# The effect of Entry Region on Thermal Field

# Flow Fractionation

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Abstract


Achieving the separation and purification of large or delicate molecules, such as

polymers or DNA, can be difficult using conventional techniques, which may require

introducing such compounds to extreme temperatures or pressures.  Ergo, developing

techniques to achieve high purity final products under mild conditions has obvious

practical purposes.  Micro thermal field-flow fractionation (TFFF) is a technique utilizing

the interactive effects of temperature and concentration gradients on molecular diffusion,

whereby large molecules can be separated with high purity by applying a very small

temperature gradient (on a range of the order of 1 to 10 K cm$^{-1}$) to a fluid flowing through

a very thin channel.[1]  Our previous work focused on an investigation into the potential

use of computational techniques to model TFFF devices.  Because previous attempts

assumed a fully-developed thermal gradient at the channel inlet, in this paper, we seek to

build on this work by investigating the effect of a thermal entry region on the results of

our computer model, in addition to fluid flow through the channel.

Objectives


The main objective of this project was to determine what effect, if any, the thermal

gradient and flow rate at the entrance of a TFFF channel would have on the functionality

of a TFFF device.  In particular, we wish to compare three cases: a fully developed

temperature gradient at the inlet with no fluid flow (diffusion only), a fully developed

temperature gradient at the inlet with fluid flow, and no temperature gradient at the inlet

with fluid flow.  In the last of the three cases, we wished to determine the distance

through the channel at which the thermal gradient between the bottom and top plates

became fully developed.  We defined this as occurring when the temperature at the

center-line approached 99% of its final value.


Theory


Micro TFFF is a process whereby a thermal field or gradient is used to create differential

flow displacement of large molecules in a stream of liquid flowing through a thin channel

(see Fig. 1).  Consider a case where the top of the channel is kept at a constant high

temperature, and the bottom of the channel is kept at a constant low temperature.  Next,

consider a solution composed of two different compounds (both compounds are made of

large molecules, such as polymers), which is injected in a small pulse at the inlet of the
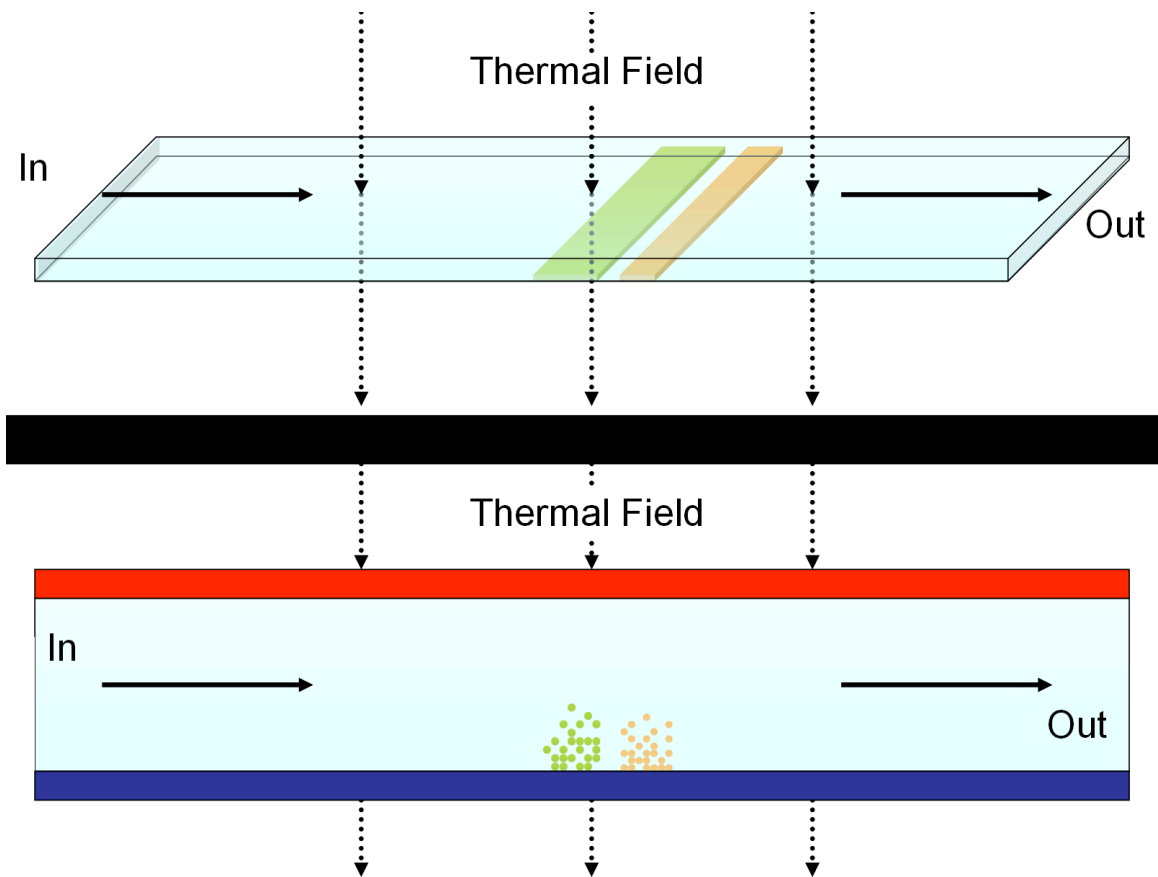
TFFF channel.

