates, while for highly charged capillaries under confinement the thermoelectric effect due to the temperature modified Boltzmann distribution of ions prevails since the thermoelectric field induced by the latter is proportional to $\zeta$ and that by Seebeck-type effect is (virtually) $\zeta$-independent (see (2.42), note that $F_{cc}$ prevails in the denominator). Besides, the TOF-induced thermoelectric effect must be taken into account for higher $\zeta$ potentials and a contain range of $\kappa_0 a \sim O(1) - O(10)$ depending on the magnitude of $\zeta$.

### 3.2. Effect of electrolytes on thermoelectric potential

In this section, we explore the effect of electrolytes on the induced thermoelectric field. To this end, we computed $\Delta \varphi/\Delta T$ versus $\kappa_0 a$ for three aqueous electrolytes: LiCl, NaCl and KCl. These results are depicted in figures 3–5, where the temperature settings follow §3.1. It is noted that, in our model, there are four variables distinguishing one kind of electrolyte from another, i.e. $\Delta S_T$, $\chi$, $S_T$ and $\Lambda$. The first two characterise the differences in Soret and in diffusion coefficients between cations and anions, respectively. The last two characterise the average values of Soret and of diffusion coefficients between cations and anions, respectively. Thus the effect of electrolytes on the induced thermoelectric field can be reflected by those of the above four variables. In what follows, we focus on the effect of $\Delta S_T$ and $\chi$, since the two remaining variables affect the induced thermoelectric field only marginally (indeed, both of them only occur in the non-dominant terms of the expression for the thermoelectric field, see (2.42)).

We first analyse the effect of $\chi$ on the thermoelectric potential. To this end, we take the aqueous lithium chloride solution as an example and compare the thermoelectric potential for the hypothetical case of $\chi = 0$ with the practical case of $\chi = -0.328$. The comparison results are displayed in figure 3. Traditionally, the equal diffusion coefficient of cations and anions (i.e. $\chi = 0$, which we refer to as identical diffusivity assumption) is widely assumed in studies on thermoelectric potential of confined electrolytes (Dietzel & Hardt 2016, 2017). Nevertheless, in real applications, the diffusivity of cation and of anion are normally different, thus a non-zero $\chi$ would be expected. It is seen from figure 3 that the
Figure 3. Thermoelectric potential per temperature difference $\Delta \phi/\Delta T$ as a function of $\kappa_0 a$ for an aqueous solution of LiCl. Results based on the identical diffusivity assumption are compared to the complete solutions with $\zeta = \pm 25, \pm 75$ and $\pm 125$ mV. The cold side temperature was set to $T_1 = T_0 = 298$K, whereas the other end was set to $T_2 = T_0 + \Delta T$ (here $\Delta T = 25$ K). All data were calculated by integrating (2.37) numerically along axial direction.

The difference in the diffusivities between cation and anion makes a substantial impact on the induced thermoelectric potential, especially when $\zeta$ potential is high. For instance, for $\zeta = -125$ mV and $\kappa_0 a = 100$, it is found that the thermoelectric potential with identical diffusivity assumption deviates from the realistic value even by 20%. Furthermore, for LiCl solutions, the identical diffusivity assumption overestimates (underestimates) the thermoelectric potential if $\zeta < 0$ ($\zeta > 0$). Such behaviour becomes more pronounced as the $\zeta$ potential increases (see figure 3). In addition, this behaviour is also affected by $\kappa_0 a$. The difference between the induced thermoelectric potential with and without the identical diffusivity assumption is strongest at a certain $\kappa_0 a$, and vanishes as $\kappa_0 a$ reduces to zero or increases towards infinity. This can be interpreted as follows: for $\kappa_0 a \to \infty$, the thermoelectric potential approaches the bulk Soret voltage (being zero for LiCl), which is independent on $\chi$. This indicates that the difference between the induced thermoelectric potential with and without the identical diffusivity assumption disappears. For small values of $\kappa_0 a$ the thermoelectric effect is primarily caused by the counterions, thus the difference in the diffusivities of the ions is of no importance.

Yet, for moderate $\kappa_0 a$, the coions get involved and make a substantial impact on the thermoelectric field. Thus we must take into account the effect of non-zero $\chi$. In fact, the chloride ions ($\text{Cl}^-$) diffuse more rapidly than the lithium ions ($\text{Li}^+$). For a fixed intrinsic péclet number (or equivalently, for constant $D_0$), the identical diffusivity assumption artificially erases the difference in the diffusion speeds between cation (here $\text{Li}^+$) and anion (here $\text{Cl}^-$), resulting in cations diffusing more rapidly and anions more slowly. It is noted that in the EDL the lithium ions are the dominant charge carriers for $\zeta < 0$. Thus, in this case, the zero-$\chi$ assumption overpredicts the current caused by the axial gradients of ion concentrations due to the temperature modified Boltzmann distribution of ions (see §3.1), leading to an overestimation of the thermoelectric potential (though the effective conductivity is overestimated as well). As for $\zeta > 0$, the dominant charge carriers turn into chloride ions, which results in an underestimation of the induced thermoelectric potential (see figure 3). Furthermore, we conclude from (2.42) and the preceding discussion that the effect of the difference in the diffusivities between cation and anion on the thermoelectric field is dependent on both the sign and magnitude of $\chi \zeta$. We also deduce that for high
for negatively charged surfaces when a κs solutions ∆ϕ/ϕ/ (at the cold end was set to κ = 25, ±75 and ±125 mV. The temperature at the cold end was set to T1 = T0 = 298K, whereas the other end was T2 = T0 + ΔT (here ΔT = 25 K). All data were calculated by integrating (2.37) numerically along axial direction. (a) ζ < 0. (b) ζ > 0.

ς potentials and a certain range of κa, the larger the χζ (with sign) is, the stronger the thermoelectric field due to the mechanism proposed by Dietzel & Hardt (2016) would be. It is evident from (2.42) that the non-zero χ also affects the Seebeck-type thermoelectric field. However, we do not discuss this trivial effect by noticing that the second term in the first round bracket of (2.42) contributes less to the thermoelectric field (neglecting it yields the χ-independent Seebeck-type effect).

Next, we examine the effect of ΔS on the thermoelectric potential. For this purpose, in figure 4, Δ/ΔT is plotted as a function of κa for different electrolytes and varying ζ. It is clear from figure 4(a) that when ζ < 0, for KCl solutions the behaviours depicted in 3.1 still hold, whereas for LiCl solutions not all of them are satisfied. In this case, for LiCl solutions Δ is always positive, i.e. the thermoelectric field is oriented toward the cold end regardless of the values of κa. This is because the Seebeck-type effect disappears (ΔS = 0) and the thermoelectric field due to the two remaining mechanisms is always orient toward the cold end under the condition of ζ < 0. Figure 4(a) also reveals that for negatively charged surfaces when κa is below the critical value (κa,cr), the induced thermoelectric fields for different solvents are sorted by their intensity as follows: LiCl > KCl > NaCl. Expectedly, the thermoelectric field for KCl/NaCl solutions would switch direction as κa exceeds the critical value. Among them, the induced thermoelectric
field of NaCl solutions reverses at a smaller \( \kappa a \) and becomes the stronger after both of them switch direction. This can be explained as follows: first, a stronger dominant (or a weaker counteracting) effect causes a stronger thermoelectric field. The Seebeck-type effect dominates when \( \kappa a > (\kappa a)_{cr} \), while acts as a counteracting effect if \( \kappa a < (\kappa a)_{cr} \). Second, tabulated data of Agar et al. (1989) listed in table 1 (see Appendix B) suggest that \( \Delta S_{T,NaCl} > \Delta S_{T,KCl}, \) which implies that the Seebeck-type effect is more significant for NaCl solutions. Accordingly, the thermoelectric field of NaCl solutions is weaker than that of KCl solutions for smaller \( \kappa a \) value and it exhibits the opposite behaviour for larger \( \kappa a \) values. To maximise the induced thermoelectric potential per temperature gradient, one would expect to choose appropriate electrolytes and surface materials as well as pH values such that the two non-adveective thermoelectric mechanisms are synergetically combined by rendering the sign of \( \zeta \) and of \( \Delta S_T \) identical (i.e. \( \zeta \Delta S_T > 0 \)). This is supported by figure 4 which reveals that for equal \( |\zeta| \) values and \( \Delta S_T > 0 \), the thermoelectric potential is higher in the case of \( \zeta > 0 \). Obviously, we can exclude effect of \( \chi \), which contributes less to the thermoelectric potential than \( \Delta S_T \) (see figure 3).4.

Finally, to see the effect of electrolytes on the thermoelectric potential more clearly, in figure 5 we display contour plots of \( \Delta \varphi/\Delta T \) as a function of \( \kappa a \) and \( \zeta \) for two typical electrolytes: (a) NaCl and (b) LiCl. As for NaCl solution, figure 5(a) clearly indicates that for positive or lowly negative charge surfaces there should be \( \Delta \varphi < 0 \) regardless of \( \kappa a \) values, while for highly charge surfaces \( \Delta \varphi < 0 \) is only present if \( \kappa a \) exceeds the corresponding \( \zeta \)-dependent critical value. Nevertheless, for an aqueous LiCl \( \Delta \varphi \) is (nearly) symmetric with respect to \( \zeta \) due to vanishing \( \Delta S_T \) (see figure 5b).

