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Nonequilibrium Plate Height for Field-Flow Fractionation in Ideal Parallel Plate Columns

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Abstract

The need for a more realistic theoretical description of peak spreading in field-flow fractionation (FFF) is shown. The lengthy derivation necessary to obtain the plate height of an ideal parallel plate column is then described in abbreviated form. Several limiting expressions are derived.

INTRODUCTION

The characterization of the elution profiles of solute peaks from field-flow fractionation (FFF) columns is necessary in order to optimize the parameters of separation. The most important peak characteristics insofar as separations are concerned are retention time and peak width, the same as in chromatography and most other fractionation techniques. Retention has been described both experimentally and theoretically for a number of subclasses of FFF (*1–8*). Peak widths are more difficult to treat theoretically, and their measurement is less reliable, again reflecting the general properties of chromatographic systems. However, a general theory of nonequilibrium has been developed for FFF, which can be applied to peak spreading in various column geometries (*9*). Unfortunately, the application of the general theory to specific geometries is rather complex, involving the integration and manipulation of numerous terms. For this reason only one specific application has been made: to linear velocity gradient flow across a flat plate, with no upper confining wall (*9*). At best this simple model provides the proper limiting expression for strong retention in parabolic flow between parallel plates. However, it does not describe the full practical retention range even for this simple geometry. It is, therefore, imperative to expand the theory so that it can be more realistically applied to practical column geometries.

In this paper we develop the theory for the ideal parallel plate column. This consists of two infinite parallel plates with parabolic flow between. All significant FFF columns developed to date consist of a parallel plate channel with a breadth-to-width ratio of 40-to-1 or greater. Except for a small perturbation at the edge, these channels should exhibit a behavior approaching that of the ideal parallel plate column.

THEORY

Peak spreading in FFF is best described in terms of plate height. The definition of plate height used here in the usual way for zonal migration systems, including chromatography (*10*), is

$$H = \sigma^2/L \tag{1}$$

where σ^2 is the variance of the eluted peak in units of distance and L is the column length. Several factors contribute to H in FFF. These can be grouped into three categories: longitudinal diffusion, extraneous disturbances, and nonequilibrium (*2*). The first of these is small because of sluggish diffusion in systems of macromolecules. The second can be made small by advances in instrumentation. The third, nonequilibrium, is the least reducible and therefore the most important influence in FFF peak spreading.

The plate height contributed by nonequilibrium processes can be written in two equivalent forms (*9*, *2*):

$$H = \psi l^2 \mathscr{V}/D \tag{2}$$

$$H = \chi w^2 \langle v \rangle / D \tag{3}$$

where l is the characteristic thickness of the solute layer, $\mathscr{V}$ is the zone velocity, $\langle v \rangle$ is the average solvent velocity, D is the diffusion coefficient, and ψ and χ are coefficients whose magnitude we seek in this paper. The first of these expressions reduces to a simpler form and is generally more useful under conditions of high retention, and the second is advantageous when retention is slight. The second is also favored by the fact that all parameters but χ are directly observable. The coefficients are related by the equation

$$\chi = \psi(\lambda^2 R) \tag{4}$$

a relationship that can be derived from Eqs. (2) and (3) by using retention ratio R for $\mathscr{V}/\langle v \rangle$ and the basic retention parameter λ for l/w.

In the earlier paper devoted to evolving a general nonequilibrium theory for FFF (*9*), it was shown that ψ is the following ratio of cross-sectional averages

$$\psi = -2\langle c^*\Phi(\mu - 1)\rangle/\langle c^*\rangle \tag{5}$$

where c^* is the quasiequilibrium concentration of solute at any given point; μ is the reduced solvent velocity, $v/\mathscr{V}$; and Φ is a nonequilibrium parameter dependent on cross-sectional position and equal to $\phi - g_1$. Here g_1 is a constant and ϕ is to be obtained as a solution to the differential equation

$$\frac{d^2\phi}{d\zeta^2} - \frac{d\phi}{d\zeta} = \mu(\zeta) - 1 \tag{6}$$

Quantity ζ is a dimensionless coordinate equal to the altitude above the lower plate x divided by characteristic thickness l. (We redefine l in this paper to equal the absolute value of l in the general paper.) Hence the first negative sign in Eq. (6) replaces a positive sign in the original equation. This equation is to be solved subject to the boundary conditions $\langle c^*\phi\rangle = 0$ and $(\partial\phi/\partial\zeta) = 0$ at the two confining walls.

