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Field-Flow Fractionation for Poiseuille Flow through a Cylindrical Tube

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Abstract

We calculate the longitudinal dispersion coefficient K for field-flow fractionation in a cylindrical tube by using a variational principle.

1. INTRODUCTION

The longitudinal dispersion of noninteracting particles suspended in a Poiseuille flow (average velocity $\bar{u}$) through a cylindrical tube (radius R, tube axis z, see Fig. 1) was first explained by Westhaver (*1*) and Taylor (*2*). They showed that this dispersion is, in the long time limit, of the diffusive type, i.e., the mean square deviation $\langle \delta z^2(t) \rangle = \langle (z(t) - \langle z(t) \rangle)^2 \rangle$ from the average motion $\langle z(t) \rangle$ grows linearly with time [see also Aris (*3*)]:

$$\lim_{t\to\infty} \frac{\langle \delta z^2(t) \rangle}{2t} = K = \frac{\bar{u}^2 R^2}{48D} + D \tag{1}$$

K is called the effective longitudinal diffusion coefficient. It is the sum of the molecular diffusion coefficient D and a contribution caused by the inhomogeneity of the flow field, with the peculiarity that it is proportional to the inverse of D. In most cases the latter contribution is dominant, and we will, in the following, completely neglect the molecular diffusion in the

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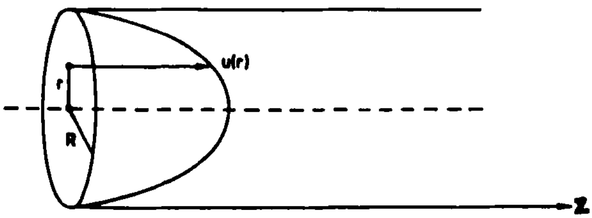

FIG. 1. Poiseuille flow through a cylindrical tube with radius R.

direction z of the flow. The motion of a single particle is thus taken to be diffusive in the directions orthogonal to the tube axis, with diffusion coefficient D, and completely deterministic in the z-direction with a velocity equal to the local flow velocity $u(r)$ (r being the distance to the tube axis):

$$\partial_t z = u(r) = 2\bar{u}[1 - (r/R)^2] \tag{2}$$

The purpose of this paper is to investigate how Taylor's result (1) is modified in the presence of a transverse field, e.g., a gravitational field. Under the influence of this field the particles will acquire a systematic motion with "sedimentation" velocity v, which has to be superimposed on the diffusive motion. The competition between diffusion and systematic motion, tending to make the particles float or sink, can be described in terms of the dimensionless Peclet number:

$$\alpha = vR/D \tag{3}$$

We will show that the correction to the result (1) is of the following form:

$$K = \frac{\bar{u}^2R^2}{48D}C(\alpha) \tag{4}$$

and we will determine the function $C(\alpha)$. This result is of importance in field-flow fractionation and chromatography (*4*, *5*), where one tries to separate particles according to this Peclet number (i.e., according to their radius, mobility, etc.) The present model was proposed by Reis and Lightfoot (*9*) as a simplified but realistic model of electropolarization chromatography, where one tries to separate protein mixtures. In this case the sedimentation is caused by a constant electric field. The average motion $\langle z(t)\rangle$ was calculated analytically. In the present paper we want to extent this result by the calculation of $C(\alpha)$. We mention first that in the case of Poiseuille flow between plane parallel plates, with a field orthogonal to these plates, the function $C(\alpha)$ can be obtained analytically (*6*, *7*). In the present geometry, the introduction of a field destroys the rotational symmetry of the problem and we are not able to obtain analytic results for $C(\alpha)$. Instead we used a variational principle that was derived in a previous paper (*8*). The following functionals $K_1(f)$ and $K_2(f)$ are lower bounds for K:

$$K_1(f) = -\frac{\langle f|\delta u\phi_0\rangle^2}{\langle f|\hat{L}f\rangle} \leq K \tag{5}$$

and

$$K_2(f) = 2\langle f|\delta u\phi_0\rangle + \langle f|\hat{L}f\rangle) \leq K \tag{6}$$