Figure 1: diagram of a TFFF device separating two compounds (orange and green) from a perspective (top) and 2D (bottom) viewpoint.

The thermal gradient of the channel drives the molecules of both compounds to the accumulation plate, but at different rates due to the different thermal diffusivity properties of both compounds. The two compounds then travel through the channel at different rates, allowing for their separation. In this fashion, TFFF functions much in the same way as chromatography.

<u>Methods</u>

We used three equation systems to model this process. The first governed the fluid dynamics of the model, and was represented by the incompressible Navier-Stokes equation, shown in Eq. 1.

$$\rho \frac{\partial u}{\partial t} + \rho \mathbf{u} \bullet \nabla \mathbf{u} = \mu \nabla^2 \mathbf{u} - \nabla p + \rho \mathbf{g} \tag{1}$$

Here, $\rho$ represents the fluid density, $\mathbf{u}$ represents the fluid velocity, $\mu$ represents the viscosity, $p$ is the differential pressure drop, and $g$ is the gravitational constant. The second equation we used governed thermal convection and conduction, and is shown in Eq. 2.

$$\rho C_p \frac{\partial T}{\partial t} + \nabla(-\kappa \nabla T) = Q - \rho C_p \mathbf{u} \bullet \nabla T \tag{2}$$

Here, $C_p$ is the heat capacity of the fluid, $\kappa$ is the thermal conductivity, $T$ is temperature, and $Q$ is heat (thermal energy that crosses the system boundary). The third and final equation shown in Eq. 3 was given by deGroot and Mazur, and governs the convection and diffusion of the large molecules in question as a result of the fluid flow, thermal gradient, and concentration gradient.

$$\nabla \bullet (c D_T \nabla T + D \nabla c - \mathbf{u} c) = 0 \tag{3}$$

Here, $c$ is the concentration of the solute, $D_T$ is the thermal diffusivity of the solute, $D$ is the mass diffusivity of the solute, and $u$ is the fluid velocity through the channel. These three equations were solved simultaneously using Comsol Multiphysics ©. The geometry of the channel was based on dimensions found in literature for actual TFFF devices. This geometry and finite element mesh is shown in Fig. 2.
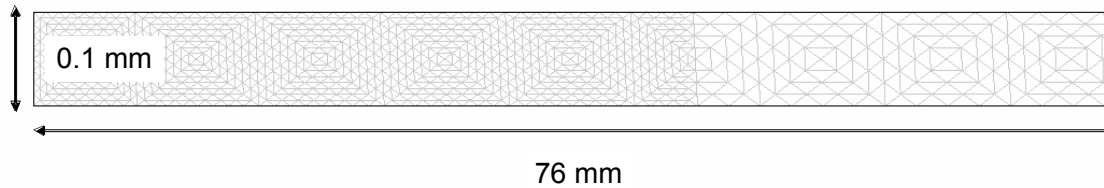


0.1 mm

76 mm

Figure 2: Depiction of the domain dimensions. Note, the entire domain is not shown, because the length of the channel is so long compared to the channel height. The mesh and vertical dimensions would not be resolved with a full picture (it would appear to be a line).

This solution involved solving for 35,876 mesh elements. This is a very large number of mesh elements, and results from the fact that in order to achieve high enough resolution at the top and bottom of the plate (so that a concentration gradient could be observed), the mesh had to be refined many times over. In order to show higher quality resolution (especially at the entrance of the channel), the mesh was refined even more, which can be observed directly from Fig. 2.

