Journal of Chromatography, 600 (1992) 133–137
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 942

Transverse particle redistribution in a flat channel for SPLITT or integral Doppler anemometry

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ABSTRACT

The solution of the convective diffusion equation for the case of a flat channel with a transverse focusing force is proposed. It is shown that in practically important situations this solution can be expressed as a series containing Hermite polynomials. Using this solution, the transversal distributions of particles at different distances and corresponding to different distributions at the channel input were calculated. The situations in which there are uniform and delta-function-like transverse distributions of particles were examined. First. these curves show that transverse non-equilibrium peaks of concentration may exist if the distance from the channel input is short enough. Second, it is confirmed that there exists a possibility of high resolution under very non-equilibrium conditions. The transversal peaks of concentration may be used for the analysis of fractions that cannot be separated under equilibrium conditions.

INTRODUCTION

Recently, methods of continuous liquid mixture separation and analysis based on field flow fractionation (FFF) principles have been developed. A splitting of the flow in an FFF channel by means of longitudinal splitters was suggested [1,2] for the separation of different fractions in a field of transverse force. This method was called SPLITT (continuous separation in split-flow thin cell) separation. The analytical variant of continuous FFF has been considered [3–5] in which photon-correlation spectroscopy is used for the visualization of transverse particle distribution, *i.e.*, integral Doppler anemometry (IDA). IDA analysis is easiest if a focusing transverse field is applied. The possibility of protein separation in a SPLITT cell with a transverse electrical field has been demonstrated [6]. IDA spectra have been registered in a flat channel where a transverse focusing hydrodynamic force was acting [7,8]. A model suspension containing relatively large (*ca.* 1 μm) particles was used, and it was shown that the transverse particle distribution was essentially non-equilibrium. Because the particle size was relatively large, the trajectories of particles were used [7,8] for the calculation of IDA spectra, neglecting the Brownian motion. The possibilities of SPLITT separation in a non-equilibrium (transfer) regime have been discussed [6]. Most experimental situations do not permit diffusion to be neglected, and the examination of the convective diffusion equation is necessary.

THE MATHEMATICAL PROBLEM

In a flat channel the dimensionless form of the convective diffusion equation is as follows:

$$\partial/\partial x_1(\partial/\partial x_1 + \partial E/\partial x_1)c = Pe(1 - x_1^2)\partial c/\partial z_1 \qquad (1)$$

where $x_1 = x/h$, $z_1 = z/h$; x, z = transverse and longitudinal coordinates ($x = 0$ is placed in the plane of symmetry and $z = 0$ at the inlet of a channel), h = half-width of a channel, c = concentration, $E(x)$ = transverse potential in kT units, kT = thermal energy and Pe = longitudinal Peclet number:

$$Pe = u_0 h/D$$

where u_0 = maximum flow velocity and D = diffusion coefficient of particles. If the transverse potential is of the focusing type, then

0021-9673/92/$05.00

$$E(x_1) = E_0(x_1 - x_0)^2 \quad (2)$$

where E_0 = transverse Peclet number and x_0 = dimensionless coordinate of a focusing point. The boundary conditions for eqn. 1 take into account the inpermeability of the walls and the constancy of concentration at the channel inlet:

$$(\partial/\partial x_1 + \partial E/\partial x_1)c = 0 \quad \text{at } x_1 = \pm 1 \quad (3)$$

$$c = c_0 \quad \text{at } z_1 = 0 \quad (4)$$

where c_0 is the initial concentration. These boundary conditions permit a search for the solution of eqn. 1 in the form

$$c = c_1(x_1)e^{-\lambda z_1} \quad (5)$$

and its transformation into an ordinary differential equation:

$$d/dx_1(d/dx_1 + dE/dx_1)c_1 + Pe\lambda(1 - x_1^2)c_1 = 0 \quad (6)$$

with the boundary conditions in eqn. 3 and eigenvalue λ. The substitution

$$c_1 = u(x_1)e^{-E(x_1)/2} \quad (7)$$

transforms eqn. 6 into an equation of the Sturm–Liouville type:

$$d^2u/dx_1^2 + [E_0 - E_0^2(x_1 - x_0)^2 + Pe\lambda(1 - x_1^2)]u = 0 \quad (8)$$

with the boundary conditions

$$du/dx_1 + E_0(x_1 - x_0)u = 0 \quad \text{at } x_1 = \pm 1 \quad (9)$$

Different solutions of a Sturm–Liouville equation are orthogonal:

$$\int_{-1}^{1} (1 - x_1^2)u_m u_n dx_1 = \delta_{mn} \int_{-1}^{1} (1 - x_1^2)u_n^2 dx_1 \quad (10)$$

where n, m = 0, 1, 2 ... and δ_{mn} = Kronecker symbol.

