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Axial Dispersion of Sedimented Colloids

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Abstract

After an ensemble of identical particles has had time to settle along the y-axis to their equilibrium distribution in a field of potential energy $\phi(y)$ by gravity, but prevented from adsorbing by double-layer repulsion, their dispersion by Poiseuille flow between two horizontal plates is predicted. The residence-time distribution of particles is obtained in terms of $\phi(y)$. For chromatographic peaks with long retention times, equations are obtained relating the elution volume and dispersion coefficient to $\phi(y)$. From such data, two pieces of information regarding $\phi(y)$ can be deduced: the location of the minimum, y_m, and $\phi''(y_m)$. However, at the opposite extreme of very short retention times, a major portion of the profile $\phi(y)$ can be deduced from a single chromatogram. Such an experiment might provide the first measurement of long-range forces between a colloid particle and a flat plate.

Several variants of liquid-exclusion chromatography (*1–4*) have been proposed or developed for analyzing mixtures of colloids. Two of these—"field-flow fractionation" (*2*) and "hydrodynamic chromatography" (*1*)—have been extensively studied. While particle size can be the basis of separation in all of these techniques, some techniques also show sensitivity to other particle properties such as the density, charge, or dielectric constant. In the case of hydrodynamic chromatography (*1*), the double-layer and van der Waals interactions between the particle and the stationary phase significantly alter the elution volume (*1, 5*). A simple explanation is that double-layer repulsion, for example, pushes particles away from the stationary phase and out into a region of higher carrier velocity so that the particles (on the average) move through the column more rapidly than in the absence of the force. Thus any property on which these colloidal forces depend could serve as a basis for particle separation.

If colloidal forces affect the separation of particle mixtures in complex columns, then the chromatogram of a monodisperse sol in a simple column (where the hydrodynamics are known) should yield information about the colloidal forces. In this paper the analysis of axial dispersion of an ensemble of identical particles is performed in some simple limiting cases to see what information about the particle/wall interaction can be gleaned from such experiments. To increase the importance of the particle/wall interactions, the particles are allowed to settle in a horizontal column before elution. If the residence time of the particle is much longer than the time needed for a particle to sample all accessible points in the cross-section by Brownian motion, then the analysis below reveals that only two pieces of information about the interaction potential profile can be obtained. But if the residence time is so short that particles only have time to diffuse a distance over which their potential energy change is much less than kT, then much of the potential energy profile can be deduced from a single chromatogram.

AXIAL DISPERSION

As an initially uniform slug of solute moves with a carrier fluid through an open capillary column, its shape becomes distorted. Solute molecules located closer to the wall of the capillary move through the column more slowly than solute molecules located on the centerline because the fluid velocity is smaller at the wall than at the center. Besides axial convection, the solute may also diffuse radially. Whether or not diffusion is important, a detector monitoring the average concentration of solute in the effluent of the column will indicate that the solute has spread over a volume of effluent which is larger than that of the injected slug. This spreading is called axial "dispersion."

Taylor (*6*) analyzed the dispersion of molecular solutes in steady Poiseuille flow through circular tubes by estimating a solution for the unsteady concentration profile. Aris (*7*) showed that only the first two moments of the residence-time distribution are needed so that a complete solution is unnecessary; he also included axial diffusion in his analysis. Gill and Sankarasubramanian (*8*) analyzed dispersion of molecular solutes when the initial slug is not of uniform concentration or when the flow is unsteady.

Dispersion of particles having colloidal size differs from dispersion of small molecules in that particle/wall interactions may be important. In addition, particles near the wall do not have the same velocity as fluid elements located the same distance from the wall as the particle's center. Furthermore, the diffusion coefficient of particles may depend on the distance from the wall. Brenner and Gaydos (*9*) used the method of Aris (*7*) to incorporate these effects in the analysis of dispersion of spherical particles in Poiseuille flow through a circular tube in the limit where the residence time is large compared to the time for a particle to sample all radial positions by Brownian motion.

Below is an analysis of the dispersion of sedimented spherical particles in steady Poiseuille flow between flat plates. The two contributions of this paper to the literature on axial dispersion are (a) the interpretation of the dispersion coefficient for long retention time in terms of particle/wall interactions, and (b) the analysis of the asymptotic behavior for short retention times. It is in the limit of very short retention time that the chromatogram yields the most information on the particle/wall interaction.

GENERAL FORMULATION

Within a few radii of the wall, a particle is carried by the fluid at a velocity which is somewhat less than the velocity of undisturbed fluid at the same distance from the wall as the particle's center. Goldman et al. (*10*) deduced a relation between these two velocities in the case of spherical particles in linear shear flow. Similarly, a particle's mobility and, consequently, its diffusion coefficient become less than their bulk values when the particle is near a wall. The amount of the reduction for motion perpendicular to the wall was computed by Brenner (*11*).

