Published in final edited form as:

Int J Heat Mass Transf. 2016 February 1; 93: 529–537. doi:10.1016/j.ijheatmasstransfer.2015.10.032.

Effect of Channel Sidewalls on Joule Heating Induced Sample Dispersion in Rectangular Ducts

Debashis Dutta*

Department of Chemistry, University of Wyoming

Abstract

In this article, we analyze the effect of channel sidewalls on the broadening of analyte bands resulting from Joule heating during their electrokinetic migration through a rectangular conduit. A method-of-moments formulation has been used to numerically evaluate the Taylor-Aris dispersivity of sample zones under these conditions for thin electrical double layers applicable to a majority of microfluidic assays. Our analysis shows that the larger surface area to volume ratio around the side regions of a rectangular channel causes these corners to stay cooler than the rest of the conduit. While such a thermal profile does not modify the electroosmotic flow in the system for a fixed temperature at the channel walls, it reduces the electrophoretic transport rate by about 10% for small temperature differentials across the channel cross-section ($<10^{\circ}\text{C}$). The effect of these thermal gradients on the hydrodynamic dispersion of analyte bands is more significant however, increasing such band broadening by nearly an order of magnitude in large aspect ratio designs. Our analyses further show that the trends noted above are magnified when a fixed heat transfer coefficient is assumed at the channel walls, in which case, the temperature along this boundary is no longer constant. The non-isothermal channel walls combined with the temperature dependence of zeta potential and other material properties in this situation leads to a non-uniform electroosmotic slip velocity in the system modifying both fluid and analyte transport rates. Again, while the resulting solute flow profile reduces the migration velocity of sample zones only to a moderate extent, it is found to increase the hydrodynamic dispersion of analyte bands by several orders of magnitude in large aspect ratio rectangular channels.

Keywords

electroosmosis; electrophoresis; Joule heating; Taylor-Aris dispersion; channel sidewalls

Corresponding Author: Debashis Dutta, Associate Professor, Department of Chemistry, (Dept. # 3838), University of Wyoming, 1000 East University Avenue, Laramie, Wyoming 82071, USA. ddutta@uwyo.edu, Fax: (307) 766-2807.

Conflict of Interest Disclosure: The author declares no competing financial interests.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Introduction

Electrokinetic transport presents a powerful method for manipulating fluid and solute samples in microfluidic networks because of its better controllability and ease of implementation at shorter length scales [1, 2]. Moreover, the plug-like velocity profile for electrokinetic flows leads to lower sample dispersion, which often translates into a higher efficiency and/or throughput of the device [3]. The use of an electric field in realizing this mode of actuation however, inherently leads to Joule heating that in turn produces an increase as well as a variation in the liquid temperature across the cross-section of the analysis column [4, 5]. While the higher temperature in these systems can be undesirable for analyzing biological samples, the non-uniformity in the temperature profile tends to introduce zone dispersion of analyte bands often deteriorating assay performance. The latter effect arises as the thermal gradients in the channel perturb the plug-like velocity profile of electrokinetic flows due to a dependence of the various material properties, e.g., fluid viscosity, fluid electrical conductivity, zeta potential, etc., on temperature.

The effect of Joule heating on the performance of electrokinetically-driven systems has been previously investigated by several researchers [6–10]. It has been shown for example, that the electroosmotic velocity profile remains plug-like in channels with thin electrical double layers (EDL) even under conditions when this source of heat generation is significant [7]. This occurs as non-uniformities in the liquid temperature affect the streamline velocity in electroosmotic flows only within the EDL, which in this case occupies a negligible fraction of the channel cross-sectional area. Electrophoretic velocities of sample species on the other hand, can vary significantly across the lateral dimensions of these systems as the liquid viscosity, and hence the hydrodynamic drag experienced by the solute particles decreases with temperature [4, 5, 11–13]. Moreover, the higher average temperature in a fluidic channel as a result of Joule heating inherently causes an increase in the axial diffusion of analyte bands. Band broadening induced by axial temperature gradients around the ends of a microchannel has been further shown to deteriorate assay performance in short conduits [14, 15].

While the literature noted above has significantly advanced our understanding of sample dispersion arising from Joule heating effects, it has focused on analyzing this problem only in simple channel geometries such as the parallel-plate device (a rectangular channel with no sidewalls) or the cylindrical tube. Consequently, the effect of channel side regions on such band broadening is not well understood in conduits with non-circular cross-sections. This understanding is particularly important for microfluidic systems where analysis ducts with rectangular or trapezoidal cross-sections are regularly employed and fluid/analyte transport within them is often controlled via electrokinetic means. It can be anticipated that the Joule heating induced variation in electrophoretic velocity across the wider transverse dimension of a large aspect ratio microfluidic channel to significantly increase the Taylor-Aris dispersivity of analyte bands relative to that in a parallel-plate device similar to that known for simple pressure-driven flows [16–20]. In addition, a fixed heat transfer coefficient at the channel walls may lead to substantial non-uniformities in temperature, and thereby, the electroosmotic slip velocity along this boundary further contributing to the sample dispersion process. In this article, we present a theoretical analysis of these effects by

considering the hydrodynamic broadening experienced by analyte bands during their electrokinetic migration through a rectangular channel. The noted problem has been examined under conditions of a constant wall temperature and a fixed heat transfer coefficient at the channel walls individually, to develop a quantitative understanding of the Joule heating induced sample dispersion process in 3-dimensional channel geometries.