Here: i) $\hat{L}$ is the operator that describes the stochastic dynamics in the plane orthogonal to the flow, i.e., to the tube's axis. In the present problem it has the following form:

$$\hat{L} = D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - v\partial y \tag{7}$$

with zero flux boundary conditions at the tube's surface $r = R$:

$$[D\partial_x\vec{e}_x + (D\partial_y - v)\vec{e}_y]\cdot\vec{r}|_{|\vec{r}|=R} = 0 \tag{8}$$

ii) ϕ_0 is the normalized steady-state distribution:

$$\hat{L}\phi_0 = 0 \tag{9}$$

i.e.,

$$\phi_0(x,y) = \frac{\alpha e^{\alpha y}}{2\pi R^2 I_1(\alpha)} \tag{10}$$

(I_1 is the first modified Bessel function).

iii) δu is the deviation of the flow velocity from its average value:

$$\delta u = u(r) - \iint_{r\leq R} u(r)\,\phi_0(x,y)\,dx\,dy \tag{11}$$

iv) The inner product is defined by

$$\langle f|g\rangle = \iint_{r\leq R} fg\phi_0^{-1}\,dx\,dy \tag{12}$$

v) The inequality (6) is valid for any function f that satisfies the boundary condition (8). The use of inequality (5) moreover requires f to be different from ϕ_0.

This paper is organized as follows: To illustrate the use and accuracy of the variational principles, in Section 2 we study the rate of dispersion of particles suspended in a Poiseuille streaming between two parallel plates with a constant transverse field, and compare variational with analytic results for the dispersion coefficient K. The agreement is found to be extremely good. In Section 3 we discuss the same problem in a cylindrical tube. We calculate a lower bound for the dispersion coefficient on the basis of a 2, 3, 6, and 13 parameter variational approach, based on Eqs. (5) and (6). The convergence is very good and the 13-parameter result is thought to be almost perfect. Series expansion for large and small α is also given.

2. THE EFFECT OF SEDIMENTATION ON WESTHAVER–TAYLOR DISPERSION BETWEEN PLANE PARALLEL PLATES

In the case of Poiseuille streaming between two parallel plates at $y = 0$ and $y = L$, respectively, the flow profile $u(y)$ is given by

$$u(y) = 6\bar{u}\frac{y}{L}\left(1 - \frac{y}{L}\right) \tag{13}$$

The dispersion coefficient K of suspended particles in the presence of a transverse field can be evaluated analytically (*6*, *7*):

$$K = \lim_{t\to\infty}\frac{\langle\delta z^2(t)\rangle}{2t} = \frac{\bar{u}^2L^2}{210D}C(\alpha) \tag{14}$$

with

$$\begin{aligned} C(\alpha) = \frac{5040}{(e^\alpha - 1)^3\alpha^6}[(3\alpha^2 - 30\alpha + 84)e^{3\alpha} + (\alpha^4 - 6\alpha^3 - 21\alpha^2 \\ + 30\alpha - 252)e^{2\alpha} + (-\alpha^4 - 6\alpha^3 - 21\alpha^2 \\ + 30\alpha - 252)e^{\alpha} + (-3\alpha^2 - 30\alpha - 84)] \end{aligned} \tag{15}$$

The function $C(\alpha)$ is schematically represented in Fig. 2. Note that, somewhat surprisingly, $C(\alpha)$ is found to have a maximum in the vicinity of $\alpha = 3.5$.

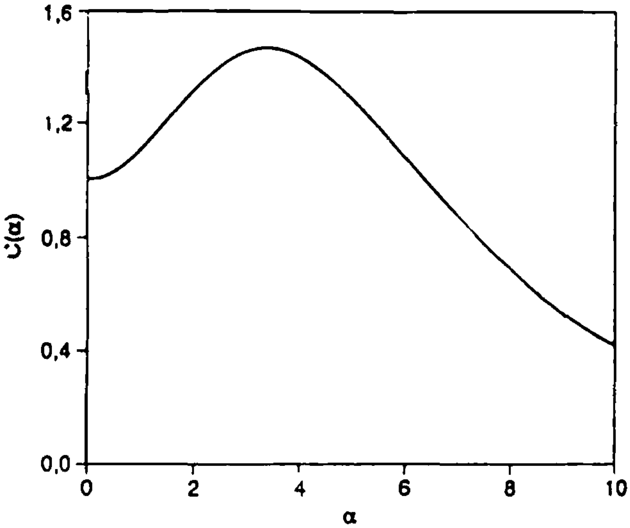

FIG. 2. The function $C(\alpha)$ (analytical result, cf. Eq. 15).