In the analysis which follows, the concentration of particles is assumed to be sufficiently dilute so that any interaction among particles can be ignored. Neglecting axial diffusion, the concentration $c(x, y, t)$ of identical Brownian particles in Poiseuille flow between horizontal plates (see Fig. 1) must satisfy

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial x} = \frac{\partial}{\partial y}\left[D\left(\frac{c}{kT}\,\frac{d\phi}{dy} + \frac{\partial c}{\partial y}\right)\right] \tag{1}$$

where $v(y)$ is the speed of a particle induced by the axial flow, $D(y)$ is the diffusion coefficient of particles in the y-direction, and $\phi(y)$ is the potential energy of one particle owing to gravity and any interaction between the particle and the plates. If the plates are impermeable to particles, then

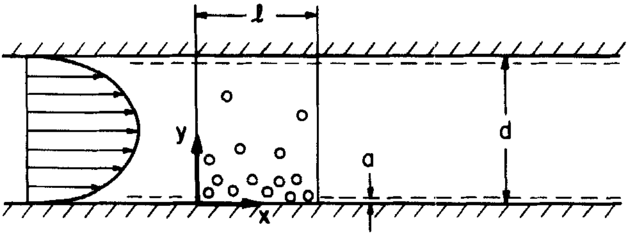

FIG. 1. The initial distribution of a slug held between two parallel plates. Before Poiseuille flow of the carrier commences at $t = 0$, the dispersed particles in the slug are allowed to settle under the influence of gravity and particle/wall interactions until a Boltzmann distribution is achieved.

$$D\left(\frac{c}{kT}\frac{d\phi}{dy}+\frac{\partial c}{\partial y}\right) \to 0 \qquad \text{as } y \to a \tag{2}$$

and as $y \to d - a$, where a is the radius of particles.

Particle/wall interactions play a secondary role in most chromatography experiments because only a small fraction of particles is close enough to the wall to experience any interaction. To make colloidal forces more apparent, let the particles settle to the wall by gravity or some applied force before starting the flow. Suppose a slug of length l, containing N particles per unit width, is injected between the plates. In the absence of flow, the concentration profile satisfying (1) and (2) at steady state is a Boltzmann distribution:

$$c = \alpha(x)e^{-\Phi(y)} \tag{3}$$

where

$$\Phi = \phi(y)/kT$$

$$\alpha(x) = \begin{cases} \alpha_0 & \text{for } 0 < x < l \\ 0 & \text{for } x < 0 \text{ or } x > l \end{cases} \tag{4}$$

and

$$\alpha_0 = \frac{N/l}{\int_a^{d-a} e^{-\Phi}\, dy}$$

If this distribution is achieved before the flow of carrier is started, then (3) and (4) can serve as the initial condition for the analysis of subsequent dispersion.

A detector located at the end of the column of length L might sense the average particle concentration in the exit plane:

$$s(t) = \frac{1}{d} \int_a^{d-a} c(L, y, t)\, dy \tag{5}$$

What information concerning the particle/wall interaction can be extracted from this signal? Two limiting cases will be analyzed to obtain the answer.

CASE 1: FULLY-DEVELOPED TAYLOR DISPERSION

Suppose that the carrier flow rate is so slow that the time required for convection to distort the slug is very long compared to the time for the concentration profile to relax vertically to a Boltzmann distribution. Then the profile in any $x =$ constant plane is nearly a Boltzmann distribution at every instant; in other words,

$$c = \psi e^{-\Phi} \tag{6}$$

where ψ varies with position and time, but much more slowly with y than $e^{-\Phi}$.

The profile in any $x =$ constant plane changes quite abruptly as the distorted slug passes through the plane; so $(\partial c/\partial t)_{x,y}$ in Eq. (1) cannot be neglected. However, the profile in a plane which moves downstream with a speed

$$\bar{v} \equiv \frac{\displaystyle\int_a^{d-a} v(y) e^{-\Phi(y)}\, dy}{\displaystyle\int_a^{d-a} e^{-\Phi(y)}\, dy} \tag{7}$$

will evolve much more slowly. Owing to the weak dependence of ψ on y, this speed is not exactly equal to the average speed of the slug, although it represents a good approximation. The instantaneous position of this moving plane is given by

$$x = \xi + \bar{v}t \tag{8}$$

where ξ is some constant. Using Eqs. (6) and (8) to eliminate c and x from Eq. (1) obtains

$$\frac{\partial \psi}{\partial t} e^{-\Phi} + (v - \bar{v}) \frac{\partial \psi}{\partial \xi} e^{-\Phi} = \frac{\partial}{\partial y}\left(D \frac{\partial \psi}{\partial y} e^{-\Phi}\right) \tag{9}$$