Mathematical formulation

We begin our analysis by considering Joule heating of an electrolytic liquid in a rectangular channel of depth d and width W (see figure 1). The fully-developed temperature distribution (T) in this system may be determined based on Fourier's law as

$$\text{B. C. } -k \frac{\partial T}{\partial x} \Big|_{x=\pm W/2} = h(T-T_0) \Big|_{x=\pm W/2} ; -k \frac{\partial T}{\partial y} \Big|_{y=\pm d/2} = h(T-T_0) \Big|_{y=\pm d/2} \quad (1)$$

where E denotes the external electric field applied along the channel length, T_0 refers to the ambient temperature and h represents the effective heat transfer coefficient at the channel walls. The quantities k and λ in equation (1) correspond to the electrical and thermal conductivity of the electrolytic liquid, respectively, under the operating conditions. It is important to point out that although these conductivity parameters are both functions of temperature, their dependence on T for aqueous solutions is significantly different from each other. For example, while the thermal conductivity of water is known to increase by less than 1% for small variations in T ($< 10^\circ\text{C}$) around room temperature (25°C), the corresponding change in λ can be as large as 25% [21–25]. In this situation, the effect of Joule heating on electrokinetic transport of aqueous samples for small temperature variations across the channel cross-section may be well described by assuming k to be a constant ($0.6 \text{ Wm}^{-1}\text{K}^{-1}$ for water at $T_0 = 25^\circ\text{C}$) at all locations within the channel [21] and the electrical conductivity to vary as $\lambda = \lambda_0 C_0 [1 + \alpha(T - T_0)]$ where $\lambda_0 = 0.014 \text{ m}^2 \text{ Smol}^{-1}$ (for aqueous KCl solutions), $\alpha = 0.025 \text{ K}^{-1}$ (for water) and C_0 denotes the ion concentration in the background electrolyte in mol/m^3 [22–25]. Notice that the current analysis ignores any axial temperature gradients in the conduit (incompletely developed thermal profile) which have been experimentally shown to exist in microchip devices only around the channel terminals extending about a few millimeters into the duct [14, 15]. The results presented here are therefore strictly applicable to the middle section of microchannels with lengths about a centimeter or more, where the end effects from the channel terminals may be neglected. Under these conditions, equation (1) reduces to

$$\text{B. C. } \frac{\partial \theta}{\partial x^*} \Big|_{x^*=\pm W/2d} = -Nu \theta \Big|_{x^*=\pm W/2d} ; \frac{\partial \theta}{\partial y^*} \Big|_{y^*=\pm 1/2} = -Nu \theta \Big|_{y^*=\pm 1/2} \quad (2)$$

where $\theta = \frac{T-T_0}{\Delta T}$, $\Delta T = \frac{\lambda_0 C_0 E^2 d^2}{k}$ and $Nu = \frac{hd}{k}$

where the x and y coordinates have been normalized as $x^* = x/d$ and $y^* = y/d$, respectively. If the heat transfer outside of the microchannel is assumed to be limited by thermal conduction through the channels walls, the quantity h can be expected to be on the order of $1 \text{ kWm}^{-2}\text{K}^{-1}$

for conduits etched on millimeter thick glass plates. Moreover, for typical microchip operations, the electric field in the channel tends to be $<1.5kVcm^{-1}$ yielding T values as large as $25^\circ C$ for a $20mM$ KCl solution filled within a $50\mu m$ deep microchannel.

It must be noted that equation (2) governing the temperature profile in a rectangular conduit for a fixed heat transfer coefficient at the channel walls reduces to the case of a fixed wall temperature when the Nusselt number (Nu) approaches infinity. In this limit, the temperature at the channel walls assumes a value of T_0 implying a negligible heat transfer resistance outside of the analysis column. Interestingly, equation (2) can be solved analytically to yield an expression for finite Nusselt numbers given by [26]

$$\theta = \frac{1}{\alpha \Delta T} \left[\frac{Nu \cos(\sqrt{\alpha \Delta T} y^*)}{Nu \cos(\sqrt{\alpha \Delta T}/2) - \sqrt{\alpha \Delta T} \sin(\sqrt{\alpha \Delta T}/2)} - 1 \right] + \sum_{n=1}^{\infty} A_n \cosh \left(\sqrt{p_n^2 - \alpha \Delta T} x^* \right) \cos(p_n y^*)$$

where p_n is n^{th} zero of the equation $z \tan(z/2) = Nu$ and

$$A_n = \frac{4Nu}{\alpha \Delta T \left[\sqrt{p_n^2 - \alpha \Delta T} \sinh \left\{ \sqrt{p_n^2 - \alpha \Delta T} (W/2d) \right\} + Nu \cosh \left\{ \sqrt{p_n^2 - \alpha \Delta T} (W/2d) \right\} \right]} \left[\frac{\sin(p_n/2)}{p_n} - \frac{Nu}{Nu \cos(\sqrt{\alpha \Delta T}/2) - \sqrt{\alpha \Delta T} \sin(\sqrt{\alpha \Delta T}/2)} \left\{ \frac{\sin \left(\frac{p_n - \sqrt{\alpha \Delta T}}{2} \right)}{2(p_n - \sqrt{\alpha \Delta T})} + \frac{\sin \left(\frac{p_n + \sqrt{\alpha \Delta T}}{2} \right)}{2(p_n + \sqrt{\alpha \Delta T})} \right\} \right] \left[\frac{1}{1 + \frac{\sin(p_n)}{p_n}} \right] \quad (3)$$