3.3. Effects of average temperature on thermoelectric potential

In this section, we analyse the effect of average temperature on the thermoelectric field in detail. For this purpose, we computed the thermoelectric potential versus the cold side temperature \( T_1 \) for NaCl solutions and temperature difference \( \Delta T = 25 \text{ K} \). The results are plotted in figure 6 where the \( \zeta \) potential is set to \( \zeta = -125 \text{ mV} \).

Figure 6(a) shows \( \Delta \varphi/\Delta T \) as a function of \( T_1 \) for \( \kappa a = [0.1, 1, 10] \). It is evident from this plot that, countervintuiely, \( \Delta \varphi/\Delta T \) decreases virtually linearly with \( T_1 \) by \( \sim 10\% \). To explain this, figures 6(b,c) respectively describe the effect of \( T_1 \) on the thermoelectric potential for two hypothetical cases: (i) the effect of the fluid flow is neglected and (ii) only the contribution of the temperature modified Boltzmann distribution of ions is taken into account. Clearly, the thermoelectric potential in these two cases also decrease nearly linearly with \( T_1 \) for fixed \( \kappa a \). Furthermore, the magnitude of the descending slope of the fitting line in the hypothetical case without consideration of the flow effect is larger than that in the other hypothetical case for a given \( \kappa a \).

To interpret, returning our attention to (2.42), which in the absence of the fluid motion can be reduced to

\[
\left( \frac{\partial \varphi}{\partial x} \right)_{(\text{DH})}^{\text{(DH)}} = - \frac{2A}{\kappa a} + \hat{\zeta} B_3 - \hat{\zeta} (1 - A^2) \frac{\zeta}{2} \frac{\partial T}{\partial x} - \frac{\Delta S_T}{2} k_B T \frac{\partial T}{\partial x}.
\]

The first term on the right-hand side of (3.2) stands for the thermoelectric field due to the temperature modified Boltzmann distribution of ions in the EDL (here denoted by \( \partial_x \varphi_S \)), and the second term presents the thermoelectric field resulting from the difference in the Soret coefficients between cation and anion (here denoted by \( \partial_x \varphi_S \)). Before going on, we would like to state here that the equation (10) in the work by Dietzel & Hardt.
are the corresponding linear fits, whose slopes are labelled in these plots. (a) Complete solution. (b) Hypothetical case, where the flow effect is absent. (c) Hypothetical case, where the flow and the Seebeck-type effect are excluded. The reference temperature was set to $T_0 = 298$ K. All data are calculated by integrating (2.37) numerically along the axial direction.

Figure 6. Induced electric potential $\Delta \varphi/\Delta T$ scaled to $k_B/(e \varepsilon)$ versus the cold side temperature $T_1$ for an aqueous solution of NaCl with $\kappa_0 a = [0.1, 1, 10]$ and $\zeta = -125$ mV. The straight lines are the corresponding linear fits, whose slopes are labelled in these plots. (a) Complete solution. (b) Hypothetical case, where the flow effect is absent. (c) Hypothetical case, where the flow and the Seebeck-type effect are excluded. The reference temperature was set to $T_0 = 298$ K. All data are calculated by integrating (2.37) numerically along the axial direction.

(2016) is problematic since they overlooked $\sinh(\Psi) + e^{-\Psi} = \cosh(\Psi)$. Also, (3.2) implies that $\partial_x \varphi_S$ is unaffected by the EDL in the absence of fluid flow.

First, it is evident from (3.2) that $\partial_x \varphi_S \propto \partial_x \ln T$. Assuming $\kappa \approx \kappa_0$ and $\zeta \approx \tilde{\zeta}$, integration of $\partial_x \varphi_S$ across the capillary manifests that the thermoelectric potential due to the temperature modified Boltzmann distribution of ions (here denoted as $\Delta \varphi_S$) is inversely proportional to $T_1$ by noting that $\ln(1 + \Delta T/T_1) \approx \Delta T/T_1$ if $\Delta T/T_1 \ll 1$. Second, denoting $T_L$ as the lowest cold side temperature we focus on here ($\sim 283$ K) and $T_1 = T_L(1 + \delta)$, then $T_L/T_1 = 1 - \delta + O(\delta^2)$. For a narrow $T_1$ range $\delta^2 \ll 1$, the $O(\delta^2)$-term can be neglected, so that $\Delta \varphi_S/\Delta T$ decreases linearly with $T_1$. In fact, when the cold side temperature goes up, the additive concentration gradients of ions resulting from the temperature modified Boltzmann distribution $\pm n_\pm \Psi \partial_x \ln T$ (see (3.1)) declines and thus the corresponding diffusion current decreases, leading to a reduction in $\Delta \varphi_S$. Next, with analogous approach one would expect that the thermoelectric potential due to Seebeck-type effect, $\Delta \varphi_S$, is proportional to the average temperature $T_{\text{avg}} = (2T_1 + \Delta T)/2$, indicating that the magnitude of $\Delta \varphi_S$ increases linearly with $T_1$. This gives rise to larger slopes (without sign) of the fitting lines (see figures 6b,c) when $\Delta \varphi_S$ is additive to $\Delta \varphi_S$ since their signs are opposite.

Finally, in the presence of the fluid transport, there are two effects on the thermoelectric field: on the one hand, the TOF-induced thermostmosic potential decreases linearly with $T_1$ (not shown), which gives rise to a slight increase in the absolute value of the slopes of the fitting lines and thereby makes $\Delta \varphi$ decrease slightly faster. On the other hand, the contribution of the electroosmotic counterflow, described by the second term in the first round bracket of (2.42), leads to a slight decrease in the magnitudes of the slopes of the fitting lines. The overall effect (see figures 6a,b) depends on their relative magnitude.

4. Analysis of fluid flow

So far, the behaviours of the thermoelectric field have been clarified, which paves a way for studying the flow behaviour of the temperature-gradient-induced electrokinetic flow. As mentioned previously, there still exists a fluid transport in a micro- or nanocapillary with an electrolyte solution and an axial temperature gradient even without an externally applied electric field and without an imposed pressure difference. In what follows, we shall discuss the behaviour of this fluid flow. Before going on, we should point out from (2.17)...
and Eq. (2.42) that the flow velocity $u_x$ is proportional to $\Delta T/l$ in the absence of $\Delta p_0$. To measure the relative magnitude of $u_x$ induced by a unit temperature gradient regardless of values of $\zeta$ potentials, we choose $u^* = u_0 \Delta T/T_0$ to normalize the liquid velocity.

4.1. Flow behaviour

In this section, we take a NaCl solution as an example to analyse the flow behaviour and adopt the same temperature settings with §3.1. Figure 7 depicts the (dimensionless) axial velocity profiles $u_x$ obtained from Eq. (2.16) (or equivalently, Eq. (3.3)) for varying $\kappa_0a$ with $\zeta = -15$ mV (a) and $-125$ mV (b). For $\zeta = -15$ mV we find that the current results agree well with those obtained from the DH approximation (i.e. Eq. (2.17), not shown), validating our numerical evaluation.

For lower $\zeta$ potentials (e.g. $\zeta = -15$ mV), as shown in figure 7(a) the flow velocity profiles are analogous to those of the conventional EOF under isothermal conditions, i.e. (roughly) exhibiting a parabolic structure for smaller $\kappa_0a$ values and a plug-like structure for larger values of $\kappa_0a$. Also, with increasing $\kappa_0a$ from 1 to 10, the axial velocity induced by a unit thermal gradient gradually increases. For $\kappa_0a \rightarrow \infty$ the fluid velocity becomes virtually constant beyond the EDL region, as if the fluid slips through capillaries. Next, for higher $\zeta$ potentials the flow behaviour becomes more complicated. When $\zeta$ potential increases to a certain value, the location where the maximum velocity occurs at probably departures from the central axis of the capillary (not shown), resulting in a circular shell surface where the velocity peak develops. If we continue to increase the value of $\zeta$ potential, it is apparent from figure 7(b) that for $\zeta = -125$ mV, a reversal in the velocity direction is present in the region close to the centre of the capillary, while the overall velocity remains along the positive axial direction adjacent to the capillary wall. As one moves away from the capillary wall along the radial direction, the overall velocity profile increases from zero (no-slip) to the largest value first and then drops to zero, afterwards continues to increase in the opposite direction up to the capillary centre. The velocity of this counterflow is a nonmonotonic function of $\kappa_0a$ within 1 to 10, which achieves its maximum at a certain $\kappa_0a$ value and decreases as $\kappa_0a$ increases or decreases. For large $\kappa_0a \gg 1$, this counterflow disappears and the overall flow velocity is always along the positive axial direction (not shown). Another interesting and essential feature captured in figure 7(b) is the presence of a cylindrical shell (here referred to as stationary surface) inside the capillary where the solvent velocity is zero. Potentially, this phenomenon can be used for investigation on the thermophoretic ion motion.