where $\partial\psi/\partial t$ is evaluated holding ξ and t fixed. If the concentration profile on an $\xi =$ constant plane evolves slowly enough, the temporal derivative may be neglected; furthermore, if ψ is nearly independent of y, then so is $\partial\psi/\partial\xi$. With these assumptions, Eq. (9) may be integrated twice with respect to y to obtain the weak dependence on y:

$$\psi = \psi_0 + \frac{\partial \psi}{\partial \xi} \int_a^y \frac{I(y')\, dy'}{D(y')e^{-\Phi(y')}} \tag{10}$$

where

$$I(y') \equiv \int_a^{y'} [v(y'') - \bar{v}]e^{-\Phi(y'')}\, dy'' \tag{11}$$

and ψ_0 is an integration constant.

Let $J(\xi, t)$ denote the rate of transport of particles across an $\xi =$ constant plane per unit width:

$$J \equiv \int_a^{d-a} (v - \bar{v})c\, dy \tag{12}$$

This differs from zero only because $\bar{v}$, defined by Eq. (7), is not equivalent to $\int_a^{d-a} vc\, dy / \int_a^{d-a} c\, dy$. Substituting Eqs. (6) and (10) into (12), taking $\partial\psi/\partial\xi$ as nearly constant, and using Eq. (7) to show that the contribution from ψ_0 vanishes, yields

$$J = \frac{\partial \psi}{\partial \xi} \int_a^{d-a} [v(y) - \bar{v}]e^{-\Phi(y)} \int_a^y \frac{I(y')\, dy'}{D(y')e^{-\Phi(y')}}\, dy \tag{13}$$

Conservation of particles in the thin slice of fluid held between planes ξ and $\xi + d\xi$ requires

$$\frac{\partial}{\partial t}\left(\int_a^{d-a} c\, dy\right)_\xi = -\frac{\partial J}{\partial \xi} \tag{14}$$

Substituting Eqs. (13) and (6) with ψ nearly independent of y, Eq. (14) becomes

$$\frac{\partial \psi}{\partial t} = \mathscr{D}\frac{\partial^2 \psi}{\partial \xi^2} \tag{15}$$

where

$$\mathscr{D} \equiv \frac{-\int_a^{d-a} [v(y) - \bar{v}]e^{-\Phi(y)} \int_a^y \frac{I(y')\,dy'}{D(y')e^{-\Phi(y')}}\,dy}{\int_a^{d-a} e^{-\Phi}\,dy}$$

is called the "dispersion coefficient." Interchanging the order of integration, this expression becomes

$$\mathscr{D} \equiv \frac{\int_a^{d-a} \frac{I^2(y)\,dy}{D(y)e^{-\Phi(y)}}}{\int_a^{d-a} e^{-\Phi}\,dy} \tag{16}$$

from which it is clear that $\mathscr{D} \geq 0$. Except for the obvious geometrical differences, Eqs. (11) and (16) are identical to Eqs. [3.50] of Brenner and Gaydos (*9*), although a different method is employed.

If the length l of the injected slug is sufficiently short, the slug may be considered initially to be concentrated in the plane $x = 0$. Then the solution of Eq. (15) is

$$\psi = \frac{\alpha_0 l}{2\sqrt{\pi \mathscr{D} t}} \exp\left(-\frac{\xi^2}{4\mathscr{D} t}\right)$$

and the detector signal of Eq. (5) is

$$s(t) = \frac{N}{2d\sqrt{\pi \mathscr{D} t}} \exp\left[-\frac{(L - \bar{v}t)^2}{4\mathscr{D} t}\right] \tag{17}$$

Interpretation of $\bar{v}$ and $\mathscr{D}$ in One Limiting Case

From the residence time corresponding to the peak of the chromatogram and from the half-width of this peak, the values of $\bar{v}$ and $\mathscr{D}$ can be deduced.

What information concerning the particle/wall interaction $\phi(y)$ can be gleaned from these values?

The general relationships between these parameters and the potential profile are stated by Eqs. (7) and (16). As a simple limiting case, suppose the forces acting on the particles are such that at equilibrium the particle centers all lie very near to a plane denoted as $y = y_m$. This would occur if the function $\phi(y)$ is a negative spike concentrated at $y = y_m$ which causes $e^{-\Phi}$ to behave like a Dirac delta function. Then Eq. (7) reduces to

$$\bar{v} = v(y_m) \tag{18}$$

If the function $v(y)$ is known, then the location y_m of the minimum in $\phi(y)$ can be deduced from the value of the average velocity.