In the limit of $Nu \rightarrow \infty$, i.e., the constant wall temperature case, equation (3) reduces to

$$\theta = \frac{1}{\alpha \Delta T} \left[\frac{\cos(\sqrt{\alpha \Delta T} y^*)}{\cos(\sqrt{\alpha \Delta T}/2)} - 1 \right] + \sum_{n=0}^{\infty} A_n \cosh \left\{ \sqrt{(2n+1)^2 \pi^2 - \alpha \Delta T} x^* \right\} \cos \{ (2n+1) \pi y^* \}$$

where

$$A_n = \frac{4}{\alpha \Delta T \cosh \left\{ \sqrt{(2n+1)^2 \pi^2 - \alpha \Delta T} (W/2d) \right\}} \left[\frac{(-1)^n}{(2n+1)\pi} - \frac{1}{\cos(\sqrt{\alpha \Delta T}/2)} \left\{ \frac{\sin \left(\frac{(2n+1)\pi - \sqrt{\alpha \Delta T}}{2} \right)}{2((2n+1)\pi - \sqrt{\alpha \Delta T})} + \frac{\sin \left(\frac{(2n+1)\pi + \sqrt{\alpha \Delta T}}{2} \right)}{2((2n+1)\pi + \sqrt{\alpha \Delta T})} \right\} \right] \quad (4)$$

Having estimated the temperature distribution in the channel, it is then possible to determine the axial electroosmotic velocity (u_{EOF}) profile under thin EDL conditions by solving the governing equation [27]

$$\text{B. C. } \frac{\partial}{\partial x^*} \left(\frac{\eta}{\eta_0} \frac{\partial u_{EOF}}{\partial x^*} \right) + \frac{\partial}{\partial y^*} \left(\frac{\eta}{\eta_0} \frac{\partial u_{EOF}}{\partial y^*} \right) = 0$$

$$u_{EOF} \Big|_{x^*=\pm W/2d, y^*=\pm 1/2} = -\frac{\varepsilon \zeta E}{\eta} \Big|_{x^*=\pm W/2d, y^*=\pm 1/2} \quad (5)$$

Here ζ denotes the zeta potential at the channel walls, ε represents the electrical permittivity of the background electrolyte and η refers to the viscosity of this liquid with $\eta|_{T=T_0} = \eta_0$. Again, if the properties of the background electrolyte are approximated by those of water, the temperature variation in the fluid viscosity and electrical permittivity may be captured using the correlations $\eta = 2.76 \times 10^{-6} \exp(1713/T) \text{ Pa}\cdot\text{s}$ and $\eta = 2.71 \times 10^{-9} \exp(-T/219) \text{ Fm}^{-1}$, respectively [10]. The temperature dependence of ζ may be taken into account for glass microchannels based on the equation $\zeta = -51.4[1+0.018(T - T_0)] \text{ mV}$ as has been reported in the literature [10, 28, 29]. Finally, the method-of-moments formulation [30] may be applied to evaluate the velocity (U) and Taylor-Aris dispersivity (K) [30, 31] of sample zones as [32–34]

$$U = \frac{1}{A^*} \int_S \left(u_{EOF} + \frac{qE}{6\pi\eta a} \right) dA^* = \frac{1}{A^*} \int_S \left(u_{EOF} + u_{EP}^0 \frac{\eta_0}{\eta} \right) dA^* = U_{EOF} + U_{EP}$$

and

$$\frac{K}{D_0} = \frac{1}{A^*} \int_S \frac{D}{D_0} dA^* + \left(\frac{Ud}{D_0} \right)^2 \frac{1}{A^*} \int_S \frac{g}{U} \left(u_{EOF} + u_{EP}^0 \frac{\eta_0}{\eta} \right) dA^*$$

where the function g is solution to the problem

$$\frac{\partial}{\partial x^*} \left(\frac{D}{D_0} \frac{\partial g}{\partial x^*} \right) + \frac{\partial}{\partial y^*} \left(\frac{D}{D_0} \frac{\partial g}{\partial y^*} \right) = 1 - \frac{1}{U} \left(u_{EOF} + u_{EP}^0 \frac{\eta_0}{\eta} \right)$$

$$\text{B. C. } \frac{\partial g}{\partial x^*} \Big|_{x^*=\pm W/2d} = \frac{\partial g}{\partial y^*} \Big|_{y^*=\pm 1/2} = 0 \quad ; \quad \int_S g dA^* = 0 \quad (6)$$

In equation (6), q denotes the electrical charge carried by the analyte molecules, a represents their effective radius and $u_{EP}^0 = qE/(6\pi\eta_0 a)$ refers to their electrophoretic velocity at the ambient temperature (T_0). The symbol D here corresponds to the diffusion coefficient of the analyte molecules with D_0 being its value at temperature T_0 . For simplicity, the variation in the electrophoretic velocity in our analysis has been assumed to be arising only due to the temperature dependence of fluid viscosity. In addition, the Stokes-Einstein equation for molecular diffusion coefficient, i.e., $D = k_B T/(6\pi\eta a)$, has been used to capture the variation in D with temperature where k_B refers to the Boltzmann constant. The symbol S used in the integrals included in equation (6) represents the cross-sectional surface of the channel with $A^* = Wd/d^2 = W/d$ being its normalized area. The governing equations presented above were solved in our current work using codes written in MATLAB.