We then defined the boundary conditions for all three equations. In the list below, we report the values for each boundary condition for the fluid dynamics (FD) model, the

thermal convection and conduction model (TCC) and the deGroot and Mazur model (DGM):

- BC 1 (inlet)
    - FD: inlet velocity of 0.13 m/s (value taken from literature).
    - TCC: $100{,}000y + 298$ K. Here, where $y$ is the dimension representing the height of the channel, we assume that the inlet temperature gradient is fully developed. Hence, this linear gradient is used, where the slope is based on the temperature of the top and bottom plates.
    - DGM: $c = 1$ unit of concentration.
- BC 2 (bottom plate)
    - FD: no slip.
    - TCC: 298 K (this was chosen because ambient temperature is a reasonable assumption).
    - DGM: no mass flux.
- BC 3 (top plate)
    - FD: no slip.
    - TCC: 308 K. Based on information reported in existing literature[2], many TFFF devices used for this purpose have a temperature gradient of approximately 100 to 1000 K per cm of height. Based on the height of the channel, this corresponds to 1-10 K difference between the top and bottom plates. We settled on a 10K temperature difference because this was still

reasonably low, but allowed for enough accumulation so that the effects of the thermophoretic phenomenon could be observed.

- o  DGM: no mass flux.
- BC 4 (channel exit)

    o  FD: outlet pressure of 101.3 kPa.

    o  TCC: convective flux.

    o  DGM: convective flux.

Results and Discussion

The following results are for a single compound in a TFFF channel having dimensions as specified by the literature[2], with a temperature gradient of 10K between the top and bottom plates.

For the case with no flow at the inlet and a fully developed temperature gradient, the resulting concentration gradient is shown below in Fig. 3.
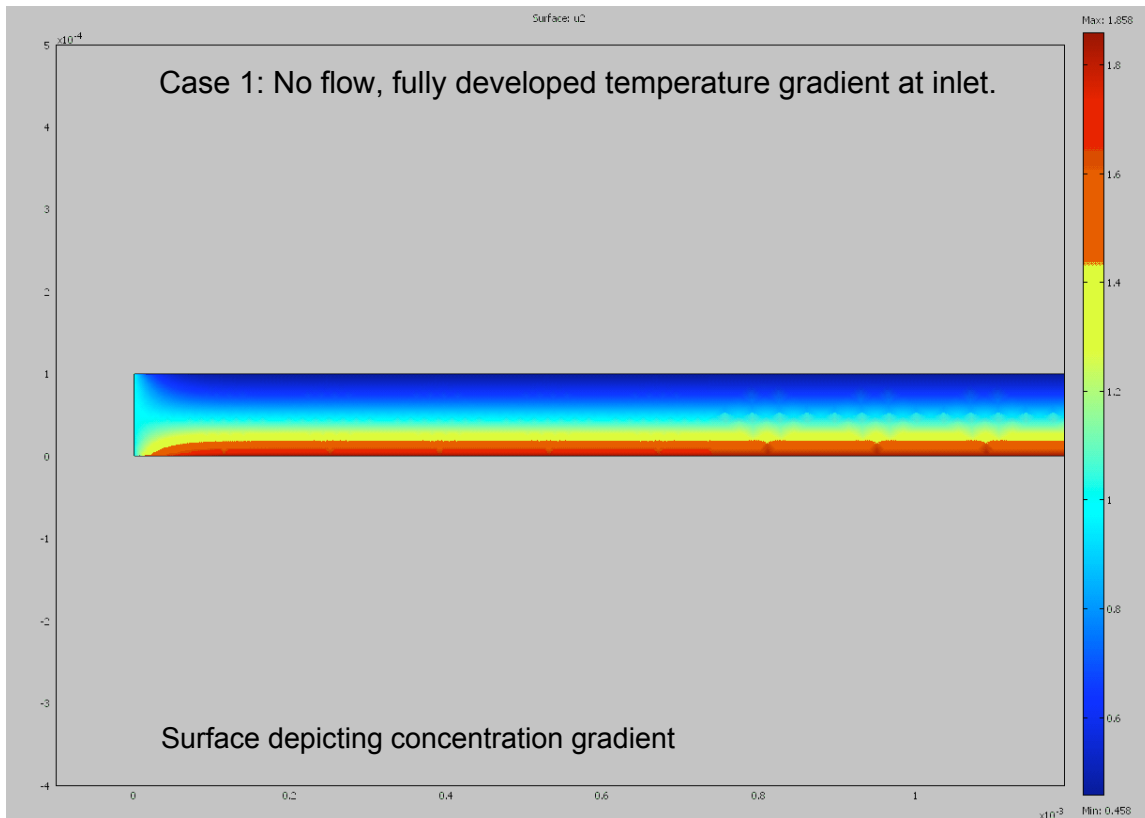
Figure 3: concentration gradient for no flow with fully developed temperature at inlet.