Eqn. 9 permits the solution of eqn. 1 with potential as in eqn. 2 to be written in the following form:

$$c(x_1,z_1) = \sum_{n=0}^{n=\infty} B_n e^{-\lambda z_1 - E_0(x_1 - x_0)^2/2} u_n(x) \quad (11)$$

where

$$B_n = \int_{-1}^{1} e^{E(x_1)/2}(1 - x_1^2)_n dx_1 / \int_{-1}^{1} (1 - x_1^2)u_n^2 dx_1 \quad (12)$$

After introducing a new coordinate:

$$y = (E_0^2 + Pe\lambda)^{1/4}[x_1 - x_0E_0^2/(Pe\lambda + E_0^2)] \quad (13)$$

we obtain the equation

$$d^2u/dy^2 + \{[(E_0 + Pe\lambda)(E_0^2 f_0 + Pe\lambda)/(E_0^2 + Pe\lambda)]/(E_0^2 + Pe\lambda)^{1/2} - y^2\}u = 0 \quad (14)$$

where $f_0 = 1 - x_0^2$, and the boundary conditions are

$$du/dy + E_0(E_0^2 + Pe\lambda)yu = 0 \quad (15)$$

at

$$y = (Pe\lambda + E_0^2)^{1/4}[\pm 1 - E_0^2 x_0(E_0^2 + Pe\lambda)] \quad (16)$$

According to eqn. 16, the boundary conditions in eqn. 15 must be satisfied at $y \approx E_0^{1/2} \gg 1$. In this situation we may assume that the boundary conditions in eqn. 15 are satisfied at $y = \pm\infty$. In addition to the conditions in eqn. 15, we must assume that $c = 0$ at the walls of channel, because for the focusing potential in eqn. 2 virtually all the particles are rejected from the walls at sufficiently short distances from the inlet. Usually $E_0 \approx$ 10–100 in FFF, but it has been shown [7,8] that $E_0 \approx 1000$. After our simplification of the boundary conditions, only Hermite functions [9] can be the solutions of eqn. 14:

$$u_n(y) = e^{-y^2/2}H_n(y) \quad (17)$$

where

$$H_n(y) = (-1)^n e^{y^2} d^n(e^{-y^2})/dy^n \quad (18)$$

is the Hermite polynomial. For the eigenvalues λ we obtain the following equation:

$$E_0 + Pe\lambda(E_0^2 f_0 + Pe\lambda)/(E_0^2 + Pe\lambda) = (2n + 1)(E_0^2 + Pe\lambda)^{1/2} \quad (19)$$

TRANSVERSE PARTICLE DISTRIBUTIONS AT $Pe\lambda \ll E_0^2$

The expression on the left-hand side of eqn. 19 rises monotonically with λ, and for this reason only one λ corresponds to any n. However, eqn. 19 has no analytical solution. Usually the channel length is *ca.* 1 cm and $h \approx 10^{-2}$ cm, so $z_1 \approx 10^2$ and $\lambda \leqslant z_1^{-1} \approx 10^{-2}$. Under usual FFF conditions E_0 = 10–100 and $Pe \approx 10^3$–10^4, so $Pe\lambda \approx (1$–$10^{-2})E_0^2$. As can be shown [7,8], $Pe \approx 10^6$ and $E_0 \approx 10^3$, so $Pe\lambda \approx 10^{-2}E_0^2$. In other words, in most situations we can assume that $Pe\lambda \ll E_0^2$, and obtain from eqns. 17–19

$$u_n = e^{-E_0(x_1 - x_0)^2/2} H_n[E_0^{1/2}(x_1 - x_0)] \quad (20)$$

$$Pef_0\lambda/E_0 = 2n \quad (21)$$

Eqns. 20 and 21 hold true for $n \ll E_0 f_0/2$. Because $H_n(y) \approx (2y)^n$ for $y \gg 1$, any member of the series 10 is *ca.* $(E_0)^{1/2} \exp(-E_0) \ll 1$ near the walls, and the solution in eqns. 20 and 21 should be considered to be true. The conditions of orthogonality of the polynomials 20 are simpler than eqn. 10:

$$\int_{-\infty}^{\infty} e^{-x^2} H_n(x) H_m(x) dx = \delta_{mn} n!(\pi)^{1/2}$$

and for coefficients B_n we obtain instead of eqn. 12

$$B_n = c_0 \int_{-\infty}^{\infty} H_n[(E)^{1/2}(x_1 - x_0)]dx_1/[2^n n!(\pi)^{1/2}] \quad (22)$$