The overall flow can be decomposed as a superimposition of a thermoosmotic flow (TOF, $\partial_x p_0 = E_x = 0$) and a thermal induced electroosmotic flow (EOF, terms in Eq. (2.16) are set to zero except the one multiplied by $E_x$) owing to the superposition rule of the Stokes flow. Figure 8 presents the comparison of the velocity profiles due to the TOF (a,b) with those due to the thermal induced EOF (c,d) for varying $\kappa_0a$. The $\zeta$ potential is set to $\zeta = -15$ mV in (a,c) and $\zeta = -125$ mV in (b,d). It is indicated from figures 8(a,b) that the TOF velocity profile also resembles the well-known conventional EOF under isothermal conditions regardless of the values of $\zeta$ potential, i.e. the velocity profile of the TOF in a capillary is a strong function of $\kappa_0a$. For smaller $\kappa_0a$ values ($\lesssim 3$), the TOF velocity profile displays a strong dependency on the radial position $r/a$, while becomes flat in the central region after a steep increase close to the wall for larger values of $\kappa_0a$ ($\gtrsim 5$). By contrast, the behaviour of the thermal induced EOF would be more complicated. As depicted in figure 8(c), for $\zeta = -15$ mV the thermal induced EOF velocity profiles are analogous to the conventional EOF to some extent, evolving from parabolic to plug-like structure as $\kappa_0a$ increases. However, this (plug-like) flow velocity beyond the EDL region is still a function of $\kappa_0a$, and gradually increases as $\kappa_0a$ is increased from 5 to 50. For significantly
Temperature-gradient-induced electrokinetic flow and thermodielectricity

Figure 7. Temperature-gradient-induced electrokinetic flow velocity profile $u_x$ normalized by $u^*$, for a dilute NaCl solution with $\kappa_0 a = [1, 2, 3, 5, 10, 75, 100]$ and $\Delta T = 25$ K. The $\zeta$ potential is set to either (a) $\zeta = -15$ mV or (b) $\zeta = -125$ mV. All results are obtained from numerical evaluation of (2.16), in which the double layer potentials are obtained by solving (2.8) numerically. In (b), the velocity profiles for $\kappa_0 a = [75, 100]$ are not shown. Moreover, $\kappa a$ is determined at average temperature $T_{avg}$.

Figure 8. Normalized velocity profiles $u_x/u^*$ of the purely thermoosmotic flow ($\partial_x p_0 = E_x = 0$, (a), (b)) and of the thermal induced electroosmotic flow (terms in (2.16) are set to zero except the one multiplied by $E_x$, (c), (d)), for an aqueous solution of NaCl with $\kappa_0 a = [1, 2, 3, 5, 10]$, and $\Delta T = 25$ K. The $\zeta$ potential is set to $\zeta = -15$ mV in (a), (c) and $\zeta = -125$ mV in (b), (d). The results were computed from (2.16), in which the double layer potentials are obtained by solving (2.8) numerically. In (c), the flow profiles for $\kappa_0 a = [50, 75, 100]$ are depicted as well.
large $\kappa_0a$, it no longer changes even though one continues to increase the value of $\kappa_0a$ (i.e. the velocity reaches a plateau). As stated previously, for $\zeta = -15$ mV the thermoelectric field $E_x$ due to the Seebeck-type effect dominates (see §3.1), which together with the excess ion distribution drives the solvent to the hot end. Since in this case $|E_x|$ increases with increasing $\kappa_0a$, the pre-factor of the expression for the thermal induced EOF velocity, given by $-\varepsilon_0\zeta E_x/\eta$, (without sign) also increases with increasing $\kappa_0a$. This behaviour is terminated when $\kappa_0a$ is sufficiently large because in this case the relative variation of $E_x$ with $\kappa_0a$ is negligibly small. Accordingly, there exists a difference between velocity profile of the thermal induced EOF and that of the conventional EOF. Figure 8(d) manifests that for $\zeta = -125$ mV, a thermal induced electroosmotic counterflow appears. In this case, the thermoelectric field is primarily induced by the temperature modified Boltzmann distribution of ions and directed toward the cold end (see §3.1), leading to a thermal induced EOF along the negative axial direction. As $\kappa_0a$ varies from 1 to 10, this counterflow is enhanced first and then reduced (which is expected to disappear for large $\kappa_0a \rightarrow \infty$, not shown). This is because increasing the value of $\kappa_0a$ on the one hand enhances an EOF induced by a unit electric field, on the other hand gives rise to a weaker thermoelectric field if $\kappa_0a < (\kappa_0a)_{cr}$ (see §3.1). Consequently, the combined effect is dependent on their competition, one would see that there exists a finite $\kappa_0a$ (as a function of $\zeta$) such that the electroosmotic counterflow is the strongest and regulating $\kappa_0a$ can lead to a reduction in this counterflow.

The reason for the behaviour of the overall flow lies on the cooperation or competition of the above two forms of flow. For lower $\zeta$ potentials (e.g. $\zeta = -15$ mV), their directions always coincide with each other, jointly driving the fluid to the hot end. For higher $\zeta$ potentials (e.g. $\zeta = -125$ mV) and not sufficiently large $\kappa_0a \sim O(1) - O(10)$, the overall velocity comes from the competition between the TOF velocity along the positive axial direction and the counteracting thermal induced EOF velocity. At the capillary wall, both TOF and thermal induced EOF velocities are zero. Within the EDL region close to the wall, the TOF velocity increases more rapidly than the thermal induced EOF velocity as one moves away from the wall (see figures 8(b,d)), thus the overall velocity in $x$-coordinate direction increases with decreasing $r$. Beyond this region, the TOF velocity becomes constant ahead of the thermal induced EOF velocity, causing a reversal in the velocity direction. In view of that with increasing $\kappa_0a$ the thermal induced EOF velocity increases first and then decreases (see figure 8(f)), thus as $\kappa_0a$ increases this counterflow is enhanced first and then is reduced, finally disappears. In short, for sufficiently large values of $\zeta$ potential a competition between the TOF and thermal induced EOF is found to occur at small $\kappa_0a$, whereas a cooperation at larger $\kappa_0a$.

To analyse the contribution to the TOF due to either the osmotic pressure (the terms multiplied by $1/T$ and $\partial T n/n$) or the dielectric body force (the term proportional to $\gamma$), in figure 9 the individual contributions to the TOF velocity $u_{TOF}$ are plotted for $\zeta = -75$ mV with $\kappa_0a = [1, 2, 3, 5, 10]$. Figure 9(a) displays the TOF velocity profile for the hypothetical case where only the contribution of the osmotic pressure is considered. As shown, this velocity profile is found to follow the qualitative behaviour of the overall TOF. With $\kappa_0a$ increasing from 1 to 10, the fluid velocity close to the wall increases monotonically, while the velocity in the central region increases first and then diminishes. The reason for this peculiar behaviour lies in two counteracting effects: for overlapping EDLs, increasing $\kappa_0a$ leads to a decrease in the driving force, whose magnitude is captured by the term proportional to $2nk BT_0$ in (A.6) (see Appendix A its qualitative behaviour with varying $\kappa_0a$ can be explicitly understood by making use of the DH approximation). Yet, a larger value of $\kappa_0a$ (i.e. the wider capillary) is beneficial for the fluid velocity to reach its bulk value. For $\kappa_0a \rightarrow \infty$, this TOF velocity appears to reach a plateau beyond
the EDL (i.e. the velocity in this region no longer changes, not shown) since the driving force is constrained to the EDL. With help of Eq. (A.5), the osmotic pressure gradient is mainly due to two mechanisms: first, a temperature gradient together with the excess ion concentrations directly induces an osmotic pressure gradient. Second, the temperature modified Boltzmann distribution of ions implies an axial gradient of salt concentration, which also gives rise to an osmotic pressure gradient. The latter primarily emerges due to the thermophoretic ion motion (i.e. intrinsic Soret effect) and a temperature-dependent electrophoretic ion mobility. Unfortunately, a more accurate quantitative description of the realistic TOF due to these mechanisms seems to be a formidable challenge since the dependencies of the Soret coefficients and of the electrophoretic mobilities on temperature and ionic strength are considerably complex (Agar & Turner 1960; Rogacs & Santiago 2013; Lecce et al. 2017), which is beyond the scope of this paper and can be left for future studies.

In addition to inducing a gradient of osmotic pressure, a temperature gradient also gives rise to a dielectric body force due to the temperature-dependent permittivity (Derjaguin et al. 1987). This dielectric body force alone can drive a TOF by acting on the fluid volume element, and corresponding velocity profiles are plotted in figure 9(b). It is seen that for all $\kappa_0a$ in the EDL the local velocity induced by the dielectric body force alone increases dramatically as one moves away from the wall and becomes virtually constant beyond the EDL region. This can be understood by considering the last term in the curly bracket of Eq. (2.17) and noting that $g_2(\xi) \sim -1 + O(\xi^4)$ as $\xi \to 0$ (asymptotic expansion). However, this coordinate-independent constant is not the same for different $\kappa_0a$ values, instead increases with $\kappa_0a$. For sufficiently large $\kappa_0a$ values, it no longer increases even though we continue to increase $\kappa_0a$, so that in this case the velocity profiles for different values of $\kappa_0a$ in the central region are expected to coincide with each other (not shown). This is because the dielectric body force is constrained to the EDL and becomes vanishing small beyond the double layer. As shown in §2 the dielectric body force originates from the temperature dependence of the permittivity, which also can lead to an axial gradient of the osmotic pressure $\partial_x \Pi$ and of the EDL potential $\partial_x \psi$. Nevertheless, the driving force due to $\partial_x \psi$ together with the free charge density $\rho_e$ is cancelled by $\partial_x \Pi$. As a result, the term in Eq. (2.14) proportional
to $\partial_x \psi$ disappears and the osmotic pressure affiliated with the temperature-dependent permittivity is cancelled as well. Consequently, the dielectric body force is the only active contribution to the TOF due to the temperature-dependent permittivity. This is different from the model developed by Dietz and Hardt (2017) because in their model the osmotic pressure gradient disappears along the midplane of the slit channel, which is invalid for overlapping EDL and thus seems to be questionable.