We will calculate a lower bound for $C(\alpha)$ on the basis of a 2, 3, 6, and 13 parameter variational approach based on Eqs. (5) and (6). The transverse stochastic operator is of the following form:

$$\hat{L} = D\frac{d^2}{dy^2} - v\frac{d}{dy} \tag{16}$$

The trial functions f have to satisfy the following reflecting boundary conditions:

$$\left(D\frac{d}{dy} - v\right)f\bigg|_{\substack{y=0\\y=L}} = 0 \tag{17}$$

The steady-state distribution is

$$\phi_0(y) = \frac{\alpha e^{\alpha y/L}}{L(e^\alpha - 1)} \tag{18}$$

As an example of a one-parameter variational function, we first consider the following trial function:

$$f_1 = \exp(\alpha y/L)(a_3y^3 + a_2y^2 + a_1y + a_0) \tag{19}$$

We can set the coefficient a_0 equal to 0 since it corresponds to a term proportional to ϕ_0, which does not contribute in the calculation of K_1 or K_2. On the other hand, the constant a_1 has to be equal to 0 to satisfy the boundary condition at $y = 0$. Finally, the constant a_2 is chosen such that f_1 satisfies the boundary condition at $y = L$. Optimization of the lower bounds (5) and (6) in terms of a_3 then gives

$$\tilde{C}(\alpha) = \frac{420}{\alpha^6(e^\alpha - 1)^3}(e^\alpha[\alpha^2 - 6\alpha + 12] + [-\alpha^2 - 6\alpha - 12])^{-1} \times (e^{2\alpha}[6\alpha^2 - 48\alpha + 108] + e^\alpha[\alpha^4 - 24\alpha - 216] + [6\alpha^2 + 48\alpha + 108])^2 \tag{20}$$

The same procedure with variational function

$$f_2 = \exp(\alpha y/L)(a_4 y^4 + a_2 y^2) \tag{21}$$

gives

$$\tilde{C}(\alpha) = \frac{945}{\alpha^6(e^\alpha - 1)^3}(e^\alpha[4\alpha^4 - 36\alpha^3 + 156\alpha^2 - 360\alpha + 360] + [-\alpha^4 + 24\alpha^2 - 360])^{-1}(e^{2\alpha}[8\alpha^3 - 76\alpha^2 + 264\alpha - 336] + e^\alpha[\alpha^5 - 24\alpha^3 + 80\alpha^2 - 216\alpha + 672] + [4\alpha^3 + 20\alpha^2 - 48\alpha - 35])^2 \tag{22}$$

A two parameter variational treatment with a linear combination of these functions (i.e., with terms in y^2, y^3, and y^4) gives a lower bound on $C(\alpha)$ which almost perfectly agrees with the exact result. This result, together with Eqs. (20) and (22), is compared with $C(\alpha)$ in Fig. 3.

Note that all these approximations have the exact asymptotic behavior for large α:

$$\tilde{C}(\alpha) \xrightarrow[\alpha\to\infty]{} \frac{15{,}120}{\alpha^4} \tag{23}$$