Note that in Fig. 3, we are only looking at the entrance of the channel (the channel is much, much longer than what is shown here), but that the concentration gradient becomes fully developed only after a short distance. This is due to the fact that this is a steady state solution, and there is no fluid flow through the channel. This means we are looking at what would happen after a long time had passed, where the solute is simply diffusing through a stagnant media.

Next, for the case with a fully developed temperature gradient at the inlet, but with flow, the concentration gradient is shown below in Fig. 4.
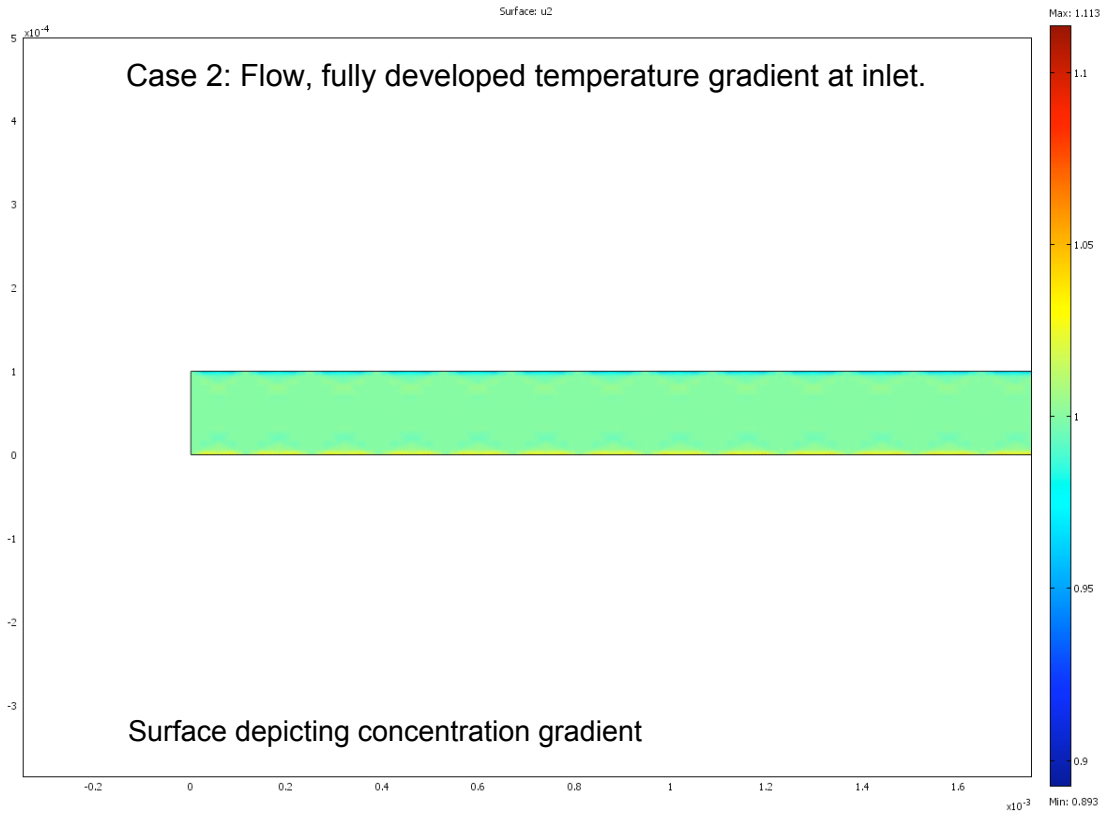
Figure 4: concentration gradient with flow and fully developed temperature gradient at inlet.

