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# Determination of the functioning parameters in asymmetrical flow field-flow fractionation with an exponential channel

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ABSTRACT

The flow conditions in normal mode asymmetric flow field-flow fractionation are determined to approach the high retention limit with the requirement $d \ll l \ll w$, where $d$ is the particle diameter, $l$ the characteristic length of the sample exponential distribution and $w$ the channel height. The optimal entrance velocity is determined from the solute characteristics, the channel geometry (exponential to rectangular) and the membrane properties, according to a model providing the velocity fields all over the cell length. In addition, a method is proposed for in situ determination of the channel height.



## 1. Introduction

Field-flow fractionation is a tool for the separation and characterization of macromolecules and particles [1,2]. Flow field-flow fractionation (FlFFF) is now mainly used in the asymmetrical configuration (AsFl-FFF or AF4) in various fields as food analysis [3], recovery of nanoparticles and proteins [4], drug delivery [5], fractionation of superferrimagnetic multicore nanoparticles [6], characterization of protein conjugate [7], analysis of starch [8,9] and liposomes [10]. It has been analyzed by several models [11–16] and a critical overview appeared recently [17]. Many publications [14–16,18] have been devoted to improve the interpretation of asymmetric flow field-flow fractionation (AsFl-FFF) data through a better description of the transverse velocity field in the domain near the wall where the solute is spread. These works are based on the assumption of a cross-flow velocity constant implying consequently the estimation of the axial transport velocity field. However taking into account the pressure variations in a recent model [19,20] led to an improved description of the flow rates through the whole system. Two cell designs were proposed to approach more accurate constancy of both velocity fields all over the length of the cell than in the usual cells. However the present manuscript proposes an analysis of data using the expression of both axial through the channel and transversal through the membrane velocity fields where we consider the usual cell geometries, i.e. membrane with constant permeability and permeate compartment of constant large height compared to the sample channel one. The analysis will examine the two cases of channel constant breadth (rectangular) and exponential decreasing breadth in the direction of axial flow (exponential).

Generally, the membranes are characterized by their molecular weight cut off, a useful parameter as they must retain the solutes, macromolecules or particles, in the sample channel. However, in the present work, the important characteristic is their resistance to the flow of solvent. The scope is to find the right balance between axial flow in the channel and transverse flow through the membrane to achieve an efficient separation, in the high retention limit. The model includes the assumption of the Poiseuille parabolic axial velocity profile.

## 2. Theory

### 2.1. Mean axial velocity and membrane (cross-flow) velocity as a function of distance

The system under study is schematically represented in Fig. 1, with the flow rate in the channel $q_c(z)$ and the flow rate through the membrane $q_m(z)$. There is no flow through the impermeable upper wall of the channel of length $L$. The height of the channel $w$ is very small with respect to the breadth, which is an exponential function of the distance (characteristic length $s^{-1}$):

$$b(z) = b(0)e^{-sz} \quad (1)$$

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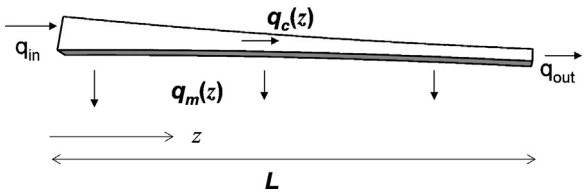


**Fig. 1.** Scheme of flow cell of length $L$ with varying channel breadth with distance $z$ to entrance. Cross-flow or membrane flow rate $q_m(z)$. Sample channel flow rate $q_c(z)$. $q_{in} = q_c(0)$. $q_{out} = q_c(L)$.

A characteristic length $\Lambda$ was previously introduced [19,20] which, for channel and membrane of same constant breadth, is the length where the channel and the membrane have the same hydraulic resistance. It depends on the channel height $w$ and a characteristic length of the membrane (+ support) $\Lambda_m$.

$$\Lambda = \left(\frac{w^3}{\Lambda_m}\right)^{1/2}, \quad L^* = \frac{L}{\Lambda} \tag{2a}$$

$$U = \left[L^{*2} + \left(\frac{sL}{2}\right)^2\right]^{1/2} \tag{2b}$$

For sake of simplicity, we will assume the pressure in the permeate compartment to be constant as in previous works [19,21]. In the writing of equations, the three variables $L^*$, $U$ and $sL$ may appear; however it should be kept in mind that there are only two independent variables. The solutions for the mean axial velocity $v_c$ and membrane (cross-flow) velocity $v_m$ were given previously (Eqs. (A11)–(A12) in Annex of [19]) as a function of the reduced distance $Z = z/L$.