Results and Discussion

Constant wall temperature case

As has been noted in the previous section, the fully-developed thermal profile within a rectangular duct can be described for a constant wall temperature T_0 using equation (4) when the heat transfer resistance outside of the channel is neglected ($Nu \rightarrow \infty$). Figure 2(a) presents a contour map of θ in such a system showing lower liquid temperatures around the channel sidewalls due to a larger surface area to volume ratio in these regions. The map also points out that the maximum temperature variation in a rectangular channel is only about 15% of T under these conditions, and is therefore $<10^\circ\text{C}$ for T values as large as 65°C . Figure 2(b) further shows that the average temperature in this cross-section, estimated as $\theta_{avg} = (\int_S \theta dA^*)/A^*$, to be a strong function of the ratio d/W . In fact, for any given value of T and channel depth, θ_{avg} is seen to reduce by nearly 60% going from a parallel-plate design ($d/W \rightarrow 0$) to a square channel ($d/W = 1$). The quantity $\theta_{avg}^{\parallel}$ in this figure refers to the average temperature in a parallel-plate geometry of gap width d (i.e., the corresponding rectangular channel without the sidewalls) and may be estimated using the expression $\theta_{avg}^{\parallel} = \{2 \tan(\sqrt{\alpha \Delta T}/2) / \sqrt{\alpha \Delta T} - 1\} / \{\alpha \Delta T\}$. In figure 2(b), it is also seen that the sidewalls of a rectangular duct reduce the maximum temperature (θ_{max}) in this cross-section by about 40 – 50% going from a parallel-plate design to a square duct. Most of this reduction however, occurs across geometries with d/W ratios ranging between 0.3 and 1. θ_{max} was evaluated in our current analysis as the value of θ at the channel center, i.e., $x^* = y^* = 0$, with $\theta_{max}^{\parallel}$ denoting the corresponding quantity in a parallel-plate device of gap width d estimated as $\theta_{max}^{\parallel} = \{\sec(\sqrt{\alpha \Delta T}/2) - 1\} / \{\alpha \Delta T\}$. Figure 2(c) shows a weak dependence of θ_{avg} and θ_{max} on the parameter T in the square and parallel-plate geometries with both these quantities assuming larger values in the latter design.

Although the sidewalls of a rectangular channel are seen to significantly modify the temperature profile in this geometry, their effect on the electroosmotic flow (EOF) is minimal for a constant wall temperature boundary condition. This occurs as the nonuniformities in the EOF profile still remain confined within the electrical double layer in such a system which in our case occupies a negligible fraction of the channel cross-section. The electrophoretic velocity of analyte molecules (u_{EP}) on the other hand, increases around the channel center due to Joule heating effects where warmer temperatures cause a reduction in the fluid viscosity. The higher average temperature in the conduit also leads to an increase in the molecular diffusion coefficient of the sample species (D) resulting in faster broadening of analyte bands during their electrokinetic transport. In figure 3(a), we have plotted the ratio of the average electrophoretic velocity in a rectangular channel (U_{EP}) to its corresponding value ($U_{EP}^{\parallel}$) in a parallel-plate device of gap width d which is seen to increase moderately with a reduction in d/W as a result of the higher average temperature in these geometries. Similarly, the ratio of the average diffusivity to its value in the corresponding parallel-plate device ($D/\bar{D}^{\parallel}$) is observed to rise by less than 10% going from a square cross-section to a large aspect ratio design for the same reason. Figure 3(b) further shows that the average electrophoretic velocity and diffusivity in rectangular channels

increase with T only by about 15% in the limit of $d/W \rightarrow 0$ even for a characteristic temperature rise (T) of 65°C. This figure also predicts that a reduction in the wall temperature from 25°C to 10°C magnifies the noted variation in $U_{EP}/U_{EP}^{\parallel}$ and $D/D_0^{\parallel}$ with T in a minor way.

The thermal gradients in a rectangular duct also affect the dispersion of analyte bands as they electrokinetically migrate through the channel at a constant wall temperature. This effect can be captured by the Taylor-Aris dispersivity (K) in the system given by

$$\frac{K}{D_0} = \frac{\bar{D}}{D_0} + \left(\frac{Ud}{D_0} \right)^2 f \quad (7)$$

where f denotes the dispersivity function under the operating conditions, and has been evaluated in this work based on the formulation outlined in equation (6). Notice that the lack of any measurable fluid shear in the electroosmotic flow profile for thin EDLs prevents this transport mechanism from contributing to the sample dispersion process. In this situation, the effect of channel sidewalls on Joule heating induced band dispersion may be quantitated in terms of the ratio $f_{EP}/f_{EP}^{\parallel}$ where f_{EP} and $f_{EP}^{\parallel}$ denote the dispersivity functions in a rectangular conduit and parallel-plate device of gap width d , respectively, for electrophoretic flow only. Figure 4(a) shows this ratio to decrease monotonically with an increase in the value of d/W nearly unaffected by the parameters T and T_0 . Interestingly, $f_{EP}/f_{EP}^{\parallel}$ assumes a value of about 8–9 in the limit of $d/W \rightarrow 0$ similar to that reported for the corresponding ratio of dispersivity functions in simple pressure-driven flow systems [16–20]. This result is a consequence of the fact that the electrophoretic flow profile closely resembles the pressure-driven velocity field in a rectangular channel for small values of T as considered in our current work. Figure 4(a) also shows that the ratio $f_{EP}/f_{EP}^{\parallel}$ assumes a value of about 0.3 for a square cross-section almost independent of the magnitude T and T_0 . The lower dispersion in small aspect ratio rectangular ducts ($d/W \sim 1$) relative to that in a parallel-plate device is a result of the weaker temperature gradients in these geometries leading to a smaller differential in the electrophoretic velocity across the channel cross-section. The dispersivity function in a square channel however, is still greater than that in a cylindrical tube which offers an even lesser resistance to heat transport. Figure 4(b) shows that the function f assumes a value on the order of 10^{-5} for $T = 10^\circ\text{C}$ in a large aspect ratio rectangular channel. In this situation, the hydrodynamic dispersion component is expected to exceed the axial diffusion contribution to band broadening for analyte species with diffusivity $D_0 = 5 \times 10^{-6} \text{ cm}^2/\text{s}$ when migrated with electrophoretic velocities greater than 3 mm/s in a 50 μm deep channel. The corresponding U_{EP} value in a square duct is about a factor 5 – 5.5 larger due to a lower mass transfer resistance in this cross-sectional geometry. It is important to point out that while the electroosmotic flow does not lead to any additional band dispersion for thin electrical double layers and a fixed wall temperature boundary condition, it modifies the sample velocity (U), and therefore, the Peclet number ($Pe = Ud/D_0$) in the system. Nevertheless, one can estimate the function f for a non-zero

electroosmotic flow in the rectangular channel with wall temperature T_0 from the results included in figure 4 using the relationship $f = U_{EP}^2 f_{EP} / U^2$.