Here we note that the concentration is nearly uniform, except at the top and bottom plates, where we witness a slight accumulation on the bottom, and a slightly lower concentration at the top. This is an expected result; since we now have flow, the fully-developed concentration gradient that we witnessed in the first case (no flow) will not take place near the inlet of the channel (and in this case, the concentration gradient at the outlet is not much different).

To illustrate the key difference between the case shown in Fig. 4 and the last case (flow with no temperature gradient at inlet), we present Figs. 5a-b, which depict the

temperature gradient for fully developed case (a) and the case with a thermal entry region
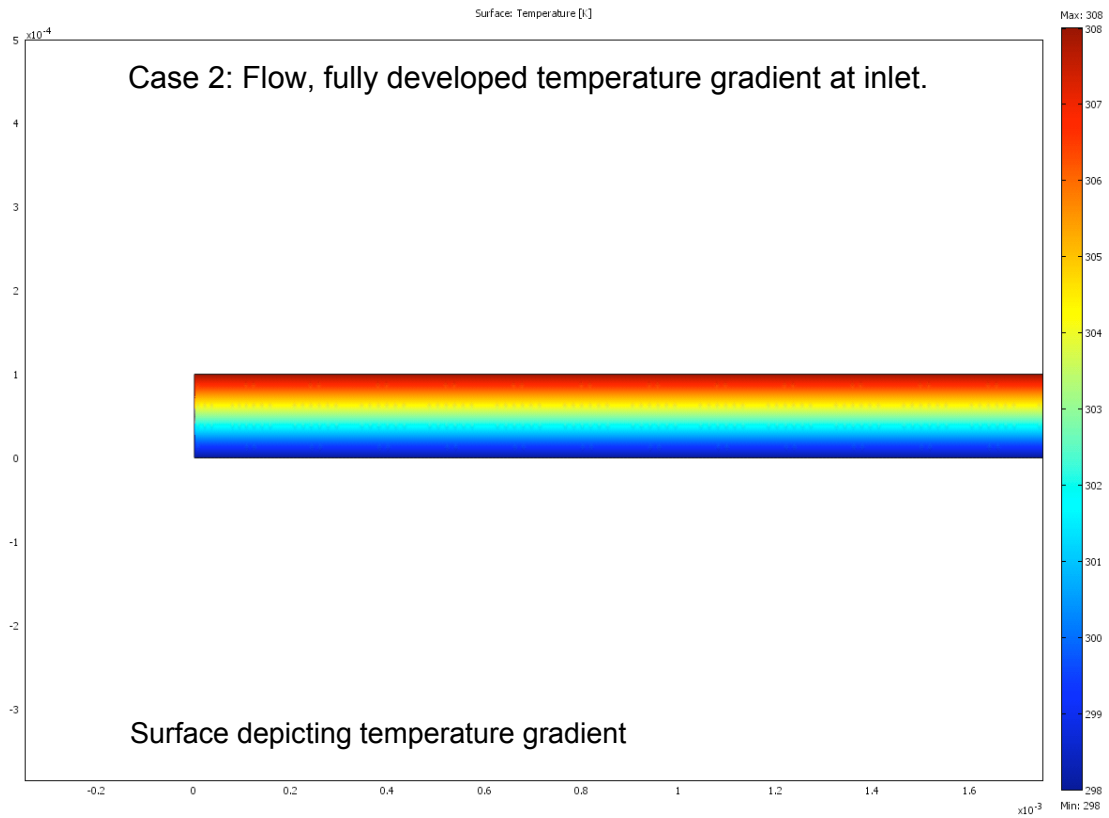
(b).



Figure 5a: temperature gradient for fully developed case – note that, as expected, the