As an aid to solving Eq. (6), we note the mathematical relationship

$$\frac{d}{d\zeta}\left(e^{-\zeta}\frac{d\phi}{d\zeta}\right) = e^{-\zeta}\left(\frac{d^2\phi}{d\zeta^2} - \frac{d\phi}{d\zeta}\right) \tag{7}$$

This along with Eq. (6) permits the reformulation of Eq. (6) into the form

$$\frac{d}{d\zeta}\left(e^{-\zeta}\frac{d\phi}{d\zeta}\right) = e^{-\zeta}(\mu - 1) \tag{8}$$

One integration and the use of the boundary condition $(d\phi/d\zeta) = 0$ at $\zeta = 0$ leads to the equation

$$\frac{d\phi}{d\zeta} = e^{\zeta}\int_0^{\zeta} e^{-\zeta}(\mu - 1)\, d\zeta \tag{9}$$

A second integration yields

$$\phi - g_1 = \int_0^\zeta e^\zeta \int_0^\zeta e^{-\zeta}(\mu - 1)\,d\zeta\,d\zeta \tag{10}$$

where constant g_1 can be identified as the ϕ value at $\zeta = 0$. Quantity $\phi - g_1$ can be identified with the nonequilibrium parameter Φ which, upon substitution into Eq. (5), yields

$$\psi = -\frac{2c_0{}^*\lambda}{\langle c^*\rangle}\int_0^{1/\lambda} e^{-\zeta}(\mu - 1)\int_0^\zeta e^\zeta \int_0^\zeta e^{-\zeta}(\mu - 1)\,d\zeta\,d\zeta\,d\zeta \tag{11}$$

where c^* in the numerator has been replaced by the exponential distribution (*4*, *5*, *9*).

$$c^* = c_0{}^*e^{-x/l} = c_0{}^*e^{-\zeta} \tag{12}$$

Equation (11) can be integrated by parts, $\int u\,dv = uv - \int v\,du$, in which we employ

$$u = \int_0^\zeta e^\zeta \int_0^\zeta e^{-\zeta}(\mu - 1)\,d\zeta\,d\zeta \tag{13}$$

$$dv = e^{-\zeta}(\mu - 1)\,d\zeta \tag{14}$$

The *uv* portion of the integral can be written as

$$\left[\int_0^{1/\lambda} e^\zeta \int_0^\zeta e^{-\zeta}(\mu - 1)\,d\zeta\,d\zeta\right]\int_0^{1/\lambda} e^{-\zeta}(\mu - 1)\,d\zeta \tag{15}$$

The integral outside the brackets spans the range from the lower wall, $\zeta = 0$, to the upper wall, $\zeta = 1/\lambda$. At both walls the boundary condition $d\phi/d\zeta = 0$ applies (see discussion following Eq. 6). Therefore, by virtue of Eq. (9), the integral under discussion vanishes. Hence the *uv* portion of the parts integration is zero. This leaves, when we combine the multiplicative constant of Eq. (11) and the integral $-\int v\,du$, the following expression for ψ

$$\psi = \frac{2c_0{}^*\lambda}{\langle c^*\rangle}\int_0^{1/\lambda} e^\zeta \left[\int_0^\zeta e^{-\zeta}(\mu - 1)\,d\zeta\right]^2 d\zeta \tag{16}$$

If now we replace $\langle c^*\rangle$ by $\lambda c_0{}^*(1 - e^{-1/\lambda})$ (derivable using Eq. 12), μ by $v/\mathscr{V}$, $\mathscr{V}$ by $R\langle v\rangle$, and v by the parabolic expression

$$v = 6\langle v\rangle\left(\frac{x}{w} - \frac{x^2}{w^2}\right) = 6\langle v\rangle(\lambda\zeta - \lambda^2\zeta^2) \tag{17}$$

we get the following working equation for ψ, valid in the parabolic flow approximation

$$\psi = \frac{2}{R^2(1 - e^{-1/\lambda})} \int_0^{1/\lambda} e^{\zeta} \left[\int_0^{\zeta} e^{-\zeta}(6\lambda\zeta - 6\lambda^2\zeta^2 - R)\, d\zeta \right]^2 d\zeta \qquad (18)$$

The evaluation of the integrals in this equation are more involved and detailed than the form of the expression might suggest. We will discuss only a few key juncture points below.