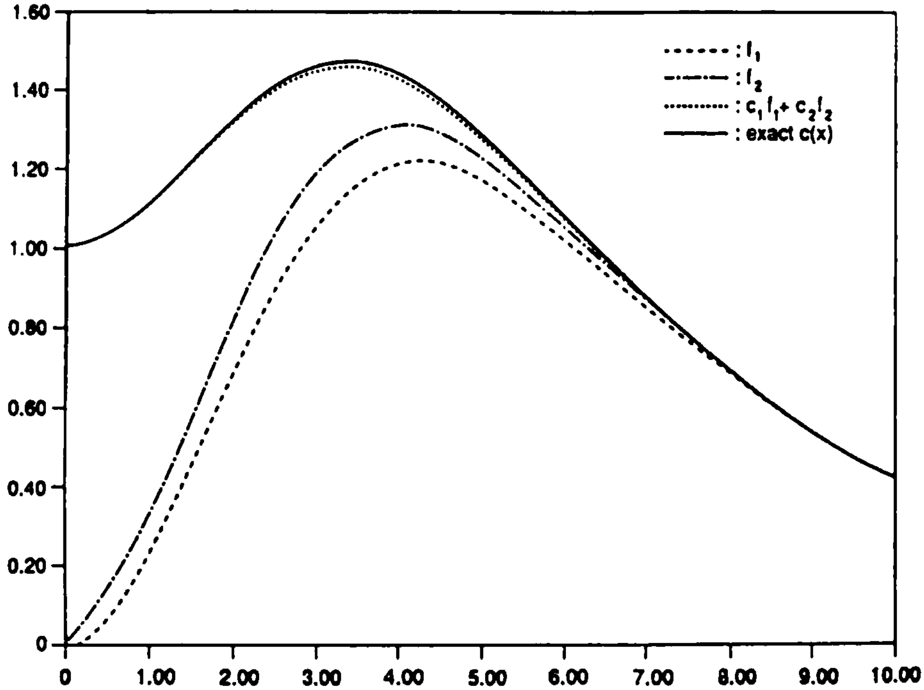

FIG. 3. Lower bounds for $C(\alpha)$ for the case of field-flow fractionation between plane parallel plates. The full line corresponds to the exact result of Eq. (15).

This is due to the fact that for α large and negative, all the particles are very close to the boundary $y = 0$, such that the effect of the higher order terms in $y^3\phi_0$, $y^4\phi_0$, ... are negligible compared to the contribution of the lowest order contained in $y^2\phi_0$.

We have also carried out calculations for variational functions with more parameters:

$$\sum_{i=2}^{N} a_i y^i \exp(\alpha y/L) \tag{24}$$

in which only the coefficient a_2 is fixed by the boundary condition at $y = L$.

A 4-parameter fit, with terms up to order y^6, already gives a result with a relative error of the order of the computing precision (10^{-6}). This gives us some confidence to apply the variational approach in problems for which the analytic solution is not available.

3. THE EFFECT OF SEDIMENTATION ON WESTHAVER–TAYLOR DISPERSION IN A CYLINDRICAL TUBE

In the case of a Poiseuille streaming through a cylindrical tube of radius R, the flow profile $u(r)$ has the following form:

$$u(r) = 2\bar{u}(1 - (r/R)^2) \tag{25}$$

The motion of the suspended particles in a direction perpendicular to the tube axis (z-axis) is the combination of diffusion, with diffusion constant D, and drift (or sedimentation), with systematic velocity v, which we take to be oriented along the (vertical) y-axis. The corresponding equation of motion is given by Eq. (7) with boundary conditions Eq. (8) and stationary state given by a Boltzmann distribution, cf. Eq. (10).

The presence of the vertical field breaks the cylindrical symmetry of the problem and makes an analytic treatment very difficult.

By introducing dimensionless variables however, it is easy to verify that the perturbation of the field can be expressed in terms of the dimensionless number $\alpha = Rv/D$, so that K is of the following form:

$$K = \frac{\bar{u}^2R^2}{48D}C(\alpha) \tag{26}$$

We now proceed to evaluate the correction factor $C(\alpha)$ as accurately as possible by using the variational principles. It is important to make a good guess for the trial functions. First, instead of working in terms of the y- and z-coordinates, we will consider polar coordinates r and θ. Since the problem is symmetrical around the vertical axis, i.e., invariant under the transformation $\theta \rightarrow \pi - \theta$, the trial function can be chosen of the following form (no cosine terms):

$$f(r,\theta) = \exp(\alpha r \sin\theta/R)[\phi_0(r) + \sin\theta\phi_1(r) + \sin^2\theta\phi_2(r) + \cdots]$$