From its definition by Eq. (11), $I(a)$ must be zero. With the help of Eq. (7), $I(d-a)$ must also vanish. Since $e^{-\Phi}$ is very small everywhere except near $y = y_m$, $I(y)$ is expected to display its extremum near $y = y_m$. To approximate $I(y)$ near $y = y_m$, we shall substitute for v and Φ the first two nonvanishing terms of their respective Taylor series:

$$v = v_m + v_m'(y - y_m) \tag{19}$$

$$\Phi = \Phi_m + \frac{1}{2}\gamma(y - y_m)^2 \tag{20}$$

where $v_m' \equiv dv/dy$ evaluated at $y = y_m$ and $\gamma \equiv d^2\Phi/dy^2$ evaluated at $y = y_m$. Equation (11) becomes

$$I(y) = -\left(\frac{v_m'}{\gamma}\right) e^{-\Phi_m} \exp\left[-\frac{\gamma}{2}(y - y_m)^2\right] \tag{21}$$

provided $\frac{\gamma}{2}(a - y_m)^2 \gtrsim 2$. Finally $D(y)$ in the numerator of Eq. (16) is a gentle function compared to

$$I^2 e^{\Phi} \approx \left(\frac{v_m'}{\gamma}\right)^2 e^{-\Phi} \tag{22}$$

which is a sharp spike concentrated at $y = y_m$, and so $D(y)$ may be replaced by D_m, the leading term of its Taylor-series expansion about $y = y_m$. Substituting D_m and Eq. (22) in Eq. (16) obtains

$$\mathscr{D} = \left(\frac{v_m'}{\gamma}\right)^2 \frac{1}{D_m} \tag{23}$$

With y_m known from Eq. (18), v'_m and D_m can be calculated. Then Eq. (23) allows γ to be deduced from the experimental value of the dispersion coefficient.

In summary, the values of $\bar{v}$ and $\mathcal{D}$ deduced from the chromatogram can be used to infer two pieces of information about the potential profile $\Phi(y)$: the location of its minimum y_m and the value of $d^2\Phi/dy^2$ at this location.

CASE 2: NEARLY NON-BROWNIAN DISPERSION

On the other hand, suppose that the carrier flow rate is so fast that upon reaching the exit plane every particle is located at the same distance from the wall as it was initially. In other words, insufficient time was allowed for Brownian motion to occur. Analysis of this completely non-Brownian case was also performed by Taylor (*6*). His result could easily be extended to account for the nonuniform initial distribution given by Eqs. (3) and (4) and for the different velocity profile denoted by $v(y)$. However, more quantitative criteria as to when this result is applicable are not self-evident. To obtain such criteria, a new analysis is presented below which estimates the distortion of the signal owing to Brownian motion.

Introducing dimensionless variables:

$$\begin{aligned} X &\equiv x/L & H &\equiv (y-a)/a \\ \Phi &\equiv \phi/kT & C &\equiv c/\alpha_0 \\ V &\equiv v/U & \tau &\equiv tU/L \end{aligned}$$

Equations (1) through (4) become

$$\frac{\partial C}{\partial \tau} + V\frac{\partial C}{\partial X} = \lambda\frac{\partial}{\partial H}\left[f\left(C\frac{d\Phi}{dH} + \frac{\partial C}{\partial H}\right)\right] \tag{24a}$$

subject to:

$$f\left(\frac{\partial C}{\partial H} + C\frac{d\Phi}{dH}\right) \to 0 \quad \text{as} \quad H \to 0, R \tag{24b}$$

and

$$C = Ae^{-\Phi} \quad \text{at} \quad \tau = 0 \tag{24c}$$

where

$$A(X) = \begin{cases} 1 & \text{if} \quad 0 \leq X \leq l/L \\ 0 & \text{if} \quad X < 0 \text{ or } X > l/L \end{cases} \tag{25}$$

$$f(H) \equiv D(y)/D_\infty \tag{26}$$

$$\lambda \equiv LD_\infty/(Ua^2) \tag{27}$$

where U is the average velocity of the carrier, D_∞ is the bulk diffusion coefficient of particles, and R is $(d - 2a)/a$.

In terms of the dimensionless variables, the limit of very small residence time, L/U, corresponds to the limit $\lambda \to 0$. Thus a regular perturbation expansion of the form

$$C(X, H, \tau; \lambda) = c_0(X, H, \tau) + \lambda c_1(X, H, \tau) + \lambda^2 c_2(X, H, \tau) + \cdots \tag{28}$$

is used to represent the asymptotic behavior of the solution to Eq. (24) in this limit.

