A chip system for hydrodynamic chromatography

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APPENDIX

The transient form of species dispersion in a rectangular channel

Exact flow profile.

The exact velocity profile in a channel of a rectangular cross-section of width w and depth h is given by[1]

$$u = -\frac{\partial p}{\partial z}\frac{h^2}{8\eta}\left[1-\left(\frac{2y}{h}\right)^2 + 32\sum_{n=1,3,5...}^{\infty}\frac{(-1)^{\frac{n+1}{2}}\cosh\frac{n\pi z}{h}\cos\frac{n\pi y}{h}}{n^3\pi^3\cosh\frac{n\pi w}{2h}}\right] \quad (1)$$

For an aspect ratio $w/h \rightarrow \infty$ the average velocity $<u>$ equals $^2/_3\, u_{max}$ as in the approximation by planparallel plates (used in Chapter 3). This approximation gives a very good estimate (~ 5 % error) for $<u>$ already for aspect ratios > 10.[1] Figure 1 shows a contour plot of the velocity profile (eq. 1) for this aspect ratio.

The hydrodynamic entrance length[2] over which this profile develops, $l \sim 0.1 Re.h$ is much smaller than the height of the channel because of the very small Reynolds number in the considered application ($Re << 1$).

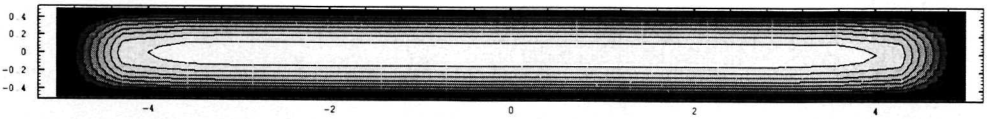

Figure 1: Contour plot of the velocity profile (eq. 1) for an aspect ratio $w/h = 10$.

Transient dispersion.

The very narrow regions along the side walls where the velocity decreases to zero can eventually cause a considerable dispersion, even in the case of very large aspect ratios. The transient form of this (cross-sectional-average) dispersion was studied by in detail by Doshi et al.[1] Their results are adapted here in the formalism of effective diffusivity and dispersion coefficient (an alternative[3] to the plate-height concept). The additional peak variance σ_x^2 created during the separation can be written as a function of an effective diffusivity D_{eff} and the time t:

$$\sigma_x^{\ 2} = 2D_{eff}t + \sigma_{x,0}^2 \tag{2}$$

The effective diffusion constant includes a contribution due to stationary diffusion effects (the true diffusion coefficient D) and a convective component:

$$D_{eff} = D\left(1 + \alpha_0 Pe_{1/2}^2\right) \tag{3}$$

where

$$Pe_{1/2} = \frac{(h/2)\langle u \rangle}{D} \tag{4}$$

The subscript 1/2 reflects that this Peclet number is defined with respect to half of the characteristic dimension, contrary to the definitions of Pe numbers used in the preceding chapters.

For large aspect ratios the effective diffusivity can be written as a sum of the separate contributions of the gradients in the x-direction (K_2) and the y-direction (K_3)

$$\left(\frac{D_{eff}}{D} - 1\right)\left(\frac{16\eta D}{h^3}\left(\frac{\partial p}{\partial z}\right)^{-1}\right)^2 = K_1(t) = K_2(t) + K_3(t) \tag{5}$$

From eq. (1) a relation between the pressure gradient and maximum velocity follows as

$$u_{max} = -\frac{\partial p}{\partial z}\frac{h^2}{8\eta} \tag{6}$$

Substituting eq. (6) into eq. (5) and comparing eq. (4) and (3) with eq. (5) gives a relation

$$\langle u \rangle = \sqrt{\frac{K_1}{\alpha_0}} u_{\max} \tag{7}$$

Because for larger aspect ratios $<u> \sim {}^2/_3\, u_{max}$, the dispersion constant can be related to K_l as

$$\alpha_0 = \tfrac{9}{4} K_1 \tag{8}$$

The solution found by Doshi for K_l can be then related to the dispersion constant α_0 as:

$$\alpha_0 = \tfrac{9}{8} \sum_{m=1}^{\infty} B_m^2 (1 - e^{-m^2\pi^2 t^*}) + \tfrac{9}{8} \sum_{n=1}^{\infty} B_n^2 (1 - e^{-n^2\pi^2 t^* (w/h)^2}) \tag{9}$$

in which:

$$B_m = \frac{256(-1)^m}{m\pi^6} \sum_{j=0}^{\infty} \frac{\tanh\left[\frac{(2j+1)\pi w}{2h}\right]}{(2j+1)^3((2j+1)^2 + 4m^2(h/w)^2)} \tag{10}$$

$$B_n = \frac{4(-1)^n}{\pi^3 n^3} + \frac{256(-1)^{n+1} h}{n\pi^6 w} \sum_{j=0}^{\infty} \frac{\tanh\left[\frac{(2j+1)\pi w}{2h}\right]}{(2j+1)^3(2n+2j+1)(2n-2j-1)} \tag{11}$$