Notice that the mathematical formulation outlined in equations 1 through 6 for estimating the Taylor-Aris dispersion of analyte bands relies on the decoupling of the energy, momentum and mass conservation equations. Although this approach reduces the computational effort involved in deriving the desired information significantly, it yields accurate results only when some simplifying assumptions are satisfied. For example, the thermal profile in a straight microchannel may be calculated independently of the velocity and solute concentration fields provided the axial temperature gradient and the transverse advective velocity components may be neglected. While the axial temperature gradients are minimized in a fully-developed thermal profile, the transverse advective velocity components may be neglected for small Reynolds number flows in the absence of any natural convection in the channel (small Grashof number). Interestingly, these two assumptions are generally satisfied in the central section of long microchannels which justifies the ignorance of the advective term in the energy equation, i.e., equation (1). Moreover, the decoupling of the energy and momentum conservation expressions from the mass conservation equation is known to be strictly valid for dilute samples for which the solute concentration profile does not influence any of the material properties in the system. Furthermore, the Taylor-Aris dispersion limit for band broadening is applicable to situations only when the transit time for the sample species through the microchannel is significantly larger than their diffusion time across the channel cross-section, i.e., $L/U \gg d^2/D_0$. These conditions again are easily met in channels that are longer than a few millimeters carrying dilute samples of small molecules with D_0 values in the range of 10^{-5} – 10^{-6} cm²/s. To substantiate our arguments on the validity of the assumptions made in our simplified model, we also carried out some full blown 3-D simulations of the concerned problem using the commercially available COMSOL package and have compared these results to those discussed in the previous paragraph. In these simulations, the energy, momentum and mass conservation equations were solved in a coupled manner within the rectangular channel geometry shown in figure 1. An infinitesimally narrow sample band was introduced at the entrance of this conduit, and its spatial variance (σ^2) evaluated along the channel axis during its electrophoretic migration through the column. The Taylor-Aris dispersivity K was later estimated from the time derivative of σ^2 as $K = (D/2)(d\sigma^2/dt)$ to enable its comparison with the results from the simpler model. As may be seen from the data included in figure 4(b), the two approaches yielded similar results for the Joule heating problem in rectangular microchannels consistent with several other reports published in the literature [4–13].

Constant heat transfer coefficient case

As has been previously noted, the fully-developed thermal profile in a rectangular duct with a fixed heat transfer coefficient h at the channel walls can be described using equation (3) for small temperature increases resulting from Joule heating effects, i.e., $\theta_{max} T < 10^\circ\text{C}$. Figure 5(a) presents a contour map of θ under these conditions depicting its variation across the channel cross-section. As may be seen from the figure, the most significant difference between this map and the one presented in figure 2(a) is the loss of isothermality at the channel walls. This occurs as the larger surface area to volume ratio in the side regions of

the rectangular conduit promotes faster heat transfer out through the channel walls lowering the local temperature compared to that in the central section of the duct. The non-uniformity in wall temperature in turn leads to a variation in the zeta potential, electrical permittivity and liquid viscosity along this boundary yielding a non-uniform electroosmotic slip velocity in the system. Consequently, the electroosmotic flow profile in the rectangular channel no longer remains plug-like even under thin EDL conditions and can contribute significantly towards the broadening of analyte bands. Interestingly, a constant heat transfer coefficient at the walls of a parallel-plate device or a circular tube, does not lead to a nonuniform electroosmotic slip velocity in those systems. This is because the surface area to volume ratio in these two cross-sectional geometries remains constant along the channel boundary resulting in higher (relative to T_0) but still a uniform wall temperature for finite Nusselt numbers. Notice that for our current analysis, Nu has been assumed to be on the order 0.1 which corresponds to the heat transfer resistance encountered in microchannels embedded between $\sim 1\text{mm}$ thick glass plates with the outer surface of the microchip maintained at a temperature of T_0 . Another important difference between the contour maps presented in figures 2(a) and 5(a) is the significantly higher liquid temperature within the channel interior in the latter case. This result is a consequence of the fact that for $Nu \sim 0(0.1)$, the overall heat transfer resistance in the system is dominated by that of the channel walls causing a majority of the temperature drop to occur across the plates (base/cover plate) between which the conduit is embedded. In fact, for $Nu = 0.1$ this temperature drop across the base/cover plate is about 90% of its overall value with the channel center being about 10°C above T_0 for a T value of 2°C . In figure 5(b), we have plotted the temperature at the center of the rectangular duct $\theta_{\max}$ (value of θ at $x^* = y^* = 0$) against its aspect ratio which shows a decrease in this quantity by as much as 55% going from a parallel plate design to a square channel for $Nu = 0.1$. A similar trend is also noticed for θ_{avg} which is seen to approach $\theta_{\max}$ for smaller Nusselt numbers. A weak variation in θ_{avg} and $\theta_{\max}$ is observed with the parameter T in figure 5(c), similar to that reported for the constant wall temperature case, with this dependence getting sharper for smaller values of Nu .