Substituting Eq. (28) into Eq. (24), then equating terms of order λ^0 yields

$$\frac{\partial c_0}{\partial \tau} + V\frac{\partial c_0}{\partial X} = 0 \tag{29a}$$

$$f\left(\frac{\partial c_0}{\partial H} + c_0\frac{d\Phi}{dH}\right) \to 0 \quad \text{as} \quad H \to 0, R \tag{29b}$$

$$c_0 = A(X)e^{-\Phi(H)} \quad \text{as} \quad \tau = 0 \tag{29c}$$

Equating terms of order λ^1 yields

$$\frac{\partial c_1}{\partial \tau} + V\frac{\partial c_1}{\partial X} = \frac{\partial}{\partial H}\left[f\left(c_0\frac{d\Phi}{dH} + \frac{\partial c_0}{\partial H}\right)\right] \tag{30a}$$

$$f\left(\frac{\partial c_1}{\partial H} + c_1\frac{d\Phi}{dH}\right) \to 0 \quad \text{at} \quad H \to 0, R \tag{30b}$$

$$c_1 = 0 \quad \text{at} \quad \tau = 0 \tag{30c}$$

Equation (29) describes the case of completely non-Brownian dispersion. The solution is easily obtained by the method of characteristics:

$$c_0(X, H, \tau) = A(\eta)e^{-\Phi(H)} \tag{31}$$

where

$$\eta(X, H, \tau) \equiv X - \tau V(H) \tag{32}$$

The solution of Eq. (30) represents the leading term of the distortion of the profile caused by Brownian motion. Using Eqs. (31) and (32) to eliminate c_0 and X from Eq. (30a) yields

$$\left(\frac{\partial c_1}{\partial \tau}\right)_{\eta,H} = \tau^2 \ddot{A}(\eta) V'^2 f e^{-\Phi} - \tau \dot{A}(\eta)[V' f e^{-\Phi}]' \tag{33}$$

where primes and dots denote derivatives with respect to H and η, respectively. If A is given by Eq. (25), with η substituted for X, then $\dot{A}$ and $\ddot{A}$ are zero everywhere except at $\eta = 0$ and $\eta = l$, where their values are not defined. Of course, the ends of a real slug will be more diffuse so that these singularities do not occur. Fortunately, the nature of these derivatives will prove to be unimportant to the conclusion of this analysis.

After integrating Eq. (33) with respect to τ, holding η and H fixed (i.e., integration along a characteristic) and using Eq. (30c) as an initial condition, the function c_1 is obtained. Substituting the result together with Eq. (31) into Eq. (28), truncating the series after the second term, and then substituting the result into Eq. (5) obtains

$$\frac{ds(t)}{a\alpha_0} = \int_0^R \left\{ A(\eta)e^{-\Phi} - \frac{\lambda\tau^2}{2} \frac{\partial}{\partial H}[\dot{A}(\eta) V' f e^{-\Phi}]_{X,\tau} - \frac{\lambda\tau^3}{6} \ddot{A}(\eta) V'^2 f e^{-\Phi} \right\} dH$$

The quantity inside the square brackets is equivalent to

$$\dot{A}(\eta) V' f e^{-\Phi} = -\frac{f}{\tau}\left(\frac{\partial c_0}{\partial H} + c_0 \frac{d\Phi}{dH}\right)$$

when c_0 is given by Eq. (31). The integral of the τ^2 term in Eq. (34) equals $-\frac{1}{2}\lambda\tau^2$ times the difference in this expression evaluated at $H = R$ and at $H = 0$; both terms of this difference must identically vanish by Eq. (29b). Integrating the τ^3 term by parts twice leaves

$$\frac{ds(t)}{a\alpha_0} = \int_0^R A(\eta)\left\{e^{-\Phi} - \frac{\lambda\tau}{6}\left[\frac{(V'fe^{-\Phi})'}{V'}\right]'\right\} dH \tag{35}$$

From Eq. (25), $A(\eta) = 0$ except for $0 \leq \eta \leq l/L$, where $\eta = 1 - \tau V(H)$ in the exit plane. Before the leading edge of the slug reaches the exit plane, this integral will equal zero. After the trailing edge of the slug on the midplane ($y = d/2$) has passed through the detector, there exist two intervals in H for which $A(\eta)$ will be nonzero in the exit plane (see Fig. 2). For any given time, let these intervals be denoted as $H_1(\tau) \leq H \leq H_2(\tau)$ and $H_3(\tau) \leq H \leq H_4(\tau)$, where the $H_i(\tau)$ are defined so that

$$\tau V(H_2) = \tau V(H_3) = 1 \tag{36a}$$

which corresponds to $\eta = 0$, and

$$\tau V(H_1) = \tau V(H_4) = 1 - l/L \tag{36b}$$

which corresponds to $\eta = l/L$. Since the particles were allowed to settle near the lower plate before elution began, there are practically no particles in the interval above the midplane. Substituting $A = 1$ for $H_1 \leq H \leq H_2$ and neglecting the contribution from the second interval, Eq. (35) becomes

$$\frac{ds(t)}{a\alpha_0} = \int_{H_1(\tau)}^{H_2(\tau)} \left\{e^{-\Phi} - \frac{\lambda\tau}{6}\left[\frac{(V'fe^{-\Phi})'}{V'}\right]'\right\} dH \tag{37}$$