The straightforward integration of the integral in brackets yields

$$[\,] = 6\{e^{-\zeta}[\lambda^2\zeta^2 + (2\lambda^2 - \lambda)\,\zeta - B] + B\} \qquad (19)$$

where

$$B = \lambda - 2\lambda^2 - R/6 \qquad (20)$$

We eventually wish to eliminate R in favor of λ, and can do so by starting with the known R expression (*2*)

$$R = 6\lambda[\coth(1/2\lambda) - 2\lambda] \qquad (21)$$

and rearranging it to

$$R = 6\lambda\left[\frac{(1 - 2\lambda)e^{1/\lambda} + 1 + 2\lambda)}{e^{1/\lambda} - 1}\right] \qquad (22)$$

This substituted into Eq. (20) simplifies to

$$B = \frac{2\lambda}{1 - e^{1/\lambda}} \qquad (23)$$

If now Eq. (19) is substituted back into Eq. (18), a considerable number of integrations and rearrangements of the latter produce

$$\psi = \frac{144\lambda^3}{R^2(1 - e^{-1/\lambda})}\left\{\frac{B}{2\lambda^3}\left(4\lambda^2 + 2\lambda - 2B - \frac{1}{3}\right) + (28\lambda^2 + 1)(1 - e^{-1/\lambda}) - 10\lambda(e^{-1/\lambda} + 1)\right\} \qquad (24)$$

Quantities B and R can be eliminated with the help of Eqs. (22) and (23), finally yielding ψ as a function of λ only:

$$\psi = \frac{4(1 - e^{-1/\lambda})}{[(1 + e^{-1/\lambda}) - 2\lambda(1 - e^{-1/\lambda})]^2}\left\{(28\lambda^2 + 1)(1 - e^{-1/\lambda}) - 10\lambda(e^{-1/\lambda} + 1) - \frac{1}{3\lambda^2} - \frac{2}{\lambda} + 4 - \frac{1/\lambda}{(1 - e^{-1/\lambda})}\left[4\lambda\left(1 + \frac{1/\lambda}{(1 - e^{-1/\lambda})}\right) - \frac{1}{3\lambda} - 6\right]\right\} \qquad (25)$$

The corresponding expression for χ can be obtained from this with the aid of Eqs. (4) and (22)

$$\chi = \frac{24\lambda^3\{\ \}}{1 + e^{-1/\lambda} - 2\lambda(1 - e^{-1/\lambda})} \tag{26}$$

where { } is identical to the expression in braces in Eq. (25). The values of ψ and χ from these two expressions are plotted in Fig. 1. An R vs λ plot (Eq. 21) appears there also.

Equations (25) and (26) involved so many algebraic steps in their derivation that, despite normal precautions, errors are not inconceivable. However, certain checks exist to help obviate the problem. First of all, the magnitude and shape of the curves generated by these equations are reasonable and are in rough accord with experimental work. Second, limiting expressions can be obtained from these two equations which can be compared with other, more limited studies. For instance, as $\lambda \rightarrow \infty$,