### 4.2. Volumetric flow rate

In this section, we discuss the effect of $\kappa_0 a$ and $\zeta$ on the VFR $\dot{Q}$. For comparison, in figures (10a,d), $\bar{u}_x = \dot{Q}/(\pi a^2)$ scaled to $u^*$ and $u_{\text{HS}}$ are respectively plotted as a function of $\kappa_0 a$ for $\zeta = [-15, -25, -50, -75]$ mV, where $u_{\text{HS}} = \bar{\zeta}^2 u^*$ is the thermal induced HS velocity. The electrolyte and temperature settings also follow (3.1). Note that the area-averaged velocity $\bar{u}_x$ is proportional to the inverse of the capillary length $l$. Thus ratios $\bar{u}_x/u^*$ and $\bar{u}_x/u_{\text{HS}}$ can measure the relative magnitude of the VFRs induced by a unit temperature gradient for varying $\kappa_0 a$. The former also can compare the VFRs for different $\zeta$ potentials. For the lowest $\zeta$ potential, the overall VFRs calculated from (2.19) and predicted by (2.20) directly match perfectly, validating our numerical evaluations.

It reveals from figures (10a,d) that for $a \ll \kappa_0^{-1}$ (i.e. $\kappa_0 a \to 0$), the overall VFR goes to zero. Indeed, this can be explained as follows: first, $\kappa_0 a \to 0$ gives rise to a uniform excess ion distribution across the capillary and an insignificant local modification of the EDL thickness (Dietz and Hardt 2017). Second, the fluid velocity is unable to develop from the no-slip boundary to a finite value for an ultraconfined capillary (i.e. $a \ll \kappa_0^{-1}$). Accordingly, the temperature gradient-induced electrokinetic flow vanishes. By contrast, for $a \gg \kappa_0^{-1}$ (i.e. $\kappa_0 a \to \infty$) the intensity of this flow not longer be enhanced or weakened since the driving forces are constrained to the EDL region. Accordingly, a saturated effect is observed as $\kappa_0 a \to \infty$ after a steep increase within $1 \lesssim \kappa_0 a \lesssim 5$.

Also, figure (10a) reveals that an increase in $|\zeta|$ from 15 mV to 75 mV causes a rise in $\dot{Q}/(\pi a^2 u^*)$. By contrast, the ratio $\dot{Q}/(\pi a^2 u_{\text{HS}})$ decreases with increasing $|\zeta|$ if $\kappa_0 a \gtrsim 0.5$ (see figure (10f)). This still holds for lower $\zeta$ range (e.g. $|\zeta| \lesssim 25$ mV) in the case of $\kappa_0 a \lesssim 0.5$, whereas in this case for higher $\zeta$ range (e.g. 50 mV $|\zeta| \lesssim 75$ mV) all curves for $\dot{Q}/(\pi a^2 u_{\text{HS}})$ nearly coincide with each other (see the inset in figure (10d)). In what follows, we account for this behaviour by isolating the VFRs due to the TOF (being denoted by $Q_{\text{TOF}}$) from those due to the thermal induced EOF (being denoted by $Q_{\text{EOF}}$). The isolated contributions of them are respectively plotted in figures (10b,e) and (c,f) for the same parameters utilized in (a). It is evident from figure (10e) that $\zeta$ potential has less effect on the magnitude of $Q_{\text{TOF}}/(\pi a^2 u_{\text{HS}})$, demonstrating that the VFR caused by the TOF is (approximately) proportional to $u_{\text{HS}}$. Then, $Q_{\text{TOF}}/(\pi a^2 u^*) \propto \bar{\zeta}^2$ and thereby $Q_{\text{TOF}}/(\pi a^2 u^*)$ significantly increases with increasing $|\zeta|$ (see figure (10b)). On the one hand, for $\kappa_0 a \to 0$ the VFR due to the TOF approaches zero because a vanishing velocity still holds. On the other hand, in the limit of $\kappa_0 a \to \infty$, one has $F_\alpha \to 3/2$. In this case, $Q_{\text{TOF}}$ reaches the maximum saturated value (under the DH approximation):

$$
\left. \frac{\dot{Q}_{\text{TOF}}}{\pi a^2} \right|_{\kappa_0 a \to \infty} = \frac{\epsilon \bar{\zeta}^2}{8\eta} \frac{\partial T}{\partial x} \left( \frac{1}{T} - \frac{\partial_T \epsilon}{\epsilon} - \frac{\partial_T \eta}{\eta} \right),
$$

which is similar to the expression for the VFR in a slit channel (see Dietz and Hardt 2017), and makes sense for $\kappa_0 a \to \infty$ since in this case a capillary channel can be regarded as a slit channel. In this case for all $\zeta$ and $\Delta T$, (4.1) is equal to ca. $0.4 u_{\text{HS}}$, which is in agreement with figure (10e). Equivalently, (4.1) also stands for the thermoosmotic...
Figure 10. Volumetric flow rate $\dot{Q}$ as a function of dimensionless Debye parameter $\kappa_0 a$ for an aqueous solution of NaCl with $\zeta = [-15, -25, -50, -75]$ mV. The $\dot{Q}$ is scaled to $\pi a^2 u^*$ in (a-c) and to $\pi a^2 u_{HS}$ in (d-f), respectively. For the smallest $\zeta$ potential, the results predicted by the Debye-Hückel approximation (DH) are compared to those calculated from (2.19), and the EDL potential is computed by solving the Poisson-Boltzmann (PB) equation numerically. (a,d) Total effect, where the contributions of thermoosmotically driven flow (TOF) and thermal induced electroosmotic flow (EOF) are taken into consideration. For $\kappa_0 a$ ranging from 0.01 to 0.5, results of (d) are enlarged in the inset. (b,e) Isolated contribution of the TOF, where the thermal induced EOF is excluded ($E_x = 0$). (c,f) Isolated contribution of the thermal induced EOF, where the TOF is absent. The temperature at the cold end is set to $T_1 = T_0 = 298$ K, whereas the other end is $T_2 = T_0 + \Delta T$ (here $\Delta T = 25$ K). The legend depicted in (a) is valid in (b-f) as well.

In what follows, we perform a detailed analysis of the VFR caused by the thermal induced EOF. First, as captured in figures 10(c,f), for all $\zeta$ potentials the VFR due to the thermal induced EOF also goes to zero as $\kappa_0 a \to 0$ even though in this case for higher $\zeta$ potentials the thermoelectric field may reach its peak value (see §3.1). Second, it is evident from figure 10(c) that for small values of $\zeta$ potential, $\dot{Q}_{\text{EOF}}/(\pi a^2 u^*)$ increases with increasing $\kappa_0 a$ until $\dot{Q}_{\text{EOF}}/(\pi a^2)$ saturates to

$$\left.\frac{\dot{Q}_{\text{EOF}}^{(DH)}}{\pi a^2}\right|_{\kappa_0 a \to \infty} = -\frac{\epsilon \zeta \Delta S_T}{2\eta} \frac{k_B T}{e z} \frac{\partial T}{\partial x} \approx -\frac{\epsilon \zeta}{2\eta T_0} \frac{1}{e z} \frac{\Delta Q}{\partial x},$$

which indicates that in this case $\dot{Q}_{\text{EOF}}$ is proportional to $\zeta$. This also holds for higher $\zeta$ potentials if $\kappa_0 a \to \infty$. It follows that when $\kappa_0 a \to \infty$ an increase in $|\zeta|$ causes a rise in $\dot{Q}_{\text{EOF}}/(\pi a^2 u^*)$, while leads to a reduction in $\dot{Q}_{\text{EOF}}/(\pi a^2 u_{HS})$. Third, in contrast to the VFR caused by the purely TOF, for higher $\zeta$ potentials it is seen from figures 10(c,f) that with increasing $\kappa_0 a$, $\dot{Q}_{\text{EOF}}$ increases in the inverse direction first and then decreases, later
The cold side temperature end is set to $T_1 - T_0 = 298$ K, whereas the hot end temperature is $T_2 = T_0 + \Delta T$ (here $\Delta T = 25$ K is utilized).

Yet, for an EOF induced by a fixed electric field, the flow is expected to increase as $\zeta$ increases with $\kappa a$ does not exceed ($\kappa a)_{cr}$ defined in (3.1). Thus in this case using (2.20) yields $\dot{Q}_{EOF} \propto \zeta^2$. Also, for $0.5 \lesssim \kappa a \lesssim 5$ the TOF-induced thermoelectric field plays a role, which is approximately proportional to $\zeta^\nu$ (see (2.22), setting $F_{cc} = 0$ yields $\nu = 1$, whereas setting $F_1 = 0$ results in $\nu = 3$, thus $1 < \nu < 3$). Therefore, the VFR due to the TOF-induced thermoelectric field alone is approximately proportional to $\zeta^\nu$ (here $2 < \nu < 4$). On the whole, the VFR caused by the purely thermal induced EOF is proportional to $\zeta^\nu$ (reduced), where $\nu$ is determined by $\zeta$ and $\kappa a$ and falls in $1 \lesssim \nu < 3$ (although a coarse analysis showing $\nu < 4$, realistic calculations indicate $\nu < 3$). It is distinctly different from the VFR due to the conventional EOF, which is proportional to $\zeta$. This can account for the behaviour that for larger values of $\zeta$ potential (e.g. $-50$ mV $\lesssim \zeta \lesssim -75$ mV) and narrow capillary (e.g. $\kappa a \lesssim 0.5$) all curves for $\dot{Q}_{EOF}/(\pi a^2 u_{HS})$ overlap. Also, if $0.5 \lesssim \kappa a \lesssim 5$ for higher $\zeta$ potentials the magnitude of $\dot{Q}_{EOF}/(\pi a^2 u_{HS})$ increases with $|\zeta|$, since in this case $\dot{Q}_{EOF} \propto \zeta^\nu$, where $2 \lesssim \nu < 3$. Then we can account for the behaviour depicted in figures (10) (a,d), which originate from the competition or cooperation of the TOF and the thermal induced EOF.