temperature gradient is completely established before entering the channel.
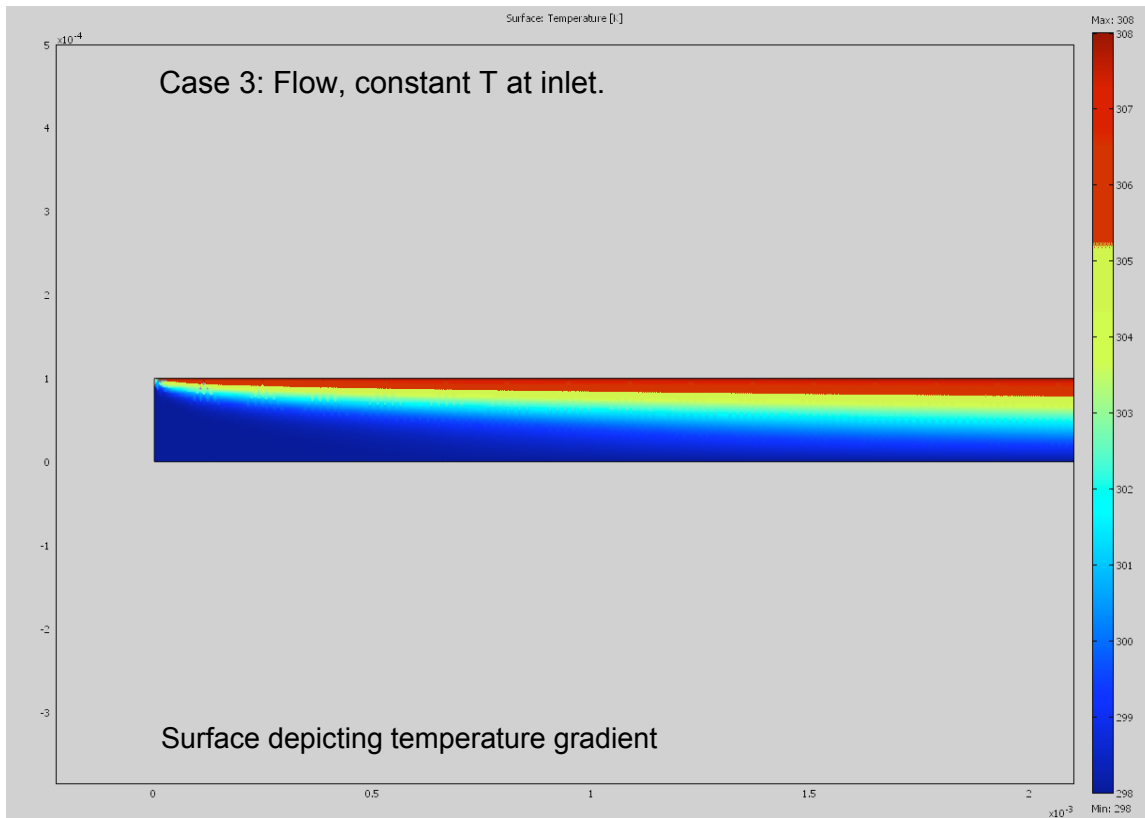
Figure 5a: temperature gradient for the thermal entry-region case – here we assume the fluid enters the channel at ambient temperature, and it takes a while as the fluid moves through the channel for the temperature gradient to become fully established.

Since one of our primary objectives was to determine the length of the thermal entry region, we present Fig. 6, which shows a graph of the centerline temperature as a function of the distance traveled through the channel.
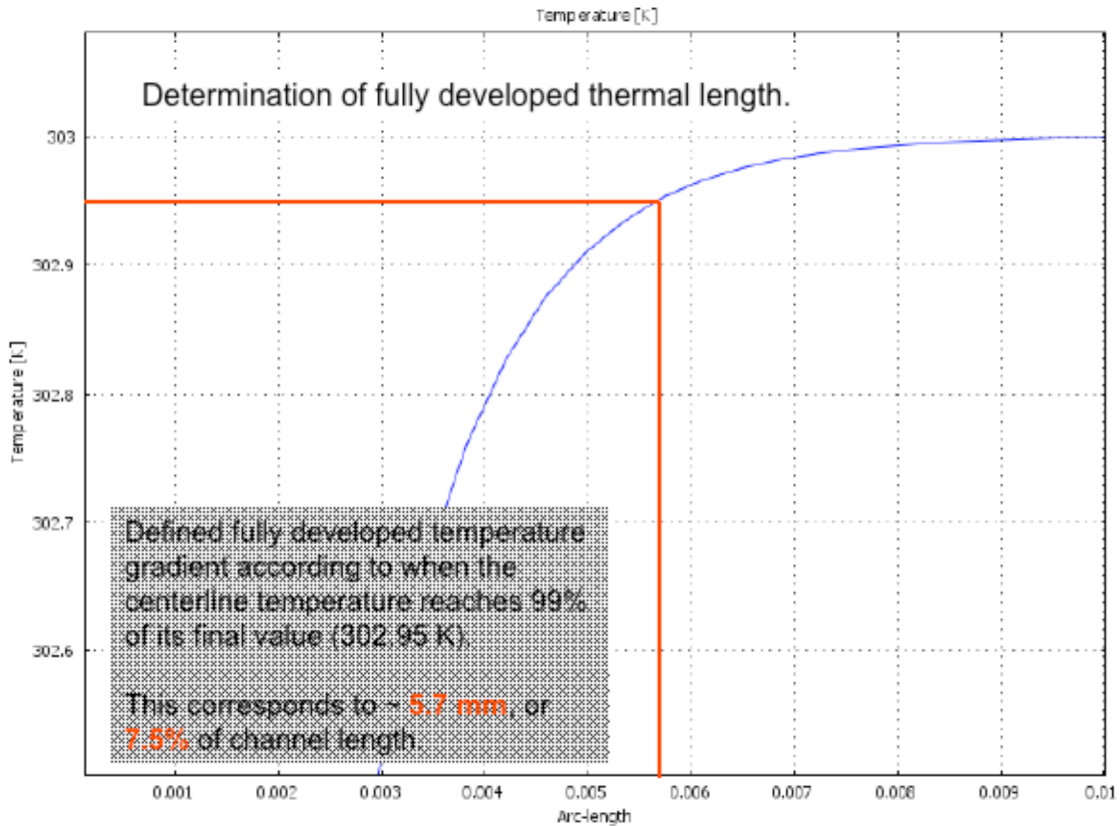
Figure 6: a graph of the centerline temperature as a function of the distance through the channel.