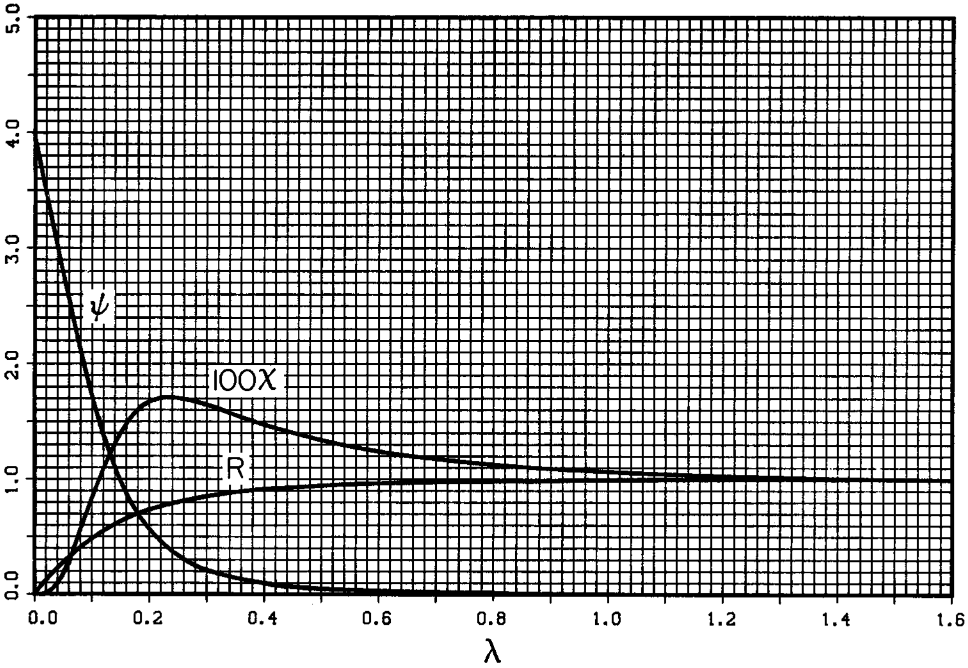

FIG. 1. Plots of ψ, χ, and R as a function of λ. The plotted values are obtained from Eqs. (25), (26), and (22), respectively.

we reach a situation in which, effectively, no field exists and thus no concentration gradients are found along axis x. In this limit, Eqs. (25) and (26) can be shown to produce

$$\lim_{\lambda \to \infty} \chi = 1/105 \tag{27}$$

$$\lim_{\lambda \to \infty} \psi = 0 \tag{28}$$

These results are easily confirmed by a simple nonfield application of nonequilibrium theory (details not shown here) as developed for chromatography (*10*).

In the limit $\lambda \to 0$, Eqs. (25) and (26) produce

$$\lim_{\lambda \to 0} \chi = 24\lambda^3 \tag{29}$$

$$\lim_{\lambda \to 0} \psi = 4 \tag{30}$$

The latter result is identical to that obtained in the general paper for a linear flow profile unbounded by an upper wall. This situation effectively occurs as l and λ approach zero. The identity of the results confirms our general equations in this limit.

APPROXIMATIONS AND DISCUSSION

The complexity of Eqs. (25) and (26), and the need for numerical and graphical calculations, make it appropriate to seek simplified, approximate expressions for these coefficients. To begin with, it is useful to look at limiting expressions in which more terms are retained than those shown in Eqs. (29) and (30). We focus here on the limit $\lambda \to 0$ because this limit is of the greatest practical importance. The limit $\lambda \to \infty$, of lesser importance, is described adequately by Eq. (27).

For $\lambda \ll 1$, Eq. (26) can be shown to reduce to

$$\chi_a = 24\lambda^3\left(\frac{1 - 10\lambda + 28\lambda^2}{1 - 2\lambda}\right) \tag{31}$$

where the subscript a is used to indicate that this is merely an approximation for any finite value of λ. Expressed purely as a power series valid to the third term,

$$\chi_a = 24\lambda^3(1 - 8\lambda + 12\lambda^2) \tag{32}$$

The first two terms, $1 - 8\lambda$, can be approximated initially by $e^{-8\lambda}$, yielding