for $\tau > 1/\max(V)$. The second term represents the distortion of the signal owing to Brownian motion of the particles. To neglect this contribution, the dimensionless residence time τ must be sufficiently short so that

$$|\lambda\tau[(V'fe^{-\Phi})'/V']'| \ll 6e^{-\Phi} \tag{38}$$

Further, if the slug length l is made sufficiently short, the interval $H_2 \leq H \leq H_1$ becomes so narrow that $e^{-\Phi}$ can be considered constant over the interval. More precisely, $e^{-\Phi}$ can be treated as a constant if the second term in a Taylor series expansion of this function is negligible compared to the first, or if

$$\left|\frac{de^{-\Phi}}{dH}\right| (H_2 - H_1) \ll e^{-\Phi} \tag{39}$$

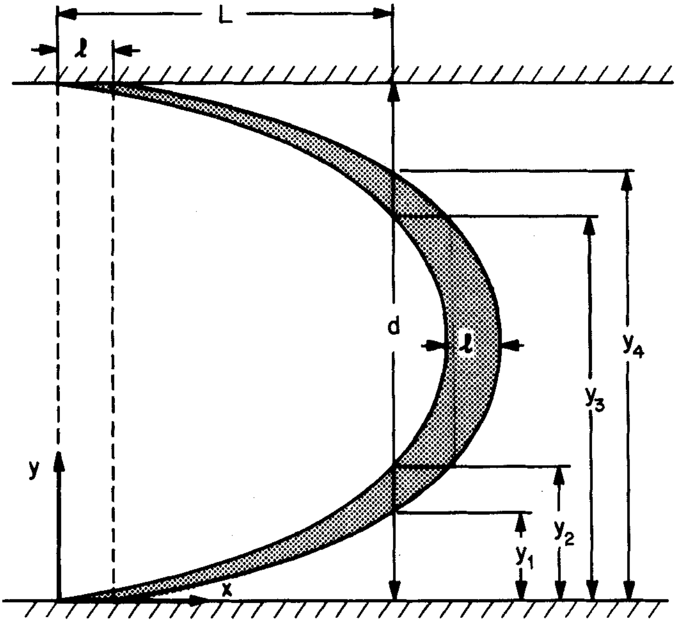

FIG. 2. Dispersion of a slug of non-Brownian particles owing to convection. (Vertical distances have been greatly exaggerated with respect to horizontal distances.) The initial shape of the slug is denoted by dashed lines, whereas the shape after t seconds of flow is denoted by the shaded region. The H_i defined by Eq. (36) are related to the y_i marked in this sketch by the expression $H_i = (y_i - a)/a$, for $i = 1, 2, 3$, or 4.

For short slugs and short residence times, Eq. (37) becomes

$$\frac{ds(t)}{a\alpha_0} = [H_2(\tau) - H_1(\tau)] \exp\{-\Phi[H_2(\tau)]\} \tag{40}$$

Thus the total potential energy of a particle located a given distance from the bottom plate may be deduced from the signal measured at a prescribed time.

Physical Interpretation of Constraints

Near the bottom plate, where $|\phi|$ is comparable to or larger than kT, $e^{-\Phi}$ can be expected to vary much more strongly with position than V' or f. Treating V' and f as constants, Eq. (38) becomes

$$Dt\left|\left(\frac{d\Phi}{dy}\right)^2 - \frac{d^2\Phi}{dy^2}\right| \ll 6 \tag{41}$$

In the usual models for colloidal forces $|d^2\Phi/dy^2| \ll (d\Phi/dy)^2$ except near extrema. Neglecting the second derivative, Eq. (41) states that the distance $\sqrt{Dt}$ over which particles can be expected to diffuse during their residence in the column must be short compared to the vertical displacement $|dy/d\Phi|$ needed to change the potential energy of the particles by kT.

If V' varies slowly, then $V(H_2) - V(H_1) \approx (H_2 - H_1)V'$. Substituting Eq. (36) and this approximation into Eq. (39) yields

$$l \ll t|dv/d\Phi| \tag{42}$$

where $dv/d\Phi$ is the ratio of dv/dy to $d\Phi/dy$. Consider two particles located at such distances from the wall that their respective potential energies differ by kT. Because they reside in planes of different velocity, these particles begin to separate at an axial speed approximately equal to $|dv/d\Phi|$. Equation (42) states that the slug length must be short compared to the axial distance accrued between these two particles when they are eluted from the column.

Approximating $H_2 - H_1$ as above, Eq. (40) becomes

$$s(t) = \alpha_0 \frac{le^{-\Phi(H_2)}}{dt\, dv/dy} \tag{43}$$

where $H_2(\tau)$ is given by Eq. (36).