Using the recurrent relationships [9]

$$d[H_n(y)]/dy = 2nH_{n-1}(y)$$

and the asymptotic expression for $H_n(y)$ at $y \gg 1$, we obtain

$$B_n = c_0(E_0)^{(n+1)/2}[(1 - x_0)^{n+1} - (-1 - x_0)^{n+1}]/[2(\pi)^{1/2}(n + 1)!] \quad (23)$$

Expressions 20, 21 and 23 permit us to obtain the function $c(x_1, z_1)$ for $E_0, Pe \gg 1$ and $n \ll E_0 f_0/2$:

$$c(x_1, z_1) = c_0(E_0/\pi)^{1/2}\{[(E_0)^{1/2} e^{-2E_0 z_1/f_0 Pe}]^n[(1 - x_0)^{n+1} - (-1 - x_0)^{n+1}](-1)^n d[e^{-E_0(x_1 - x_0)^2}]/dx_1\}/(n + 1)! \quad (24)$$

With the help of eqn. 24 we can explain most of the phenomena that take place in the process of redistribution of particles in a flat laminar flow and transverse focusing potential.

RESULTS AND DISCUSSION

In the non-equilibrium (transfer [6] regime, transverse peaks of concentration appear owing to the decrease in the transverse force and velocities of particles on approaching the focusing point. In this situation the particles, which are released from the walls, are concentrated in the regions where the transverse force is small. The positions of non-equilibrium peaks, as shown [7,8], can be different at the same distance z for particles with different values of E_0, even if they have the same focusing point, for example $x_0 = 0$. In this case,

$$c(x_1, z_1) = c_0(E_0/\pi)^{1/2} \sum_{n=0}^{n=\infty} [a^n d^{2n}(e^{-E_0 x_1^2})/dx_1^{2n}]/[(2n + 1)!(E_0)^n] \quad (25)$$

where $a = E_0 e^{-(4E_0 z_1/Pe)}$.

Eqn. 25 gives the possibility of calculating approximately the maximum distance at which the non-equilibrium peaks still exist. At large distances z_1, where $a \ll 1$, eqn. 25 transforms into the Boltzmann exponent, which has the maximum at $x_1 = 0$. At smaller distances two members of the series 25 should be taken into account:

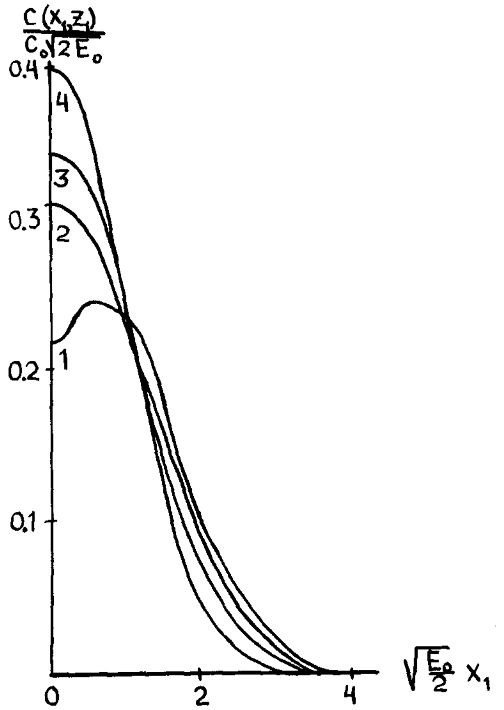

Fig. 1. Transverse particle distributions with a uniform particle distribution at the channel input. $E_0 = 20$; $Pe = 2 \cdot 10^3$. (1) $a = 2.0$; (2) $a = 1.0$; (3) $a = 0.5$; (4) Boltzmann distribution. $a = E_0 e^{-4E_0 z_1/Pe}$.

$$c(x_1, z_1) \approx c_0(E_0/\pi)^{1/2}e^{-E_0x_1^2}[1 + + (a/6)(4E_0x_1^2 - 2)] \quad (26)$$

This expression has a maximum at $x = 0$ if $a > 1$, tht is, the non-equilibrium peak is possible at the distances