$$v_c(Z) = v_c(0)\frac{U\cosh[U(1-Z)] + (\beta L^{*2} - (sL/2))\sinh[U(1-Z)]}{U\cosh U + (\beta L^{*2} - (sL/2))\sinh U} e^{sLZ/2} \tag{3}$$

$$v_m(Z) = v_m(0)\frac{\beta U\cosh[U(1-Z)] + (\beta(sL/2)+1)\sinh[U(1-Z)]}{\beta U\cosh U + (\beta(sL/2)+1)\sinh U} e^{sLZ/2} \tag{4}$$

In the configuration of a spacer of constant breadth, hence $s = 0$ and $U = L^*$, these expressions become:

$$v_c(Z) = v_c(0)\frac{\cosh[L^*(1-Z)] + \beta L^*\sinh[L^*(1-Z)]}{\cosh L^* + \beta L^*\sinh L^*} \tag{5}$$

$$v_m(Z) = v_m(0)\frac{\beta L^*\cosh[L^*(1-Z)] + \sinh[L^*(1-Z)]}{\beta L^*\cosh L^* + \sinh L^*} \tag{6}$$

$\beta$ is the ratio of the resistance of the circuit after the channel exit over the channel resistance of a channel of constant breadth $b(L)$. It is linked to the split of the entrance flow rate into the two exit flow rates out of the channel and permeate compartments.

### 2.2. Ratio $r_q$ of channel exit flow rate over entrance flow rate. Connection to parameter $\beta$

Let $r_q$ be the ratio of channel exit flow rate $q_{c,out}$ over channel entrance flow rate $q_{c,in}$.

$$r_q = \frac{q_{c,out}}{q_{c,in}} = \frac{v_c(1)}{v_c(0)}e^{-sL} = r_v e^{-sL} \tag{7}$$

From Eq. (3), we deduce:

$$r_q = \frac{q_c(1)}{q_c(0)} = \frac{U}{U\cosh U + (\beta L^{*2} - (sL/2))\sinh U}\exp\left(-\frac{sL}{2}\right) \tag{8}$$

which becomes in the configuration of a spacer of constant breadth:

$$r_{q,s=0} = \frac{1}{\cosh L^* + \beta L^*\sinh L^*} \tag{9}$$

hence

$$\beta(sL) = \frac{Ue^{-sL/2}r_q^{-1} - (U\cosh U - (sL/2)\sinh U)}{L^{*2}\sinh U} \tag{10a}$$

$$\beta(0) = \frac{r_q^{-1} - \cosh L^*}{L^*\sinh L^*} \tag{10b}$$

The condition $\beta \geq 0$ provides the upper boundary of $r_q$ which corresponds to the same pressure at the exit of the channel and in the permeate compartment:

$$r_{q,\max}(sL) = \frac{Ue^{-sL/2}}{U\cosh U - (sL/2)\sinh U} \tag{11a}$$

$$r_{q,\max}(0) = \frac{1}{\cosh L^*} \tag{11b}$$

Such a domain corresponds to a positive membrane velocity (i.e. from sample channel to permeate compartment): the condition $\beta > 0$ is equivalent to the condition $v_m(1) > 0$. Additional resistance at the exit of permeate compartment would allow to increase $r_q$ above $r_{q,max}$ by increasing pressure in that compartment and inducing inverse flow through the membrane. Closing of that exit corresponds indeed to the absolute limit $r_q = 1$, for instance used recently to determine the void-time [21]. It can be also verified that the upper limit (Eqs. (11)) is the unity when $L^* \to 0$ (impermeable membrane).

### 2.3. Elution time in the high retention limit over the full length of the cell

In the limit of high retention (characteristic length of the solute exponential distribution from the wall much smaller than the channel height), elution time is independent of the flow rate but dependent on the ratio of channel exit over entrance flow rates. Indeed, an increase of axial flow rate thus of axial velocity is counterbalanced by the transverse displacement of the solute towards the wall (membrane) induced by the simultaneous increase of the (cross-flow) membrane velocity (Fig. 2).

The solute velocity averaged over its exponential distribution from the wall (characteristic length $D/v_m$, assumption of half infinite space: see details on approximations in Appendix A or [15]) is:

$$V_s(Z) = \frac{6D}{w}\frac{v_c(Z)}{v_m(Z)} \tag{12}$$

The elution time over the cell length is:

$$t = \int_0^1 \frac{LdZ}{V_s(Z)} = \frac{wL}{6D}\int_0^1 \frac{v_m(Z)dZ}{v_c(Z)} \tag{13}$$

Let us consider the general case of a breadth $b$ varying with distance. The conservation of the mass of the incompressible fluid leads to the relation between membrane transverse velocity $v_m$ and axial channel velocity $v_c$:

$$v_m(Z) = -\frac{w}{L}\left(\frac{dv_c}{dZ} + \frac{1}{b}\frac{db}{dZ}v_c(Z)\right) \tag{14}$$

which, put in Eq. (13), leads to:

$$t = \left(\frac{w^2}{6D}\right)\ln\frac{q_{c,in}}{q_{c,out}} \tag{15}$$