For a constant heat transfer coefficient at the channel walls, Joule heating affects both the electrophoretic (U_{EP}) and electroosmotic velocity (U_{EOF}) of analyte bands in the rectangular conduit. Because the overall sample transport rate (U) is determined by the algebraic sum of these two contributions, i.e., $U = U_{EP} + U_{EOF}$, it is possible to analyze the effect of the various operating parameters on U by characterizing their influences on U_{EP} and U_{EOF} individually. In figure 6(a) we have plotted the quantity $U_{EP}/U_{EP}^{\parallel}$ as a function of the channel aspect ratio which shows the electrophoretic velocity to drop by about 15% for $Nu = 0.1$ and $T = 2^\circ\text{C}$ going from a parallel-plate device to a square duct due to lower liquid temperatures in the latter design. Moreover, this effect is diminished for larger Nusselt numbers and magnified for smaller values of T_0 for all rectangular geometries. Similar trends are also noticed for the molecular diffusion coefficient of analyte species which is seen to grow superlinearly with T for all values of Nu , T_0 and d/W (see figure 6(b)). In figure 7(a), we have depicted the variation in the EOF profile across the cross-section of a rectangular channel through a contour map of U_{EOF}/u_{EOF}^0 where $u_{EOF}^0 = \varepsilon_0 \zeta_0 / \eta_0$ denotes the electroosmotic slip velocity at the ambient temperature T_0 . This map shows only about a 2 –

3% variation in the EOF velocity across the lateral dimensions of a conduit with $W/d = 3$, $Nu = 0.1$ and $T = 2^\circ\text{C}$ with an area averaged value for this quantity that is 30% higher compared to the situation when $Nu \rightarrow \infty$ (see figure 7(b)). The cooler side-regions however lead to a decrease in the ratio $U_{EOF}/U_{EOF}^{\parallel}$ by about 20% under the same operating conditions, i.e., $Nu = 0.1$, $T = 2^\circ\text{C}$ going from a parallel-plate device to a square duct (see figure 7(c)).

Hydrodynamic dispersion of analyte bands during their electrokinetic transport through a rectangular conduit with a constant heat transfer coefficient at the channel walls arises due to both electrophoresis and electroosmosis, unlike in the case of a fixed wall temperature. Moreover, these contributions are not additive as was the situation for the sample transport rate discussed in the previous paragraph. In this situation, we have estimated the Taylor-Aris dispersivity function for pure electrophoretic and electroosmotic flow individually to assess the effect of Joule heating on hydrodynamic dispersion in these two asymptotic limits. Figure 8(a) shows a drastically different variation in f with the channel aspect ratio for pure electrophoretic flow compared to the fixed wall temperature case. While the dispersivity function varied by about a factor of 30 going from high aspect ratio geometries to a square channel in the latter situation, the corresponding factor is nearly 4 orders of magnitude for a constant heat transfer coefficient boundary condition. Moreover, this quantity is seen to assume values over an order of magnitude larger than that for the constant wall temperature case when $d/W \ll 1$. Careful analysis of the contour maps shown in figures 2(a) and 5(a) suggests that a complete absence of the slow moving streamlines in the central section of a high aspect ratio channel leads to such large dispersion in the latter case. Figure 8(b) shows that the dispersivity function f for pure electroosmotic flow varies by nearly 5 orders of magnitude across channel geometries with d/W ratio ranging between 0 and 1. While this quantity is seen to assume large values compared to the electrophoretic flow case for $d/W \ll 1$, the opposite is true for small aspect ratio designs. In fact, our analysis suggests that the overall band broadening in a large aspect ratio $50\mu\text{m}$ deep channel to be completely dominated by the hydrodynamic dispersion contribution from electroosmotic flow for analyte species with $D_0 = 5 \times 10^{-6}\text{cm}^2/\text{s}$ when this transport rate exceeds a few $100\mu\text{m}/\text{s}$. In figure 9, we have shown the variation in f as a function of the channel aspect ratio for the situation when EOF contributes 80% towards the overall sample flow rate in the system. As may be seen, the noted curve approaches the pure electroosmotic flow case for $d/W \rightarrow 0$ as $f_{EOF} \gg f_{EP}$ in this limit. For nearly square cross-sections on the other hand, the dispersivity function follows the pure electrophoretic flow case as $f_{EP} \gg f_{EOF}$ for these geometries. The figure also shows that the actual dispersivity function may be approximated using the expression $0.8f_{EOF} + 0.2f_{EP}$ although this estimate over-predicts the true value of f for all d/W ratios.

As a final note, we would like to point out that although the assumption of a constant heat transfer coefficient at the channel walls captures the effect of a finite resistance to heat transport at this boundary, it is not strictly valid for a microfluidic channel embedded between two glass/plastic plates. This is because the distance over which heat needs to be conducted through the base/cover plate in such a system tends to be slightly different for the sidewalls and the ceiling/floor of the conduit. In this situation, the results included in the

manuscript are expected to more accurately capture the effect of Joule heating on band broadening in rectangular capillaries where the wall thickness along the entire channel boundary is held constant. Nevertheless, the present analysis should closely describe band dispersion due to Joule heating effects in microfluidic channels provided the depth of these ducts is significantly smaller compared to the thickness of the base/cover plate used to etch/seal them, and the conduit is located far away from the lateral edges of the microchip. Under these conditions, a majority of the heat produced in the microchannel dissipates from the top and bottom surface of the microchip where the temperature is held at the ambient value (T_0). Fortunately, this condition is satisfied for most microchip devices in which the same material is used for the base and cover plates.