$z_1 < z_1^* = Pe \ln E_0/4E_0$

For $Pe \approx 10^6$ and $E_0 \approx 10^3$, we obtain $z_1^* \approx 1727$. If the half-width of a channel $h \approx 10^{-2}$ cm, then the distance corresponding to this value is equal to *ca.* 17.3 cm. Although the comparison is very conditional, these parameters are in accordance with specified conditions [7,8], where non-equilibrium peaks were observed. The transverse distributions of concentration t different values of a (*i.e.*, at different distances from the channel input) are shown in Fig. 1. These curves are obtained using first four members of series 25 with $n = 0, 1, 2, 3$. It can be shown that the maximum error is less that 5% even at $a = 2$. The curves in Fig. 1 confirm the possibility of the existence of non-equilibrium transverse peaks of concentration at $a > 1$. A special inlet has been proposed [10,11] to make the initial transverse distribution of particles narrower and to increase the resolution of FFF. If the initial transverse distribution of particles is much narrower that $E_0^{-1/2}$, we can write the initial concentration in eqn. 4 as

$$c = 2c_0\delta(x) \text{ at } z_1 = 0 \quad (27)$$

where δ is the Dirac delta function. The distribution 27 is normalized to obtain the same number of particles in any cross-section of the channel that gives eqn. 4. Using eqns. 22 and 27 we can find coefficients B_n:

$$B_n = 2c_0(E_0/\pi)^{1/2}H_{2n}(0)/[2^{2n}(2n!)] \quad (28)$$

Substituting the values of $H_{2n}(0)$ obtained from the recurrence relationship

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x)$$

$$H_{2n}(0) = (-2)^n(2n - 1)!! \quad (29)$$

where $(2n - 1)!!$ is the product of all uneven numbers $< 2n$, we obtain

$$B_n = 2c_0(E_0/\pi)^{1/2}(-2)^{-n}/[2^n(2n)!!] \quad (30)$$

where $(2n)!!$ is the product of all even numbers from 2 to $2n$. Using eqn. 30, the transverse distribution of particles can be written as

$$c(x_1, z_1) = 2c_0(E_0/\pi)^{1/2}\sum_{n=0}^{n=\infty}[b^n/(2n!!)]d^{2n}(e^{-E_0x_1^2})/d(E_0^{1/2}x_1)^{2n} \quad (31)$$

Transverse distributions corresponding to eqn. 31 with different values of $b = (e^{-4E_0z_1/Pe})/2$ (*i.e.*, at different distances from the channel input) are shown in Fig. 2. A characteristic feature of these curves is the increase in their width with increasing distance from the channel input. Only at large distances, when $b \ll 1$, does the transverse distribution reach the maximum width $E_0^{-1/2}$ and a Boltzmann transverse distribution is established. This is in good agreement with the suggestion [10,11] that a "pinched" inlet must be used to increase the resolution of FFF or SPLITT in the non-equilibrium regime when the transverse particle distribution is narrow.

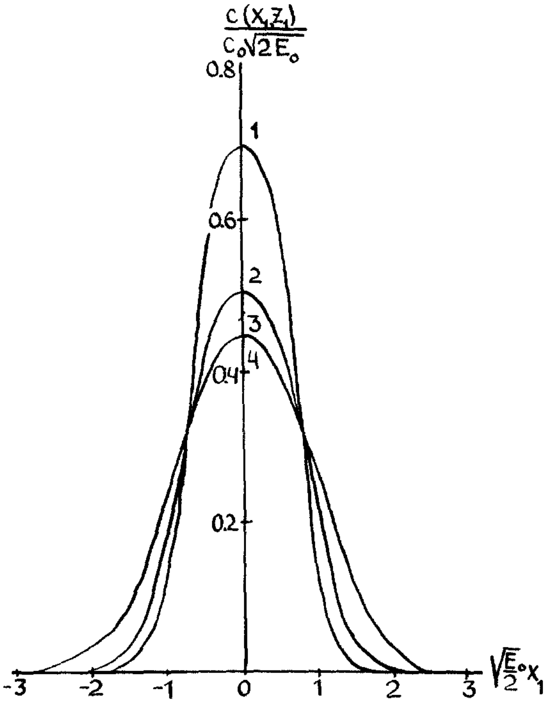

Fig. 2. Transverse particle distributions with a delta-function-like particle distribution at the channel input. $E_0 = 20$; $Pe = 2 \cdot 10^3$. (1) $b = 2.0$; (2) $b = 1.0$; (3) $b = 0.5$; (4) Boltzmann distribution. $b = (1/2)e^{-4E_0z_1/Pe}$.

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