To further understand the behaviour of the VFR, in figure (11) we display contour plots of $\dot{Q}$ as a function of $\kappa a$ and $\zeta$ for different aqueous electrolytes: (a) NaCl and (b) LiCl. The temperature settings are the same with figure (10). It is evident from (11) (a) that for an aqueous NaCl, altering the polarity of surface charge may lead, in general, to a reverse in the VFR, i.e. the VFR may change from $\dot{Q} > 0$ to $\dot{Q} < 0$ as $\zeta$ varies from $-200$ mV to $200$ mV ($-8 \lesssim e\zeta/(k_B T_0) \lesssim 8$). This can be understood by considering the direction and relative magnitude of the thermal induced EOF and the TOF. For an aqueous solution of NaCl (there should be $\Delta S_T > 0$), if $\zeta > 0$ the thermoelectric field due to two non-adveotive effects (see (3.1)) cooperate with each other, while cancel each other if $\zeta < 0$ (see (3.2)). Consequently, in the case of $\zeta > 0$ the overall thermoelectric field is stronger compared with the case of $\zeta < 0$ and thus the electroosmotic counterflow probably becomes stronger than the TOF (it should be noted that the electric body force does not...
switch direction since both the polarity of the interfacial charge and the direction of the induced thermoelectric field change), causing a reverse in the sign of $\dot{Q}$. Nevertheless, this does not hold for the following two cases: (i) high negative surface charge and $\kappa_0 a \sim O(1)$; (ii) moderate positive surface charge and very large $\kappa_0 a$ values (i.e. $\kappa_0 a \gg 1$). In case (i), the VFR due to the thermal induced electroosmotic counterflow perhaps excesses that due to the TOF, leading to a domain where $\dot{Q} < 0$. With increasing $|\zeta|$, this domain is gradually extended to a broader $\kappa_0 a$ range. This can be explained by figure 10(c), for higher $\zeta$ potentials $\dot{Q}_{EOF}$ dominates within a comparatively broader range of $\kappa_0 a$. As for case (ii), $\dot{Q} > 0$ can be explained by considering (4.1) and (4.2). Since in this case the VFR caused by the TOF (described by (4.1), which always has a positive sign) prevails, the overall VFR is oriented toward the hot end. Also, this domain of $\dot{Q} > 0$ seems to be present within much wider range of $\zeta$ potential. This is because if $\kappa_0 a \to \infty$ there should be $\dot{Q}_{TOF} > \dot{Q}_{EOF}$ for the chosen aqueous electrolyte. By contrast, for an aqueous LiCl $\dot{Q} < 0$ occurs at comparatively small $\kappa_0 a$, while $\dot{Q} > 0$ is present at relatively large $\kappa_0 a$ (see figure 11b). The reason for this behaviour lies in the disappearance of the Seebeck-type thermoelectric effect (due to $\Delta S_T = 0$). Indeed, for an aqueous LiCl if $\zeta < 0$ and smaller values of $\kappa_0 a$, the thermoelectric field becomes large enough to cause a stronger counteracting EOF, which can cancel the TOF and thus $\dot{Q} < 0$. In addition, for $0 < \varepsilon z \zeta/(k_B T_0) \lesssim 2$ and $\kappa_0 a = O(1) - 100$, the thermoelectric field becomes weaker compared with the case of $\Delta S_T > 0$, giving rise to a weaker thermal induced EOF and thus $\dot{Q} > 0$.

5. Conclusions and remarks

We have derived a semi-analytical model for the temperature-gradient-induced electrokinetic flow and the thermoelectric field of an electrolyte solution in a charged capillary with lubrication approximation. In analogy to the work by Dietzel & Hardt (2017), our model takes into account not only the temperature dependencies of bulk properties such as the permittivity, viscosity, diffusion coefficients and electrophoretic ion mobilities, but also the thermophoretic ion motion (i.e. intrinsic Soret effect or ion thermodiffusion), while contributions due to the variances of the density, heat capacity and heat conductivity of solvent with temperature are demonstrated to be negligible small. Then, the relative significance of each effect on the induced thermoelectric field and flow behaviour are analysed as either $\zeta$ potential or (dimensionless) nominal Debye parameter $\kappa_0 a$ varies. Moreover, the influences of electrolytes on the induced thermoelectric field and the fluid flow are discussed as well. The main conclusions are summarised as follows:

To begin with, the induced thermoelectric field is found to be a superimposition of three contributions: the first is due to the difference in the Soret coefficients between cation and anion (i.e. Seebeck-type effect); the second is due to the temperature modified Boltzmann distribution of ions, which implies polarity-dependent axial gradient of ion concentrations and trigger a diffusive current; and the last is caused by the thermoosmotic flow. For lowly charged surfaces and relatively thin double layer (i.e. the ratio of capillary radius $a$ to the nominal Debye screening length $\kappa_0^{-1}$, $\kappa_0 a$, is sufficiently large) the Seebeck-type effect has an essential effect. By contrast, the contribution of the temperature modified Boltzmann distribution of the ions becomes the dominant for higher $\zeta$ potentials and very small $\kappa_0 a$. The thermoosmotic flow (TOF) can also induce an electric field by causing a streaming current and charge separation. This effect is similar to the well-known streaming potential to some extent, however, reaching the maximum thermoelectric field at ca. $\kappa_0 a = 2.5$. In addition, the TOF-induced thermoelectric field increases with increasing $|\zeta|$.

The thermoelectric field is also shown to vary from electrolyte to electrolyte. In our
model, there exist four variables distinguishing one kind of electrolyte from another: the difference in Soret coefficients between cation and anion $\Delta S_T$, the normalized difference in the diffusivities between cation and anion $\chi$, the intrinsic Péclet number $\Lambda$ and the average Soret coefficient of cation and anion $S_T$. Though the temperature dependencies of the diffusivities have no effect on the thermoelectric field, the difference in the diffusivities of the ions does play a role. In particular, for higher $\zeta$ potentials and a certain $\kappa_0 a$ range $\chi$ makes a more pronounced impact on the thermoelectric field. From the microscopic viewpoint, we pointed out that $\chi$ can enhance or weaken the induced thermoelectric field depending on both the sign and magnitude of $\chi \zeta$. Finally, it follows that different electrolytes would induce different Seebeck-type thermoelectric fields since their $\Delta S_T$ differ. In addition, we demonstrated that the thermoelectric field due to the Seebeck-type effect and that due to the temperature modified Boltzmann distribution of the ions probably cooperate with or compensate each other depending on the sign of $\zeta \Delta S_T$. Furthermore, our model indicates the thermoelectric potential would be affected by the average temperature for the same temperature difference. Counterintuitively, an increase in the average temperature causes a reduction in the thermoelectric potential. This is because, expect the Seebeck-type effect, the induced thermoelectric field due to another two mechanisms decrease as the average temperature increases.

Next, we pointed out that the temperature-gradient-induced electrokinetic flow can be decomposed as the superimposition of a purely TOF and a thermal induced EOF. The $\zeta$ potential and the nominal Debye parameter $\kappa_0 a$ have essential effects on the total solvent flow. Indeed, the overall VFR appears to be a non-trivial function of $\kappa_0 a$ and $\zeta$. For a narrow capillary (i.e. smaller $\kappa_0 a$) and all $\zeta$ potentials, both the purely TOF and the thermal induced EOF vanish, leading to a vanishing overall VFR. As $\kappa_0 a$ increases, there exist two situations: first, for higher $\zeta$ potentials the thermal induced EOF switches direction at a certain $\kappa_0 a$ since the thermoelectric field reverses. Second, for smaller values of $\zeta$ potential the thermal induced EOF is always directed toward the hot end. By contrast, the TOF always drives the fluid to the hot end regardless of $\zeta$ potentials and $\kappa_0 a$ as long as $S_T > 0$. Therefore, these two kinds of fluid transports may cooperate with or counteract each other, which depends on the $\zeta$ potential and $\kappa_0 a$. Consider the TOF alone, two comparable origins are of importance, i.e. the osmotic pressure gradient and the dielectric body force. Also, the dielectric body force is the only active effect of the temperature-dependent permittivity. In quantitative, the TOF velocity and the VFR induced by the purely TOF are proportional to $\zeta^2$. Furthermore, it should be noted that the thermoelectric field due to the Seebeck-type effect, the temperature modified Boltzmann distribution of the ions and the thermosmotically driven flow are (approximately) proportional to $\zeta^0$, $\zeta^1$ and $\zeta^\nu$ ($1 < \nu < 3$), respectively. Thus thermal induced EOF velocity and the corresponding VFR arising from the above three effects are (approximately) proportional to $\zeta^1$, $\zeta^2$ and $\zeta^{1+\nu}$ ($1 < \nu < 3$), respectively. On the whole, the VFR caused by the thermal induced EOF is proportional to $\zeta^\nu$, where $\nu$ primarily depends on $\zeta$ and $\kappa_0 a$. This is distinctly different from the conventional EOF. Finally, for different electrolytes, the predicted VFR might be quite different mainly because their $\Delta S_T$ differ.