$$= \exp(\alpha r \sin\theta/R) \sum_{k,1} a_{kl}\, r^k \sin^1\theta \tag{27}$$

The question is how far one should go in the Taylor expansion in terms of r and $\sin\theta$, respectively. A first answer will, of course, come from the rate of convergence that one observes as one increases the number of variational parameters a_{kl}. Another guiding hint is obtained by writing the "optimal" trial function ψ (i.e., the function that gives the exact result for K) as a series expansion in α:

$$\psi = \psi_0 + \alpha\psi_1 + \alpha^2\psi_2 + \cdots \tag{28}$$

The functions ψ_0, ψ_1, etc. can be found exactly as follows. The "optimal" trial function ψ that maximizes Eqs. (5) and (6) is the solution of the following equation:

$$L\psi = -\delta u \phi_0 \tag{29}$$

with ψ satisfying the boundary conditions. By straightforward expansion, one finds

$$\psi_0 = \frac{\bar{u}}{24DR^2}[-3r^4 + 6r^2R^2 - 2R^4]\phi_0$$

$$\psi_1 = \frac{\bar{u}}{48DR^3}[r^5 - 3r^3R^2 + 4rR^4] \sin\theta\phi_0$$

$$\psi_2 = \frac{\bar{u}}{(48)^2DR^4}[(-r^6 + 6r^4R^2 - 9r^2R^4 - 29R^6) + 6(-r^6 + 4r^4R^2 - 5r^2R^4)\sin^2\theta]\phi_0 \tag{30}$$

$$\psi_3 = \frac{\bar{u}}{48 \times 320DR^5}[(2r^7 - 15r^5R^2 + 47r^3R^4 - 80rR^6)\sin\theta + (4r^7 - 20r^5R^2 + 24r^3R^4)\sin^3\theta]\phi_0$$

$$\psi_4 = \frac{\bar{u}}{(48)^2 320DR^6}[(-r^8 + 12r^6R^2 - 72r^4R^4 + 112r^2R^6 + 1203R^8) + 8(-2r^8 + 18r^6R^2 - 69r^4R^4 + 92r^2R^6)\sin^2\theta + 16(-r^8 + 6r^6R^2 - 7r^4R^4)\sin^4\theta]\phi_0$$

The corresponding exact series expansion for K reads:

$$K = \frac{\bar{u}^2R^2}{48D}\left(1 + \frac{13}{120}\alpha^2 - \frac{1711}{48 \times 960}\alpha^4 + O(\alpha^6)\right) \tag{31}$$

In analogy to the expressions for the functions ψ_k, we have considered a trial function of the following form:

$$f(r,\theta) = \phi_0 \sum_{k=0}^{N} \sum_{\substack{l=k \\ l+k=\text{even}}}^{N+4} a_{kl}r^l \sin^k\theta = \phi_0 \sum_k f_k(r) \sin^k\theta \tag{32}$$

For similar reasons as those discussed when setting a_0 equal to zero in Eq. (19), a_{00} can be set equal to zero. Furthermore, the boundary condition (8) can be satisfied by choosing the coefficients a_{ii} ($i > 0$) and a_{02} such that:

$$(\partial_r f_j)|_{r=R} = 0, \qquad j = 0, \ldots, N \tag{33}$$

A one- and two parameter trial function of the form given by Eq. (32) are thus, respectively,

$$\begin{aligned} f_0(r) &= a_{04}(r^4 - 2r^2R^2) \\ f_i(r) &= 0, \qquad \forall_i \geq 1 \end{aligned} \tag{34}$$

and

$$\begin{aligned} f_0(r) &= a_{04}(r^4 - 2R^2r^2) \\ f_1(r) &= a_{13}(r^3 - 3R^2r) \\ f_i(r) &= 0, \qquad \forall i \geq 1 \end{aligned} \tag{35}$$