Concluding remarks

To summarize we have shown that the sidewalls of a rectangular channel can significantly alter the broadening of analyte bands during their electrokinetic transport under operating conditions when Joule heating is significant. For a fixed temperature at the channel walls, the cooler side-regions only influences the electrophoretic flow profile under thin EDL conditions. While the effect of channel geometry on the analyte speed is modest in this case, the hydrodynamic dispersion of sample zones can increase by factors of 8–10 in large aspect ratio designs, i.e., $d/W \ll 1$, as compared to that predicted for a parallel-plate device. Interestingly, the effect of the side-regions is even more prominent in systems with a fixed heat transfer coefficient h at the channel walls. The results presented here show that this boundary condition leads to a non-uniform wall temperature in the channel affecting both the electrophoretic and the electroosmotic transport rates for the samples. The sidewalls in this case can increase sample dispersion by several orders of magnitude for both pure electrophoretic and electroosmotic flows in channels with $d/W \ll 1$. Finally, it is important to point out that while the side-regions of a rectangular channel can significantly deteriorate the performance of analytical separations in large aspect ratio geometries, they tend to improve the peak efficiency in these systems (compared to that in a parallel-plate design) in the limit of $d/W \sim 1$. This is because the side-regions more effectively conduct heat out of the channel thereby yielding lower liquid temperatures in the system. Under all operating conditions however, the tubular geometry always yields the least sample dispersion compared to the parallel-plate and rectangular channel design.

Acknowledgments

This research work was supported by grants from the National Science Foundation (DBI 0964211) and the National Institutes of Health (1R15AG045755-01A1).

References

1. Auroux PA, Iossifidis D, Reyes DR, Manz A. Micro total analysis systems. 2. Analytical standard operations and applications. *Anal Chem.* 2002; 74:2623–2636. [PubMed: 12090653]
2. Stone HA, Stroock AD, Ajdari A. Engineering flows in small devices: Microfluidics toward a lab-on-a-chip. *Annu Rev Fluid Mech.* 2004; 36:381–411.
3. Ghosal S. Electrokinetic flow and dispersion in capillary electrophoresis. *Annu Rev Fluid Mech.* 2006; 38:309–338.

4. Grushka E, McCormick RM, Kirkland JJ. Effect of temperature gradients on the efficiency of capillary zone electrophoresis separations. *Anal Chem.* 1989; 61:241–246.
5. Knox JH, McCormack KA. Temperature effects in capillary electrophoresis. 1. Internal capillary temperature and effect upon performance. *Chromatographia.* 1994; 38:207–214.
6. Gas B, Stedry M, Kennedler E. Peak broadening in capillary zone electrophoresis. *Electrophoresis.* 1997; 18:2123–2133. [PubMed: 9456027]
7. Ghosal S. Fluid mechanics of electroosmotic flow and its effect on band broadening in capillary electrophoresis. *Electrophoresis.* 2004; 25:214–228. [PubMed: 14743475]
8. Petersen NJ, Nikolajsen RPH, Mogensen KB, Kutter JP. Effect of Joule heating on efficiency and performance for microchip-based and capillary-based electrophoretic separation systems: A closer look. *Electrophoresis.* 2004; 25:253–269. [PubMed: 14743478]
9. Cetin B, Li DQ. Effect of Joule heating on electrokinetic transport. *Electrophoresis.* 2008; 29:994–1005. [PubMed: 18271065]
10. Xuan XC. Joule heating in electrokinetic flow. *Electrophoresis.* 2008; 29:33–43. [PubMed: 18058768]
11. Knox JH. Thermal effects and band spreading in capillary electro-separation. *Chromatographia.* 1988; 26:329–337.
12. Knox JH, McCormack KA. Temperature effects in capillary electrophoresis 2. Some theoretical calculations and predictions. *Chromatographia.* 1994; 38:215–221.
13. Xuan XC, Li DQ. Joule heating effects on peak broadening in capillary zone electrophoresis. *J Micromech Microeng.* 2004; 14:1171–1180.
14. Xuan XC, Sinton D, Li DQ. Thermal end effects on electroosmotic flow in a capillary. *Int J Heat Mass Transfer.* 2004; 47:3145–3157.
15. Xuan XC, Xu B, Sinton D, Li DQ. Electroosmotic flow with Joule heating effects. *Lab Chip.* 2004; 4:230–236. [PubMed: 15159784]
16. Doshi MR, Daiya PM, Gill WN. 3-dimensional laminar dispersion in open and closed rectangular conduits. *Chem Eng Sci.* 1978; 33:795–804.
17. Golay MJE. The height equivalent to a theoretical plate of retentionless rectangular tubes. *J Chromatogr.* 1981; 216:1–8.
18. Chatwin PC, Sullivan PJ. The effect of aspect ratio on longitudinal diffusivity in rectangular channels. *J Fluid Mech.* 1982; 120:347–358.
19. Dutta D, Leighton DT. Dispersion reduction in pressure-driven flow through microetched channels. *Anal Chem.* 2001; 73:504–513. [PubMed: 11217754]
20. Dutta D, Ramachandran A, Leighton DT. Effect of channel geometry on solute dispersion in pressure-driven microfluidic systems. *Microfluid Nanofluid.* 2006; 2:275–290.
21. Incropera, FP.; Dewitt, DP. *Fundamentals of Heat and Mass Transfer.* Wiley; New York: 1990.
22. Jones AE, Grushka E. Nature of temperature-gradients in capillary zone electrophoresis. *J Chromatogr.* 1989; 466:219–225.
23. Bello MS, Righetti PG. Unsteady heat transfer in capillary zone electrophoresis 1. A mathematical model. *J Chromatogr A.* 1992; 606:95–102.
24. Bello MS, Righetti PG. Unsteady heat transfer in capillary zone electrophoresis 2. Computer simulations. *J Chromatogr A.* 1992; 606:103–111.
25. Landers, JP. *Handbook of capillary electrophoresis.* CRC; New York: 1996.
26. Horiuchi K, Dutta P. Joule heating effects in electroosmotically driven microchannel flows. *Int J Heat Mass Transfer.* 2004; 47:3085–3095.
27. Probstein, RF. *Physicochemical Hydrodynamics.* 2. John Wiley & Sons; New York: 1994.
28. Somasundaran P, Kulkarni RD. New streaming potential apparatus and study of temperature effects using it. *J Colloid Interface Sci.* 1973; 45:591–600.
29. Ishido T, Mizutani H. Experimental and theoretical basis of electrokinetic phenomena in rock-water systems and its applications to geophysics. *J Geophys Res.* 1981; 86:1763–1775.
30. Aris R. On the dispersion of a solute in a fluid flowing through a tube. *Proc R Soc A.* 1956; 235:67–77.