and

$$t^* = \frac{4Dt}{w^2} \tag{12}$$

is the dimensionless time (Fourier number) for the channel width. Thus the dispersion at a certain time t^* is specified by the aspect ratio w/h solely (Figure 2). First the dispersion develops caused by the gradients in the y-direction. For later times the dispersion caused by gradients in the x-direction is added which for $t^* \rightarrow \infty$ leads to a constant dispersion coefficient:

$$\alpha_0 \approx \frac{16}{105} \tag{13}$$

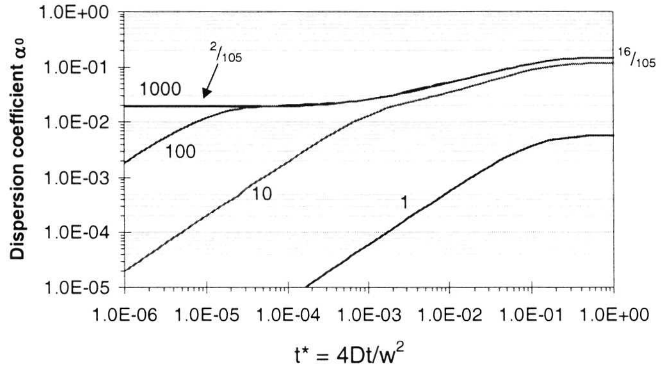

Figure 2: The dispersion coefficient according to eq. (9) for different aspect ratios.

The dispersion curves in Figure 2 are given for instantaneous dispersion constants. The dispersion coefficient averaged over a complete analysis would be:

$$\overline{\alpha_0} = \frac{1}{t}\int_0^t \alpha_0(t)dt \tag{14}$$

Plotting the time-averaged dispersion for a real HDC channel for relevant analysis times is shown in Figure 3. It is clear that this is located in the transient region in which the gradients in the x-direction are starting to add to the dispersion:

$$\frac{h^2}{D} << t << \frac{w^2}{D} \tag{15}$$

It is convenient to approximate the time-averaged dispersion constants for the region $0 < t < 240$ s by using a fit of the form:

$$\alpha_0 = \frac{2}{105}\left[1 + c\left(\frac{Dt}{D_0}\right)^d\right] \qquad (16)$$

In this fit a diffusivity of $D_0 = 3 \times 10^{-11}$ m^2/s is used. The scaling factor D/D_0 can be applied to species with a different diffusion constant D. For an aspect ratio of 500, $c = 0.28$ and $d = 0.47$; for an aspect ratio of 1000, $c = 0.082$ and $d = 0.58$.

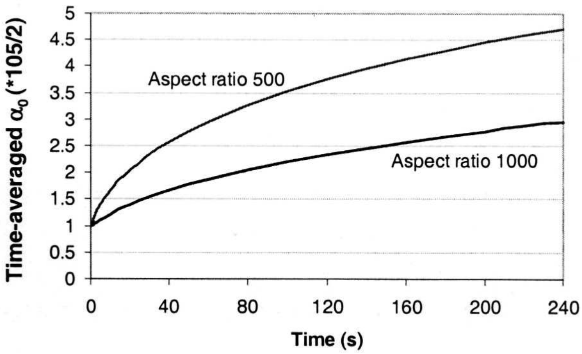

Figure 3: The time-averaged dispersion coefficient for an analyte with $D = 3 \times 10^{-11}$ m^2/s for different channel aspect ratios.

However, in the transient region (eq. 15) this dispersion theory is still overestimating the role of the side wall effect for an actual separation, at least for shorter times. The concentration profile of the sample zone, averaged over the cross-section would not be a Gaussian one, because of the long but narrow tailing along the side walls (Figure 4). This long narrow tail contributes largely to the standard deviation of the corresponding peak but less to its effective width, relevant for the resolution. In practice, large part of this tailing would merge with the baseline.

Nevertheless, although there is clearly a practical region (for slower diffusing species) where the dispersion is lower than that in the long time solution given by eq. (13), further reduction[4,5] or even elimination of the effect (as suggested in Chapter 6) is preferable.

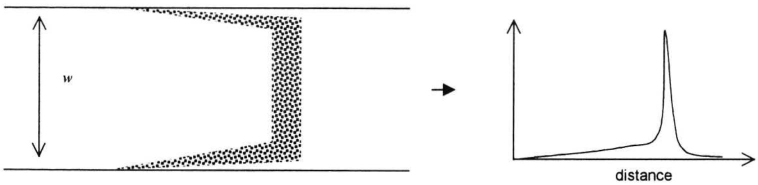

Figure 4: A schematic illustration of the effect of the side walls on the peak shape, in the early parts of the transient region.

[1] M.R. Doshi, P.M. Daiya, W.N Gill, Chem. Eng. Sci., 33, 1978, 795–804.
[2] R.B. Byrd, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, Wiley, New York, 1966.
[3] R. Aris, Proc. Roy. Soc. A, 252, 1959, 538.
[4] M.J.E. Golay,. J. Chromatogr., 216, 1981, 1–8.
[5] D. Dutta, D.T. Leighton Jr., Anal. Chem., 73, 2001, 504–513.