In Fig. 4 we show the results that are thus obtained, together with those for trial functions with 6 parameters [including terms up to ($r^6 \sin^2 \theta$)], with 9 parameters [including terms up to ($r^8 \sin^2 \theta$)], and with 13 parameters [including terms up to ($r^8 \sin^4 \theta$)]. The best lower bound is also shown for α values ranging from 0 to 5. Note that both variational principles gave results that were identical within the numerical accuracy. For comparison, we also show some results in Table 1. Note the fast convergence as the number of parameters is increased, especially for small values of α. Between the 9-parameter and the 13-parameter results, the difference is smaller than 0.1%. No significant improvement could be made by including two higher terms in $\sin \theta$, or two higher terms in r. Furthermore, the results from the series expansion given in Eq. (31) is in excellent agreement with the variational results for small values of α. Finally, we note that all the variational results give the same asymptotic result for α large, namely:

$$C(\alpha) \xrightarrow[\alpha \to \infty]{} 1536/\alpha^4 \tag{36}$$

4. DISCUSSION

We have calculated the longitudinal dispersion coefficient K for field-flow fractionation in a cylindrical tube, using a variational principle. The

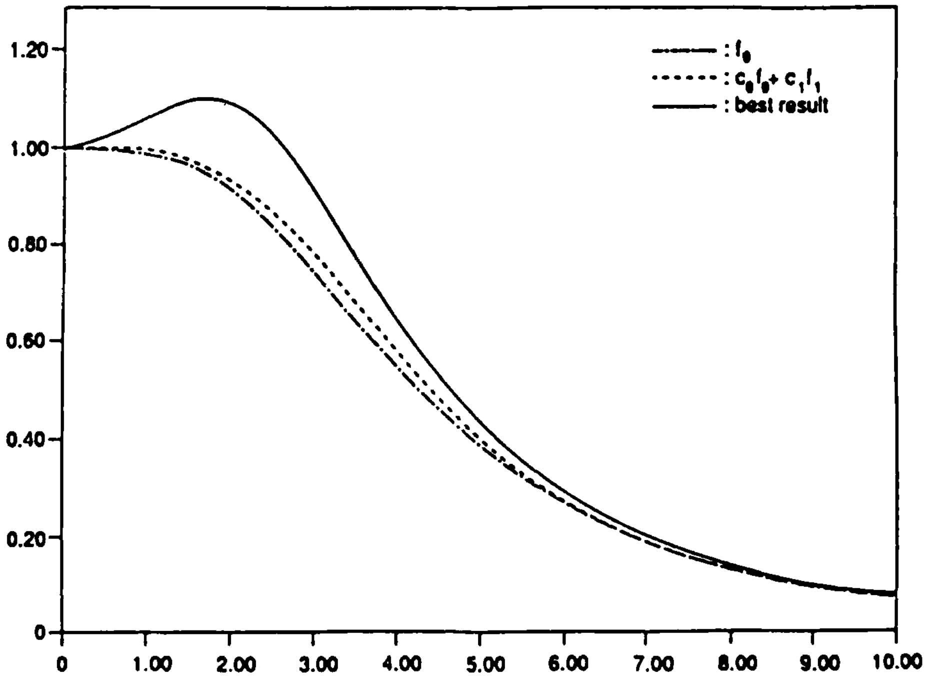

FIG. 4. Lower bounds for $C(\alpha)$ for the case of field-flow fractionation in a cylindrical tube. The full line corresponds to the best obtained result (with the 13-parameter fit).

TABLE 1

α	6 parameter	9 parameter	13 parameter	Eq. (31)
0.0	0.99979	0.99999	0.99999	1.00000
0.5	1.02485	1.02485	1.02485	1.02476
1.0	1.07603	1.07638	1.07638	1.07120
1.5	1.10718	1.10747	1.10749	
2.0	1.08563	1.08564	1.08572	
2.5	1.00611	1.00868	1.00909	
3.0	0.89544	0.89580	0.89608	
3.5	0.76624	0.76846	0.76911	
4.0	0.64395	0.64473	0.64511	
4.5	0.53168	0.53324	0.53358	
5.0	0.43666	0.43782	0.43813	

results are very similar to those obtained in the case of Poiseuille flow between plane parallel plates. K has a small maximum of 10% above the zero field result for $\alpha = 1.5$, and decreases for α large as α^{-4}. We have shown that the value of K can be obtained from the variational calculation with high accuracy, so that the latter can be used with some confidence to obtain the result for the dispersion coefficient in problems where an analytic treatment is difficult (e.g., when the eigenfunctions of the problem under consideration are not known).

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