31. Taylor GI. Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc R Soc A*. 1953; 219:186–203.
32. Dutta D. Electroosmotic transport through rectangular channels with small zeta potentials. *J Colloid Interface Sci*. 2007; 315:740–746. [PubMed: 17761188]
33. Dutta D. Electrokinetic transport of charged samples through rectangular channels with small zeta potentials. *Anal Chem*. 2008; 80:4723–4730. [PubMed: 18476719]
34. Dutta D. Solutal transport in rectangular nanochannels under pressure-driven flow. *Microfluid Nanofluid*. 2011; 10:691–696.

Highlights

- sidewalls can increase thermal dispersion by 8–10 fold for isothermal channel walls
- both EOF and electrophoresis disperse solute for fixed Biot number at channel walls
- these dispersion contributions vary by factors of 10^4 – 10^5 with channel aspect ratio

Figure 1. Schematic of the Joule heating problem in a long rectangular channel as considered in the current analysis.

Figure 2.

(a) A contour plot of dimensionless temperature (θ) in a rectangular channel of aspect ratio $W/d = 3$ for a constant wall temperature. This figure was generated setting $T = 25^{\circ}\text{C}$ and $T_0 = 25^{\circ}\text{C}$. (b) Effect of channel sidewalls on the average and maximum temperature in a rectangular conduit. (c) Variation in the average and maximum temperature in a rectangular channel with the characteristic temperature rise (ΔT) in the system. The wall temperature was assumed to be T_0 in all the figures.

Figure 3.

Effect of channel sidewalls on the electrophoretic velocity and diffusivity of solute molecules in a rectangular duct under conditions when Joule heating is significant. In these figures, the walls of the rectangular channel has been assumed to be isothermal (at T_0). The solid and dotted lines correspond to the ratios U_{EP}/U_{EP}^0 and $\bar{D}/\bar{D}^0$, respectively, evaluated at $T_0 = 25^\circ\text{C}$. The solid circle and diamond symbols on the other hand correspond to the ratios U_{EP}/U_{EP}^0 and $\bar{D}/\bar{D}^0$, respectively, evaluated at $T_0 = 10^\circ\text{C}$.

Figure 4.

Effect of channel sidewalls on the dispersivity function f in a rectangular duct under conditions of pure electrophoretic flow and a constant wall temperature T_0 . The solid circles in (b) represent the estimated values of the dispersivity function using the COMSOL package. The energy, momentum and mass conservation equations were solved in a coupled manner in these simulations in order to validate the underlying assumptions of the simplified mathematical model described in this work for analyzing Joule heating effects in rectangular channels.

Figure 5.

(a) A contour plot of dimensionless temperature (θ) in a rectangular channel of aspect ratio $W/d = 3$ for a constant heat transfer coefficient at the channel walls. This figure was generated setting $T = 2^\circ\text{C}$, $T_0 = 25^\circ\text{C}$ and $Nu = 0.1$. (b) Effect of channel sidewalls on the average and maximum temperature in a rectangular conduit. (c) Variation in the average and maximum temperature in a rectangular channel with the characteristic temperature rise (ΔT) in the system.

Figure 6.

Effect of channel sidewalls on the electrophoretic velocity and diffusivity of solute molecules in a rectangular duct for finite Nusselt numbers. In these figures, the outer surface of the microchip device has been assumed to be isothermal (at T_0). The solid and dotted lines correspond to the ratios $U_{EP}/U_{EP}^{\parallel}$ and $\bar{D}/\bar{D}^{\parallel}$, respectively, evaluated at $T_0 = 25^\circ\text{C}$. The solid circle and diamond symbols on the other hand correspond to the ratios $U_{EP}/U_{EP}^{\parallel}$ and $\bar{D}/\bar{D}^{\parallel}$, respectively, evaluated at $T_0 = 10^\circ\text{C}$.

Figure 7.

(a) A contour map of the ratio U_{EOF}/u_{EOF}^0 for finite Nusselt numbers where $u_{EOF}^0 = \varepsilon_0 \xi_0 / \eta_0$ denotes the electroosmotic slip velocity at the ambient temperature T_0 . (b) and (c) Effect of channel aspect ratio on the electroosmotic velocity of solute molecules in a rectangular duct under different operating conditions.

Figure 8. Effect of channel sidewalls on the dispersivity function f in a rectangular duct under conditions of a pure (a) electrophoretic and (b) electroosmotic flow for finite Nusselt numbers.

Figure 9.

Effect of channel sidewalls on the dispersivity function f in a rectangular duct under conditions of combined electrophoretic and electroosmotic flow for $Nu = 0.1$. In this figure, the electroosmotic component was assumed to contribute 80% towards the overall sample velocity.