Note in Fig. 6 that the centerline temperature approaches its final value (303K) approximately 5.7 mm through the 76 mm channel, which corresponds to 7.5% of its total length.  Hence, we can conclude that for a temperature difference of 10K, based on the dimensions of this TFFF device, for approximately 7.5% of the channel length, the temperature gradient is not yet established.

We also want to investigate the degree of accumulation that we are achieving with this final case; the concentration gradient for this case is shown below in Figs. 7a-b.
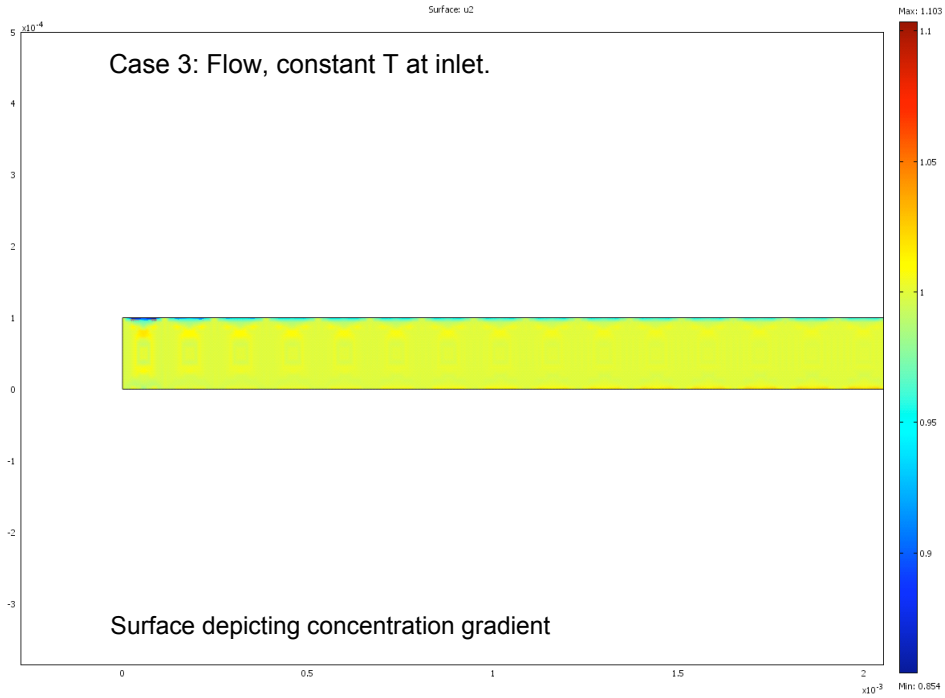
Figure 7a: concentration gradient for case with flow and constant T at inlet.
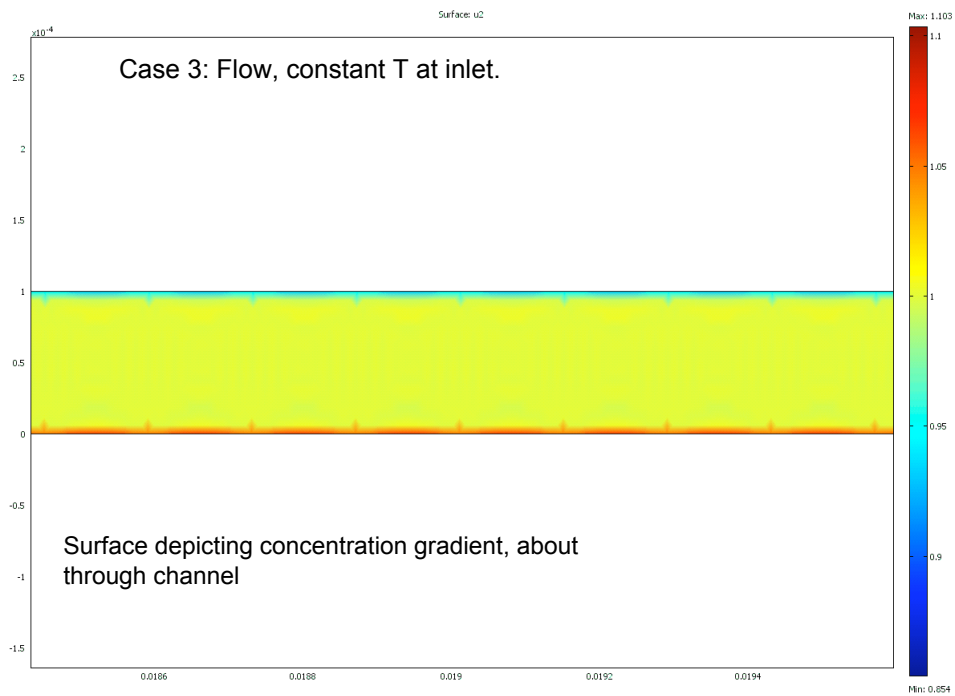