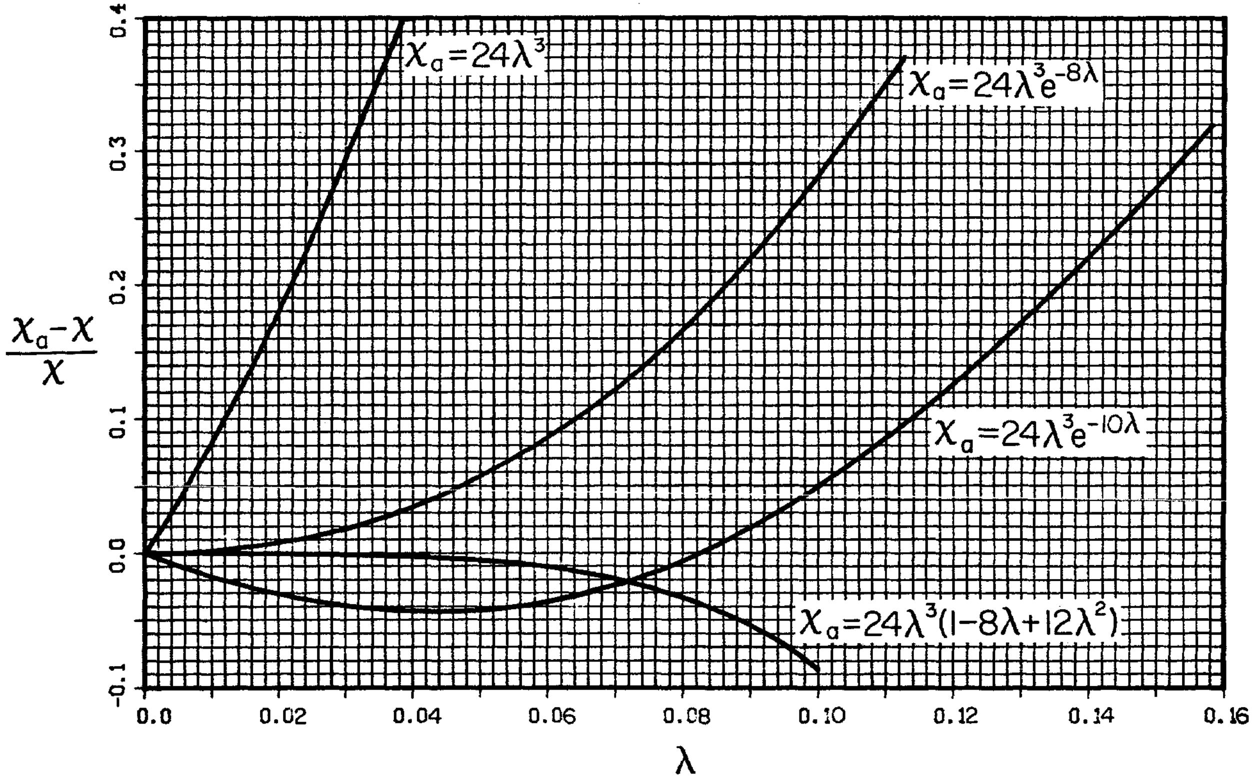

FIG. 2. The fractional difference between various approximate χ values, χ_a, and the exact value, χ, as a function of λ.

the approximation

$$\chi_a = 24\lambda^3 e^{-8\lambda} \tag{33}$$

Figure 2 shows the error incurred by the above approximations and others.

Similar approximations can be devised for ψ. Using Eqs. (4) and (31), we get

$$\psi_a = \frac{4(1 - 10\lambda + 28\lambda^2)}{(1 - 2\lambda)^2} \qquad \lambda \ll 1 \tag{34}$$

where R has been replaced by its limiting form

$$R = 6\lambda(1 - 2\lambda) \qquad \lambda \ll 1 \tag{35}$$

A series expansion of ψ yields

$$\psi_a = 4(1 - 6\lambda) \qquad \lambda \ll 1 \tag{36}$$

This is valid up to the λ^2 term in that the coefficient of that term is zero. One can also use various exponential approximations for ψ, similar to those employed for χ. The results are illustrated in Fig. 3. The simple approximation designated by $\psi = 4(1 - 6\lambda)$, Eq. (36), is valid within 10% to $\lambda = 0.1$, equivalent to $R = 0.48$ (see Fig. 1). This is an excellent and simple approximation, valid for most practical FFF work. Reasonable consistency over a broader range of λ values is provided by various exponential approximations, as shown in the figure.

It is necessary to emphasize here that the basic variable of FFF is retention. Approached from the theoretical side, retention is described most simply in terms of λ, and approached experimentally, retention is best described in terms of retention ratio R. The connection between theoretical parameter λ and experimental parameter R is provided by Eq. (21) or Eq. (22). The connection between the plate height parameter χ and ψ and retention parameter λ has now been adequately covered, and we turn our attention to variations with R.

Unfortunately, the complexity of the ψ and χ equations is such that, combined with the modest complexity of Eq. (22), a closed expression for the dependence of ψ and χ on R cannot be readily obtained. Yet the variation of ψ and χ with R is the most important relationship for the experimentalist studying peak broadening factors. In order to facilitate such studies, we have plotted in Fig. 4 the dependence of χ and ψ on R. These curves were obtained by combining the R vs λ curve of Fig. 1 with the ψ and χ expressions of Eqs. (25) and (26).