In the realm of fundamental research, the present results are beneficial to understanding different sources and relative significance of each effect of the fluid flow and induced thermoelectric field due to the non-isothermal electrokinetic transport through micro- or nanocapillary tubes. For technological applications, the present finding is of importance in the design of novel waste-heat recovery devices. For further work, the contributions of van der Waals force and water structure (Derjaguin 1980; Gallo et al. 2011; Bregulla et al. 2016; Barragán & Kjelstrup 2017) can be included to develop a more refined model so
as to obtain more accurate predictions and to explain the fluid transport phenomena in electroneutral systems. Furthermore, the present work can be extended to situations where the multiple of thermodynamic forces get involved or the Péclet number is larger than unity.

**Appendix A. Derivation of axial velocity profile**

Here, we shall show the derivation procedure of the axial velocity. First of all, for binary symmetric $z : z$ electrolyte, making use of the leading-term of $(2.7)$, one has

$$
\frac{\varepsilon}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) \approx -ez(n_+ - n_-). \tag{A 1}
$$

Additionally, from the leading-term of $(2.3)$, it follows that

$$
ez n_i D_i \frac{\partial \psi}{\partial r} + D_i \frac{\partial n_i}{\partial r} = 0. \tag{A 2}
$$

Substituting $(A 1)$ and $(A 2)$ into $(2.13)$, after rearrangement, we then have

$$
\frac{\partial}{\partial r} \left[ p - k_B T(n_+ + n_-) \right] = 0, \tag{A 3}
$$

which indicates the term in the square brackets of $(A 3)$ is independent of the $r$ coordinate and is a constant for a fixed $x$ coordinate, its value equals the pressure in the bulk electrolyte solution, i.e. $p_0 - k_B T \sum_i n_{i,\infty}$ (Masliyah & Bhattacharjee 2006), hence one gains

$$
p = p_0 + k_B T(\bar{n}_+ + \bar{n}_-), \tag{A 4}
$$

where $\bar{n}_i = n_i - n_{i,\infty}$ ($i = \pm$) denote the so-called excess ion concentration. Thus the derivative of pressure, $p$, with respect to $x$ is

$$
\frac{\partial p}{\partial x} = \frac{\partial p_0}{\partial x} + k_B T \left( n_+ \frac{\partial \ln n_+}{\partial x} + n_- \frac{\partial \ln n_-}{\partial x} - 2n \frac{\partial \ln n}{\partial x} \right) + 2k_B (\bar{n}_+ + \bar{n}_-) \frac{\partial T}{\partial x}. \tag{A 5}
$$

Substituting the modified Boltzmann distribution of each ionic species $(2.4)$ into $(A 5)$, and noting that $\bar{n}_+ + \bar{n}_- = 2n[cosh(\Psi) - 1]$ and $\bar{n}_+ - \bar{n}_- = -2n \sinh(\Psi)$, $(A 5)$ can be transformed to

$$
\frac{\partial p}{\partial x} = \frac{\partial p_0}{\partial x} + 2nk_B T_0 \left\{ [cosh(\Psi) - 1] \left( 1 + T \frac{\partial T}{n} \right) - \Psi \sinh(\Psi) \right\} \frac{1}{T_0} \frac{\partial T}{\partial x}
$$

$$
- \varepsilon z(n_+ - n_-) \frac{\partial \psi}{\partial x}. \tag{A 6}
$$

As will be shown later, the last term on the right-hand side of $(A 6)$ and the second term on the right-hand side of $(2.14)$ might counteract each other. Inserting $(A 4)$ into $(2.14)$ and rearranging, one derives

$$
\frac{1}{r} \frac{\partial}{\partial r} \left( \eta \frac{\partial u_x}{\partial r} \right) = \frac{\partial p_0}{\partial x} + \frac{\varepsilon}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) E_x
$$

$$
+ 2nk_B T_0 \left\{ [cosh(\Psi) - 1] \left( 1 + T \frac{\partial T}{n} \right) - \Psi \sinh(\Psi) \right\} \frac{1}{T_0} \frac{\partial T}{\partial x} + \frac{\gamma \varepsilon}{2} \left( \frac{\partial \psi}{\partial r} \right)^2 \frac{\partial T}{\partial x}. \tag{A 7}
$$
It is evident that the four terms on the right-hand side of (A 7) respectively refer to the contributions of the externally applied pressure gradient, the externally applied or induced electric field, the osmotic pressure gradient and the dielectric body force. Multiplying (A 7) by \( r \), and integrating on both sides once, then dividing by \( r \) and implementing another integral, at the same time, combining the corresponding boundary conditions, one obtains (2.16). Albeit the fact that the frictionless flow in some specific nanotubes was reported (Majumder et al. 2005; Holt et al. 2006), implying invalidation of no-slip boundary, in the course of our derivation the assumption of zero relative liquid-solid velocity was employed, which is valid for a multiple of realistic micro- or nanocapillaries that the slip length can be neglected.

Appendix B. Details of numerical approaches

To capture the induced thermoelectric field and axial velocity profiles, one needs the information of electrostatic potential distribution firstly. However, solving the ordinary differential equation (2.8) is the prerequisite for the EDL potential. With the dimensionless group defined in the main text, (2.8) can be rewritten as

\[
\frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left( \hat{r} \frac{\partial \Psi}{\partial \hat{r}} \right) = (\kappa a)^2 \sinh(\Psi),
\]

subject to the following dimensionless boundary conditions

\[
\Psi|_{\hat{r}=1} = \hat{\zeta}, \quad \left. \frac{\partial \Psi}{\partial \hat{r}} \right|_{\hat{r}=0} = 0.
\]

Actually, one can divide the continuum solving interval into a series of discrete subintervals, then (B 1) is solved numerically for discrete values of \( \kappa a \) in the endpoint of each subinterval along \( x \) direction. For fixed \( \kappa a \), the two points boundary value problem given by (B 1) together with the symmetric boundary at \( \hat{r} = 0 \) (in practice, we adopted infinitesimal value, for instance, \( 1 \times 10^{-8} \), instead of zero so as to maintain non-zero divisor, an analogous manipulation was used to avoid vanishing denominator when calculating velocity profile based on (2.16)) and (B 2b), was solved by using BVP4C-function carried out in Matlab (Version 9.2.0.538062, R2017a). To validate the numerical results, we compare the numerical and analytical solutions for lower \( \zeta \) potential (e.g. \( e \zeta (k_B T_0) = 0.1 \)) and for several selected \( \kappa a \). The results indicated not only the numerical solution of the dimensionless EDL potential but of its derivative with respect to \( \hat{r} \) achieve an excellent agreement with the DH approximation. To obtain the local EDL potential along axial direction, we made use of (2.9) to calculate local value of \( \kappa a \) based on \( \kappa_0 a \) and local temperature.

Furthermore, the integrals \( B_i \) (\( i = 1, 2, 3 \)) were calculated using INTEGRAL-function, while the rest discrete numerical integrals, including \( 2.25 \), \( 2.26 \), \( 2.31 \) and \( 2.32 \), were evaluated by using TRAPZ- or CUMTRAPZ-function. Finally, the local induced thermoelectric field given by (2.37) or (2.42) was integrated numerically across the capillary channel to access the induced thermoelectric potential. And the numerical evaluations of these integrals were implemented by TRAPZ-function as well. For sake of numerical evaluation, (2.37) can be explicitly given as

\[
\frac{e \zeta}{k_B} \frac{E_x}{\partial_x T} = \left\{ \int_0^1 [\cosh(\Psi) - \chi \sinh(\Psi)] \hat{r} d\hat{r} + \frac{\epsilon}{\epsilon_0} \frac{T}{T_0} \frac{1}{(\kappa a)^2} \int_0^1 \hat{r} \left( \frac{\partial \Psi}{\partial \hat{r}} \right)^2 d\hat{r} \right\}^{-1}
\]
of integration, we then see that (2.37) can be further simplified as

\[
\frac{\epsilon z E_x}{k_B \partial_x T} = \left\{ \int_0^1 \Psi [\cosh(\Psi) - \chi \sinh(\Psi)] \, \hat{r} \, d\hat{r} + \frac{\Delta S_T T}{2} \int_0^1 \left[ \cosh(\Psi) - \chi \sinh(\Psi) \right] \, \hat{r} \, d\hat{r} \right\}^{-1} 
\]

\[
\times \left\{ \int_0^1 \Psi [\cosh(\Psi) - \chi \sinh(\Psi)] \, \hat{r} \, d\hat{r} + \frac{\Delta S_T T}{2} \int_0^1 \left[ \cosh(\Psi) - \chi \sinh(\Psi) \right] \, \hat{r} \, d\hat{r} \right\} 
\]

\[
- \frac{\epsilon}{\varepsilon_0} \frac{T}{T_0} \int_0^1 \hat{r} \left[ \cosh(\Psi) - 1 - \Psi \sinh(\Psi) \right] \, d\hat{r} 
\]

\[
- \frac{\epsilon}{\varepsilon_0} \frac{T}{T_0} \frac{\partial n}{\partial T} \int_0^1 \hat{r} \left( \frac{\partial \Psi}{\partial \hat{r}} \right)^2 \, d\hat{r} 
\]

\[
- \frac{\epsilon}{\varepsilon_0} \frac{T}{T_0} \frac{\gamma_T}{(\kappa a)^2} \int_0^1 \hat{r} \left( \frac{\partial \Psi}{\partial \hat{r}} \right)^2 \left( \Psi - \zeta \right) \, d\hat{r} 
\].