DISCUSSION

Long Retention Time: FFF

Field-flow fractionation or FFF (*2*) is a class of techniques for separating mixtures of colloids which closely resembles the situation analyzed above. A short slug of particles is injected into Poiseuille flow of the carrier fluid held between two large parallel plates (as in Fig. 1). While the particles are in the column a force field (e.g., gravity) is applied perpendicular to the flow to cause particles to migrate into the slower fluid near one of the plates. This causes the average velocity of the particles to differ from the average velocity of the carrier. When the force felt by an individual particle depends upon some property of the particle (e.g., mass or charge), then particles with different values of the property will be carried through the column at different average velocities—permitting their separation by this technique.

Two examples in this class which employ gravity as the force field are "sedimentation FFF" (*12*) and "steric FFF" (*13*). In both, the retention time is long enough for the predictions of Case 1 to be applicable. Indeed, when injecting mixtures of particles, chromatograms are reported with several peaks in which the general shape of each seems to conform to Eq. (17). The two techniques differ mainly in the order of elution of particles having different sizes. When all the particles are much smaller than 1 μm, small particles are eluted before larger ones and the technique is called sedimentation FFF. When all the particles are much larger than 1 μm, the opposite elution order is observed and the technique is called steric FFF.

Both behaviors can be predicted by Eq. (7). As an exercise, let's assume that gravity and hard-sphere steric exclusion are the only forces contributing to $\Phi(y)$. Then the potential profile is

$$\Phi(y) = \begin{cases} (y - a)/\mathscr{L} & \text{for} \quad y \geq a \\ \infty & \text{for} \quad y < a \end{cases} \tag{44}$$

where

$$\mathscr{L} \equiv \frac{kT}{\dfrac{4}{3}\pi a^3(\rho_s - \rho)g} \tag{45}$$

is the ratio of the particle's thermal energy to the gravitational force it feels. This profile is plotted as the solid lines in Fig. 3. Let's further assume that the axial velocity of a particle equals the axial velocity of fluid the same distance from the wall as the particle's center. Then

$$v(y) = 6Uy/d \qquad (y \ll d/2) \tag{46}$$

where U is the average velocity of the carrier. Substituting (44) and (46) into (7) obtains

$$\frac{\bar{v}}{U} \approx 6\,\frac{a + \mathscr{L}}{d} \tag{47}$$

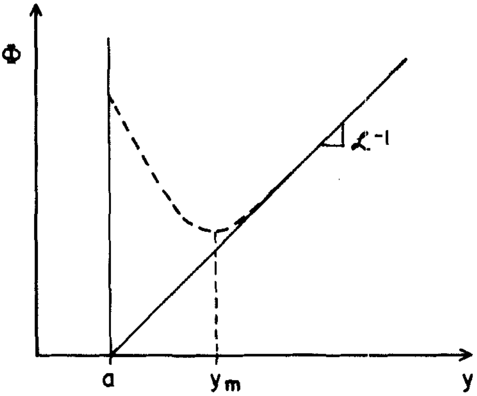

FIG. 3. The shape of the potential profile when only gravitational attraction and steric exclusion act (solid line) or when these two forces plus double-layer repulsion act (dashed line).

for the "retention ratio" when $\mathcal{L} \ll d/2$. Note that if the particles are small enough so $\mathcal{L} \gg a$, then $\bar{v} \propto \mathcal{L} \propto a^{-3}$. In this case *smaller* particles move at a higher velocity than larger particles and will be eluted first (sedimentation FFF). On the other hand, for very large particles, $\mathcal{L} \ll a$ and (47) predicts $\bar{v} \propto a$. Then *larger* particles will be eluted first (steric FFF). For $\rho_s - \rho = 1$ g/cm^3 at T = 300 K, Eq. (45) predicts $\mathcal{L} = a$ when $2a = 1.12$ μm, which is the correct order of magnitude for the particle size separating the two techniques. This critical size is not sensitive to the particle density. Thus Eq. (7) can be used to rationalize these two techniques. The corresponding prediction of the dispersion coefficient

$$\mathcal{D} = 72\frac{U^2\mathcal{L}^4}{Dd^2} \tag{48}$$

is obtained from Eq. (16) with $D(y)$ taken as a constant. On this basis, we predict $\mathcal{D} \propto a^{-11}$, which would make the half-widths of the chromatogram peaks exquisitely sensitive to particle size—they are not.