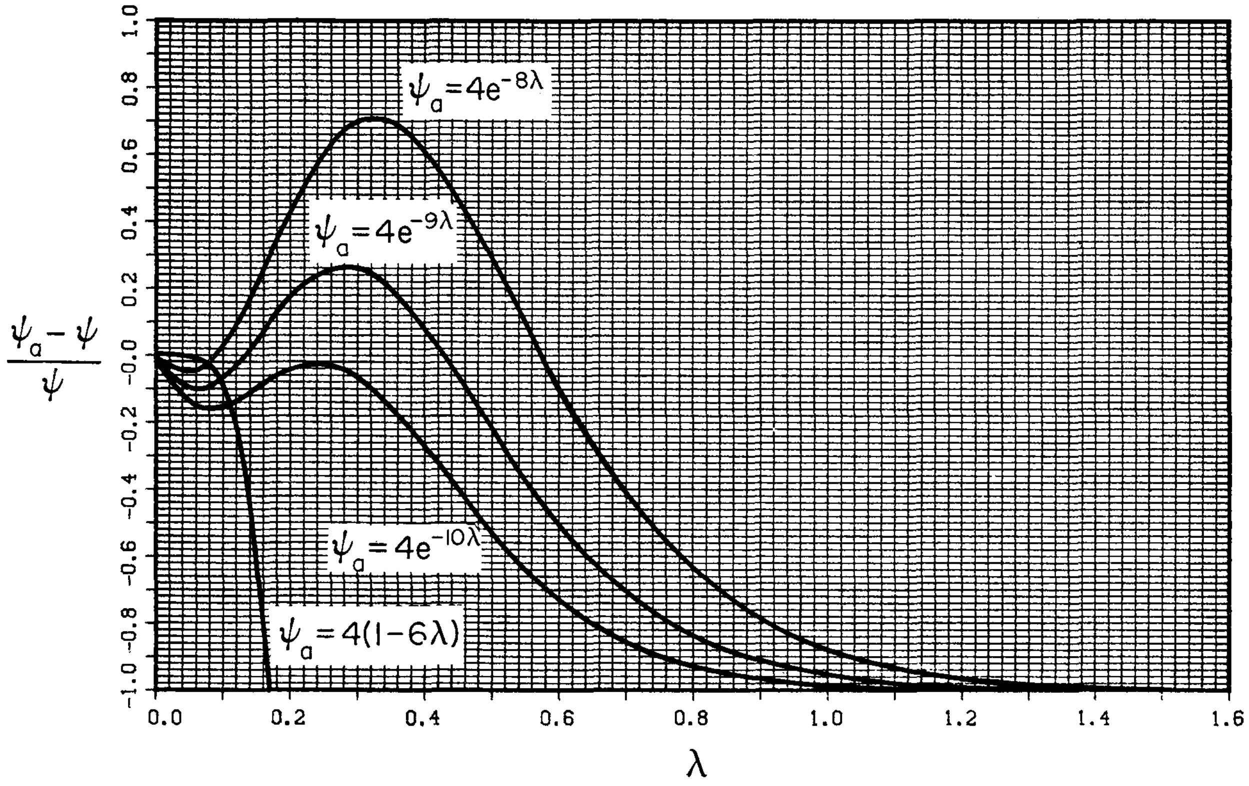

FIG. 3. Fractional difference between approximate ψ values, ψ_a, and the exact value, ψ, as a function of λ.