Interestingly, following the work by Peters et al. (2016), with interchanging the order of integration, we then see that (2.37) can be further simplified as

\[
\frac{\epsilon z E_x}{k_B \partial_x T} = \left\{ \int_0^1 \Psi [\cosh(\Psi) - \chi \sinh(\Psi)] \, \hat{r} \, d\hat{r} + \frac{\epsilon T}{\varepsilon_0 T_0} \frac{1}{(\kappa a)^2} \int_0^1 \hat{r} \left( \frac{\partial \Psi}{\partial \hat{r}} \right)^2 \, d\hat{r} \right\}^{-1} 
\]

\[
\times \left\{ \int_0^1 \Psi [\cosh(\Psi) - \chi \sinh(\Psi)] \, \hat{r} \, d\hat{r} + \frac{\Delta S_T T}{2} \int_0^1 \left[ \cosh(\Psi) - \chi \sinh(\Psi) \right] \, \hat{r} \, d\hat{r} \right\} 
\]

\[
- \frac{\epsilon}{\varepsilon_0} \frac{T}{T_0} \int_0^1 \hat{r} \left[ \cosh(\Psi) - 1 - \Psi \sinh(\Psi) \right] \, d\hat{r} 
\]

\[
- \frac{\epsilon}{\varepsilon_0} \frac{T}{T_0} \frac{\partial n}{\partial T} \int_0^1 \hat{r} \left( \cosh(\Psi) - 1 \right) \left( \Psi - \zeta \right) \, d\hat{r} 
\]

\[
- \frac{\epsilon}{\varepsilon_0} \frac{T}{T_0} \frac{\gamma_T}{(\kappa a)^2} \int_0^1 \hat{r} \left( \frac{\partial \Psi}{\partial \hat{r}} \right)^2 \left( \Psi - \zeta \right) \, d\hat{r} 
\].

All calculations of (2.37) in main text are carried out by computing indeed (B.4), unless otherwise stated.

To implement the above calculations, the values of diffusion coefficient and heat of transport for single ion are requisite, which are summarised in the first four columns of table 1. In the last six columns, some derived values used in this paper based on the preceding data are listed. All data tabulated refer to infinite dilute aqueous solution at 25 °C (~298 K). Albeit the salt concentration in the present study being set to 0.01 mM, the use of solute properties at infinite dilution does not cause a considerable difference, in particular, ΔST derives from the value at 0.01 M solutions (Snowdon & Turner 1960).
by not more than 1% except LiCl, which shows a departure by less than 4%, let alone a 0.01 mM aqueous solution.

The calculation of the flow velocity for arbitrary \( \zeta \) potential, expressed by \( (2.16) \), can be implemented by an analogous approach. The induced electric field and the EDL potential obtained from the preceding numerical evaluation were used in this process. For simplicity, the velocity expression \( (2.16) \) can be rewritten as

\[
 u_x = \frac{a^2(1 - \hat{r}^2)}{4 \eta} \frac{\partial p_0}{\partial x} - \frac{\epsilon \zeta E_x}{\eta} \left( 1 - \frac{\Psi}{\zeta} \right) \\
- \frac{\epsilon (\kappa a)^2}{\eta} \left( \frac{k_B T}{e z} \right)^2 \frac{\partial T}{\partial x} \left\{ \frac{1}{T} \int_1^{\hat{r}} \frac{1}{\tilde{r}} \int_0^{\tilde{r}} \tilde{r}[\Psi \sinh(\Psi) - \cosh(\Psi) + 1] d\tilde{r} \right\} d\hat{r} \\
- \frac{\partial T n}{n} \int_1^{\hat{r}} \frac{1}{\tilde{r}} \int_0^{\tilde{r}} \tilde{r}[\cosh(\Psi) - 1] d\tilde{r} d\hat{r} - \frac{\gamma}{2(\kappa a)^2} \int_0^{\hat{r}} \frac{1}{\tilde{r}} \int_0^{\tilde{r}} \frac{\partial (\frac{\Psi}{\partial \tilde{r}})}{\partial r} d\tilde{r} d\hat{r} \right\} \right . \}
\]

In the present work, a grid independence study had been carried out and showed that a mesh size of 500 grid points in \( r \) direction with a element ratio of 100 in reverse \( r \) direction, and 250 grid points in \( x \) direction (which is valid for \( \kappa_0 a \lesssim 100 \) and \( \Delta T \lesssim 25 \) \( K \), whereas for larger \( \kappa_0 a \) and \( \Delta T \) more refined grids should be used) can capture robust results, and the relative tolerance was set to \( 10^{-6} \).

REFERENCES

Agar, J. N., Mou, C. Y. & Lin, J. L. 1989 Single-ion heat of transport in electrolyte solutions: a hydrodynamic theory. J. Phys. Chem. 93 (5), 2079–2082.

Agar, J. N. & Turner, J. C. R. 1960 Thermal diffusion in solutions of electrolytes. Proc. R. Soc. Lond. A 255, 307–330.

Anderson, J. L. 1989 Colloid transport by interfacial forces. Annu. Rev. Fluid Mech. 21 (1), 61–99.

Baldessari, F. 2008 Electrokinetics in nanochannels part i. electric double layer overlap and channel-to-well equilibrium. J. Colloid Interface Sci. 325 (2), 526–538.

Barragán, V. & Kjelstrup, S. 2017 Thermo-osmosis in membrane systems: a review. J. Non-Equilib. Thermodyn. 42 (3), 217–236.

Behrens, S. H. & Grier, D. G. 2001 The charge of glass and silica surfaces. J. Chem. Phys. 115 (14), 6716–6721.

Benneker, A. M., Wendt, H. D., Lammertink, R. G. H. & Wood, J. A. 2017 Influence of temperature gradients on charge transport in asymmetric nanochannels. Phys. Chem. Chem. Phys. 19 (41), 28232–28238.

Braun, D. & Libchaber, A. 2002 Trapping of dna by thermophoretic depletion and convection. Phys. Rev. Lett. 89, 188103.

Bregulla, A. P., Würger, A., Günter, K., Mertig, M. & Cichos, F. 2016 Thermo-osmotic flow in thin films. Phys. Rev. Lett. 116, 188303.

Caldwell, D. R. & Eide, S. A. 1981 Soret coefficient and isothermal diffusivity of aqueous solutions of five principal salt constituents of seawater. Deep Sea Research A 28 (12), 1605–1618.

Carr, C. W. & Sollner, K. 1962 New experiments on thermoosmosis. J. Electrochem. Soc. 109 (7), 616–622.

Dariel, M. S. & Kedem, O. 1975 Thermoosmosis in semipermeable membranes. J. Phys. Chem. 79 (4), 336–342.

Derjaguin, B. V. 1980 Structural and thermodynamic peculiarities of the boundary layers of liquids. Pure Appl. Chem. 52 (5), 1163–1178.

Derjaguin, B. V., Churaev, N. V. & Muller, V. M. 1987 Surface Forces. New York: Plenum.
Temperature-gradient-induced electrokinetic flow and thermoelectricity

DERJAGUIN, B. V. & SIDORENKOV, G. P. 1941 On thermo-osmosis of liquid in porous glass. CR Acad. Sci. URSS 32 (9), 622–626.

DIETZEL, M. & HARDT, S. 2016 Thermoelectricity in confined liquid electrolytes. Phys. Rev. Lett. 116 (22), 225901.

DIETZEL, M. & HARDT, S. 2017 Flow and streaming potential of an electrolyte in a channel with an axial temperature gradient. J. Fluid Mech. 813, 1060–1111.

DUKHIN, S. S. 1993 Non-equilibrium electric surface phenomena. Adv. Colloid Interface Sci. 44, 1–134.

ELIMELECH, M., CHEN, W. H. & WAYPA, J. J. 1994 Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer. Desalination 95 (3), 269–286.

FU, L., MERABIA, S. & JOLY, L. 2017 What controls thermo-osmosis? molecular simulations show the critical role of interfacial hydrodynamics. Phys. Rev. Lett. 119, 214501.

FU, L., MERABIA, S. & JOLY, L. 2018 Understanding fast and robust thermo-osmotic flows through carbon nanotube membranes: Thermodynamics meets hydrodynamics. J. Phys. Chem. Lett.

GALLO, P., CORRADINI, D. & ROVERE, M. 2011 Ion hydration and structural properties of water in aqueous solutions at normal and supercooled conditions: a test of the structure making and breaking concept. Phys. Chem. Chem. Phys. 13 (44), 19814–19822.

GANTI, R., LIU, Y. & FRENKEL, D. 2017 Molecular simulation of thermo-osmotic slip. Phys. Rev. Lett. 119, 038002.

GHONGE, T., CHAKRABORTY, J., DEY, R. & CHAKRABORTY, S. 2013 Electrohydrodynamics within the electrical double layer in the presence of finite temperature gradients. Phys. Rev. E 88 (5), 053020.

de GROOT, S. R. & MAZUR, P. 1984 Nonequilibrium Thermodynamics. Dover Publication.