Figure 7b: surface concentration for the same conditions above, but farther through the channel.

We can see from Figs. 7a-b that, although the temperature gradient takes slightly longer to establish itself, the degree of accumulation is more or less negligible. In the case with the fully developed temperature at the inlet, we noted in Fig. 4 that the concentration gradient maxed out at the bottom plate at approximately 1.05, and had a minimum at the top plate of approximately 0.95; the same effect that we witness in the case shown in Figs. 7a-b. We can conclude from this analysis that the maximum degree of accumulation achievable under these conditions likely takes place long before the terminal outlet of the channel.

As a cautionary note – here we are investigating the degree of accumulation of one species on the bottom of the plate – not the ability of the device to separate two different species – which relies much more on the interactions between the individual species and the surface of the bottom plate. The accumulation process is merely what enables what is analogous to chromatography by driving the species down to the bottom plate with different forces.

Conclusions

From these results, we can infer that the thermal entry region does not appear to have a significant effect on the degree of accumulation of a single species in a TFFF device *under these specific conditions*. It is possible that the entry region of a device may need to be taken into account under other conditions (such as for molecules with much bigger

or smaller thermal/mass diffusivities, or at different temperatures), but here, we can not see any qualitative or quantitative effect.

We were able to conclude, however, that although the thermal entry region may have a near negligible impact on the fully developed concentration gradient, it is most certainly non-negligible in length.  For these conditions we found very clearly that the temperature will not be fully developed until the fluid has passed through approximately 7.5% of the channel length.  This is a quantity, however, that depends on the magnitude of the temperature difference, the thermal conductivity of the fluid, and the distance between the top and bottom plates.

Finally, it is worth noting that in order to properly model a TFFF device in order to assess its ability to separate two or more solutes, more equation systems must be solved (one deGroot & Mazur system for every solute in question), and likely, a transient solution will be needed.  Transient solutions can be quite difficult, and although this is possible to do with Comsol ©, we were not able to achieve these sorts of solutions due to the logistical limitations of this project.

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[1] Giddings, J. Calvin. "Science." Field-Flow Fractionation: Analysis of Macromolecular, Colloidal, and Particulate Materials 260(1993): 1456-1465.

[2] Janca, Josef. "Micro-Thermal Field-Flow Fractionation in the Analysis of Polymers and Particles: A Review." International Journal of Polymer Anal. Charact. 11(2006): 57-70.