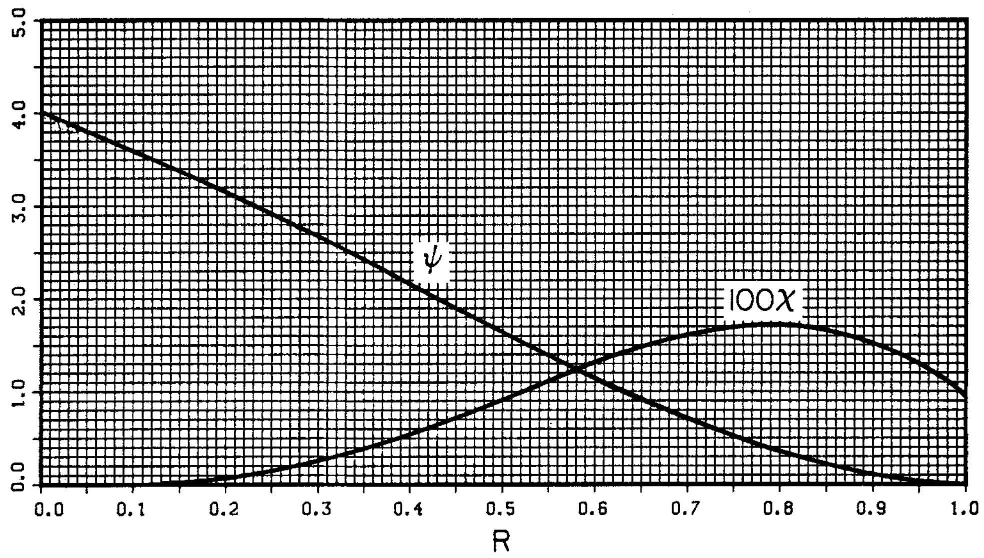

FIG. 4. Plots of ψ and χ as a function of retention ratio R.

Useful approximations can be developed to deal with these complicated dependencies. The simplest stem from utilizing the lead term of Eq. (35), $R = 6\lambda$, to convert a λ dependency to an R dependency. When this is combined with the two lead terms of Eq. (32), the following approximation is obtained:

$$\chi_a = \frac{R^3}{9}(1 - 4R/3) \tag{37}$$

When combined with Eq. (36), there results the approximation

$$\psi_a = 4(1 - R) \tag{38}$$

These two approximations are shown in Fig. 5. Equation (38) works moderately well over the entire retention range while Eq. (37) does not. However, as noted before, the most significant region for practical FFF is near $R = 0$, and both expressions serve a useful function in this vicinity. When a greater retention range requires description, it is possible to develop series approximations for χ and ψ. The following series utilizes terms up to the seventh power in R:

$$\chi_a = R^3 \sum_{i=0}^{4} a_i R^i \tag{39}$$

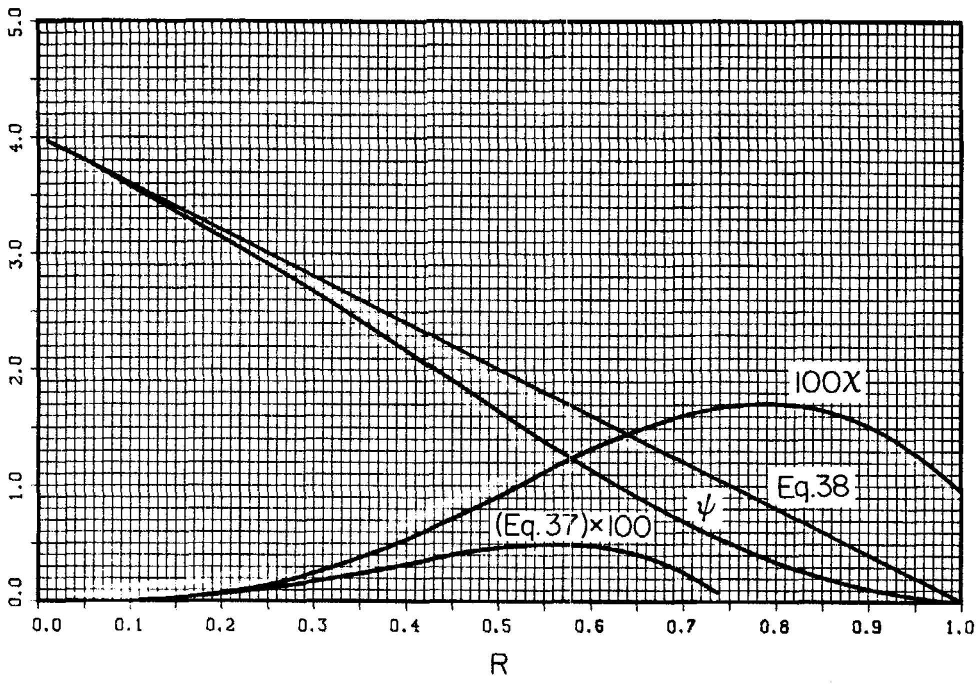

FIG. 5. Approximations to χ and ψ as provided by Eqs. (37) and (38).