GROSU, F. P. & BOLOGA, M. K. 2010 Thermoelectrohydrodynamic methods of energy conversion. Surf. Eng. Appl. Electrochem. 46 (6), 582–588.

GUTHRIE, G., WILSON, J. N. & SCHOMAKER, V. 1949 Theory of the thermal diffusion of electrolytes in a clusius column. J. Chem. Phys. 17 (3), 310–313.

HAYNES, W. M., LIDE, D. R. & BRUNO, T. J. 2014 CRC handbook of chemistry and physics. Boca Raton: CRC press.

HOLT, JASON K, PARK, HYUNG GYU, WANG, YINMIN, STADERMANN, MICHAEL, ARTYUKHIN, ALEXANDER B, GRIGOPOULOS, COSTAS P, NOY, ALEKSANDR & BAKAJIN, OLIGCA 2006 Fast mass transport through sub-2-nanometer carbon nanotubes. Science 312 (5776), 1034–1037.

HUANG, X., GORDON, M. J. & ZARE, R. N. 1988 Current-monitoring method for measuring the electroosmotic flow rate in capillary zone electrophoresis. Anal. Chem. 60 (17), 1837–1838.

ISHIDO, T., MIZUTANI, H. & BABA, K. 1983 Streaming potential observations, using geothermal wells and in situ electrokinetic coupling coefficients under high temperature. Tectonophysics 91 (1-2), 89–104.

ISRAELACHVILI, J. N. 2011 Intermolecular and surface forces. Academic press.

JIANG, H.-R., WADA, H., YOSHINAGA, N. & SANO, M. 2009 Manipulation of colloids by a nonequilibrium depletion force in a temperature gradient. Phys. Rev. Lett. 102, 208301.

KANG, T. J., FANG, S., KOZLOV, M. E., HAINES, C. S., LI, N., KIM, Y. H., CHEN, Y. & BAUGHMAN, R. H. 2012 Electrical power from nanotube and graphene electrochemical thermal energy harvesters. Adv. Funct. Mater. 22 (3), 477–489.

KIM, M., BESKOK, A. & KIH, K. 2002 Electro-osmosis-driven micro-channel flows: a comparative study of microscopic particle image velocimetry measurements and numerical simulations. Exp. Fluids 33 (1), 170–180.

KNOX, J. H. & MCCORMACK, K. A. 1994 Temperature effects in capillary electrophoresis. 1: Internal capillary temperature and effect upon performance. Chromatographia 38 (3-4), 207–214.

KOBATAKE, Y. & FUJITA, H. 1964 Osmotic flows in charged membranes. ii. thermo-osmosis. J. Chem. Phys. 41 (10), 2963–2966.

LECCE, S. D., ALBRECHT, T. & F., BRESME 2017 A computational approach to calculate the heat of transport of aqueous solutions. Sci. Rep. 7 (1), 44833.
Levine, S., Marriott, J. R. & Robinson, K. 1975 Theory of electrokinetic flow in a narrow parallel-plate channel. J. Chem. Soc., Faraday Trans. 2 71, 1–11.

Li, L. & Wang, Q. 2018 Thermoelectricity in heterogeneous nanofluidic channels. Small 14 (21), 1800369.

Majumder, Mainak, Chopra, Nitin, Andrews, Rodney & Hinds, Bruce J 2005 Nanoscale hydrodynamics: enhanced flow in carbon nanotubes. Nature 438 (7064), 44.

Masliyah, J. H. & Bhattacharjee, S. 2006 Electrokinetic and colloid transport phenomena. John Wiley & Sons.

Maynes, D. & Webb, B. W. 2004 The effect of viscous dissipation in thermally fully-developed electro-osmotic heat transfer in microchannels. Int. J. Heat Mass Transfer 47 (5), 987–999.

Onsager, L 1931a Reciprocal relations in irreversible processes. i. Phys. Rev. 37, 405–426.

Onsager, L. 1931b Reciprocal relations in irreversible processes. ii. Phys. Rev. 38, 2265–2279.

Patankar, N. A. & Hu, H. H. 1998 Numerical simulation of electroosmotic flow. Anal. Chem. 70 (9), 1870–1881.

Peters, P. B., van Roij, R., Bazant, M. Z. & Biesheuvel, P. M. 2016 Analysis of electrolyte transport through charged nanopores. Phys. Rev. E 93, 053108.

Putnam, S. A. & Cahill, D. G. 2005 Transport of nanoscale latex spheres in a temperature gradient. Langmuir 21 (12), 5317–5323.

Rasuli, S. N. & Golestanian, R. 2008 Soret motion of a charged spherical colloid. Phys. Rev. Lett. 101, 108301.

Reppert, P. M. & Morgan, F. D. 2003 Temperature-dependent streaming potentials: 1. theory. J. Geophys. Res. 108 (B11).

Revil, A., Schwaeger, H., Cathles, L. M. & Manhardt, P. D. 1999 Streaming potential in porous media: 1. theory of the zeta potential. J. Geophys. Res. 104 (B9), 20021–20031.

Rogacs, A. & Santiago, J. G. 2013 Temperature effects on electrophoresis. Anal. Chem. 85 (10), 5103–5113.

Ruckenstein, E. 1981 Can phoretic motions be treated as interfacial tension gradient driven phenomena? J. Colloid Interface Sci. 83 (1), 77–81.

Ruiz-Cabello, F. J. M., Trefalt, G., Maroni, P. & Borkovec, M. 2014 Electric double-layer potentials and surface regulation properties measured by colloidal-probe atomic force microscopy. Phys. Rev. E 90 (1), 012301.

Russel, W. B., Saville, D. A. & Schowalter, W. R. 1989 Colloidal dispersions. Cambridge Univ. Press.

Sadeghi, A. & Saidi, M. H. 2010 Viscous dissipation effects on thermal transport characteristics of combined pressure and electroosmotically driven flow in microchannels. Int. J. Heat Mass Transfer 53 (19-20), 3782–3791.

Sasidhar, V. & Ruckenstein, E. 1982 Anomalous effects during electrolyte osmosis across charged porous membranes. J. Colloid Interface Sci. 85 (2), 332–362.

Saville, D. A. 1977 Electrokinetic effects with small particles. Annu. Rev. Fluid Mech. 9 (1), 321–337.

Scales, P. J., Grieser, F., Healy, T. W., White, L. R. & Chan, D. Y. C. 1992 Electrokinetics of the silica-solution interface: a flat plate streaming potential study. Langmuir 8 (3), 965–974.

Schnitzer, O., Frankel, I. & Yariv, E. 2012 Streaming-potential phenomena in the thin-debye-layer limit. part 2. moderate péclet numbers. J. Fluid Mech. 704, 109–136.

Snowdon, P. N. & Turner, J. C. R. 1960 The soret effect in some 0.01 normal aqueous electrolytes. Trans. Faraday Soc. 56, 1409–1418.

Squires, T. M. & Bazant, M. Z. 2004 Induced-charge electro-osmosis. J. Fluid Mech. 509, 217252.

Stone, H. A., Stroock, A. D. & Ajdari, A. 2004 Engineering flows in small devices: microfluidics toward a lab-on-a-chip. Annu. Rev. Fluid Mech. 36, 381–411.

Tasaka, M. 1986 Thermal membrane potential and thermoosmosis across charged membranes. Pure Appl. Chem. 58 (12), 1637–1646.

Tasaka, M. & Nagasawa, M. 1978 Thermoosmosis through charged membranes. theoretical analysis of concentration dependence. Biophys. Chem. 8 (2), 111–116.
Vigolo, D., Buzzaccaro, S. & Piazza, R. 2010 Thermophoresis and thermoelectricity in surfactant solutions. *Langmuir* **26** (11), 7792–7801.

Wiegand, S. 2004 Thermal diffusion in liquid mixtures and polymer solutions. *J. Phys.: Condens. Matter* **16** (10), R357.

Wood, J. A., Benneker, A. M. & Lammertink, R. G. H. 2016 Temperature effects on the electrohydrodynamic and electrokinetic behaviour of ion-selective nanochannels. *J. Phys.: Condens. Matter* **28** (11), 114002.

Würger, A. 2008 Transport in charged colloids driven by thermoelectricity. *Phys. Rev. Lett.* **101**, 108302.

Würger, A. 2009 Temperature dependence of the soret motion in colloids. *Langmuir* **25** (12), 6696–6701.

Würger, A. 2010 Thermal non-equilibrium transport in colloids. *Rep. Prog. Phys.* **73** (12), 126601.

Yang, J., Lu, F., Kostiuk, L. W. & Kwok, D. Y. 2003 Electrokinetic microchannel battery by means of electrokinetic and microfluidic phenomena. *J. Micromech. Microeng.* **13** (6), 963.

Yariv, E., Schnitzer, O. & Frankel, I. 2011 Streaming-potential phenomena in the thin-debye-layer limit. part 1. general theory. *J. Fluid Mech.* **685**, 306–334.

Zhao, C., Ebeling, D., Siretanu, I., Van den Ende, D. & Mugele, F. 2015 Extracting local surface charges and charge regulation behavior from atomic force microscopy measurements at heterogeneous solid-electrolyte interfaces. *Nanoscale* **7** (39), 16298–16311.

Zhao, T. S. & Liao, Q. 2002 Thermal effects on electro-osmotic pumping of liquids in microchannels. *J. Micromech. Microeng.* **12** (6), 962.