$$\psi_a = \sum_{i=0}^{7} b_i R^i \tag{40}$$

These equations were fitted, except for restraints on the lead terms as dictated by terms in Eqs. (37) and (38), to the computer-derived values utilizing a least squares procedure described by University of Utah Computer Center Program Library No. 0032. The coefficients derived by this procedure are $a_0 = 1/9$, $a_1 = -0.03295$, $a_2 = -0.05328$, $a_3 = -0.1090$, $a_4 = 0.09406$; $b_0 = 4.0$, $b_1 = -4.0$, $b_2 = 1.642$, $b_3 = 3.585$, $b_4 = -18.479$, $b_5 = 35.195$, $b_6 = -24.484$, and $b_7 = 5.8212$.

The errors produced by these approximations are shown in Fig. 6. For the most part, these approximations are valid to within 1%.

The above approximations, combined with the theoretical equations, provide a range of options which should make it convenient to predict the behavior of FFF columns under the most diverse circumstances. In this way, this work may serve a very practical purpose as well as filling a major theoretical gap.

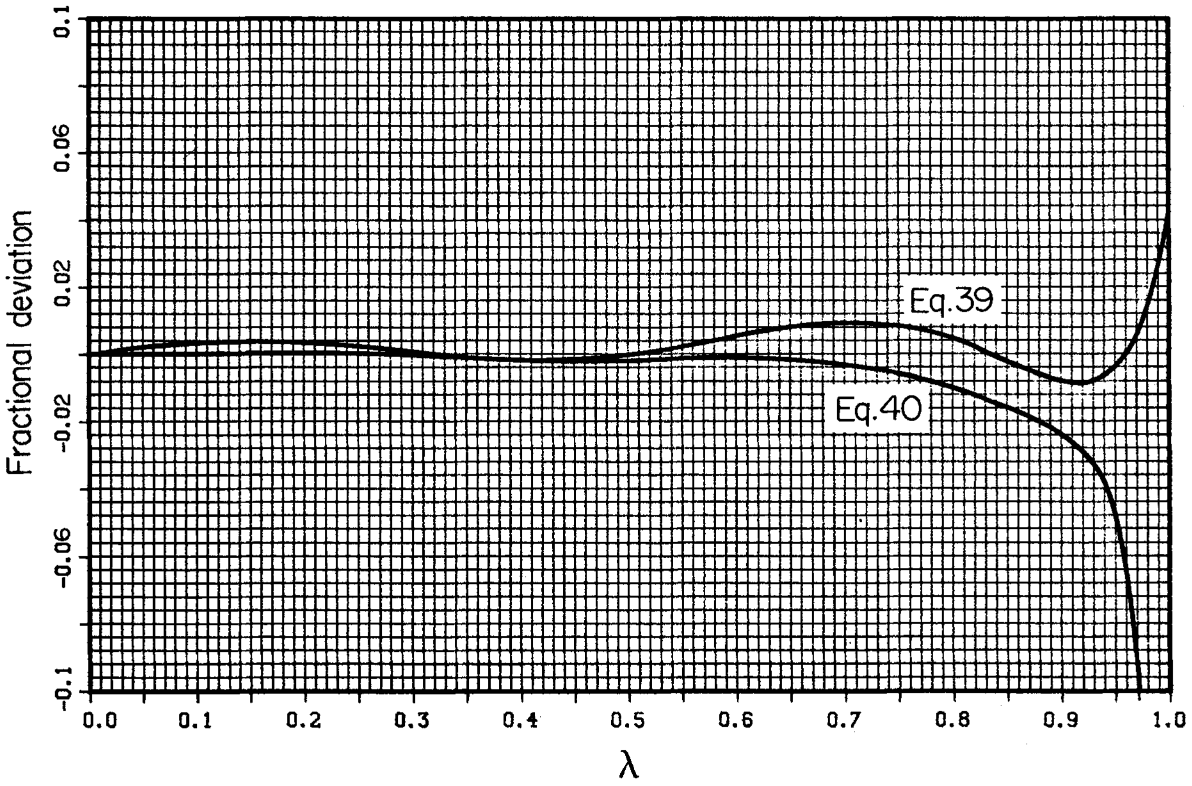

FIG. 6. Percentage deviation from exact values provided by Eqs. (39) and (40) and the associated coefficients given in the text.

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