Let's modify the above analysis by adding double-layer repulsion to the potential profile of Eq. (44):

$$\Phi(y) = \begin{cases} B\exp\left(-\dfrac{y-a}{\lambda}\right) + \dfrac{y-a}{\mathcal{L}} & (y \geq a) \\ \infty & (y < a) \end{cases} \tag{49}$$

$$B = 16\varepsilon \frac{akT}{e^2} \tanh\left(\frac{e\psi_1}{4kT}\right) \tanh\left(\frac{e\psi_2}{4kT}\right) \tag{50}$$

$$\lambda = \left(\frac{\varepsilon kT}{8\pi z^2 e^2 c}\right)^{1/2} \tag{51}$$

where ε is the dielectric constant, c is the concentration of a z-z electrolyte, and ψ_i are the Stern potentials of the particle and lower plate. [Use of the electrostatic system of units is assumed in the form of these equations: $\varepsilon = 78$ for water, $e = 4.803 \times 10^{-10}$ statcoul, ψ_i expressed in statvolts (300 volts = 1 statvolt), c expressed in ions/cm^3, with all other symbols expressed in the appropriate c.g.s. units.] This expression for the double-layer repulsion is almost identical to one used by Verwey and Overbeek (*14*) to determine the critical coagulation concentration of an electrostatically stabilized hydrosol, except it has been modified to account for the sphere-plane geometry. The total potential profile is plotted as the dotted line in Fig. 3. Equation (49) has a minimum at $y = y_m$:

$$y_m = a + \lambda \ln (B\mathscr{L}/\lambda) \tag{52}$$

$$\gamma \equiv \left.\frac{d^2\Phi}{dy^2}\right|_{y_m} = \frac{1}{\mathscr{L}\lambda} \tag{53}$$

As $\mathscr{L} \to 0$ (large dense particles), $e^{-\Phi}$ behaves like a delta function, having a spike at $y = y_m$. Then we can approximate Eqs. (7) and (16) by Eqs. (18) and (23) which yield

$$\frac{\bar{v}}{U} = 6\frac{y_m}{d} = \frac{6}{d}\left[a + \lambda \ln\left(\frac{B\mathscr{L}}{\lambda}\right)\right] \tag{54}$$

$$\mathscr{D} = 36 \frac{U^2\lambda^2\mathscr{L}^2}{D_m d^2} \tag{55}$$

These assumptions are more likely to be valid in steric FFF than in sedimentation FFF.

When $a \gg \lambda$ and $\mathscr{L}$, the second term in Eq. (54) can be neglected and the retention ratio becomes the same as that predicted by ignoring double-layer repulsion. However, the dispersion coefficient is quite different. If $y_m - a \ll a$, then $D_m \approx (y_m - a)D_\infty/a$. This result was deduced from the asymptotic form of the friction coefficient for a rigid sphere near to a plane wall (*11*). Substituting this expression and y_m from Eq. (52) into Eq. (55) yields

$$\mathscr{D} = \frac{36U^2 a\lambda\mathscr{L}^2}{\ln(B\mathscr{L}/\lambda)D_\infty d^2} \tag{56}$$

where D_∞ is the diffusion coefficient of particles evaluated far from any wall. Owing to the dependence upon λ, Eq. (56) predicts that the dispersion coefficient should decrease with the concentration of salt in the carrier. Equation (56) also predicts a dispersion coefficient which is less sensitive to particle size than Eq. (48), but still more sensitive than that observed. For example, the chromatogram of Caldwell et al. (*15*) displays almost no dependence of peak width on particle size for silica beads of 5–10 μm. However, Eq. (56) applies to dispersion of an ensemble of *idential* particles. Perhaps the peak width of real samples is more a measure of the variance in size of particles composing the sample than of the dispersion coefficient of particles having the mean size.

Besides analyzing particle mixtures, this type of experiment can be used to probe colloidal forces. Suppose that an ensemble of identical particles is injected, allowed to settle, and eluted. From the residence time and half-width of the peak, two pieces of information about the potential profile can be deduced: y_m and $d^2\phi/dy^2$ at $y = y_m$. In principle, the entire potential profile could be determined through a series of experiments in which the applied force is varied by adding an adjustable centripetal field. Increasing the applied force can be expected to shift y_m closer to a, thus allowing $d^2\phi/dy^2$ to be determined at different y. When the applied force is spatially uniform, it does not contribute to $d^2\phi/dy^2$, so that integrating $d^2\phi/dy^2$ as a function of y_m yields the profile of the net colloidal force.

Short Retention Time

By contrast, the opposite extreme of very short residence time seems to afford a major advantage for the determination of the potential profile. In particular, Eq. (43) suggests that the entire profile can be deduced from a single chromatogram.

Of particular concern is whether the particles can be eluted fast enough so they do not have time to diffuse that very short vertical distance over which their potential energy changes appreciably. The closer to the wall a particle is, the longer its residence time t will be and the stronger the colloidal force $|d\phi/dy|$ it feels; thus the closer to the wall a particle is, the more difficult it is to satisfy Eq. (41).

How close to the wall could such an experiment probe the particle/wall interactions? To obtain a rough estimate of the answer, consider a parallel plate column whose dimensions are $d \times W \times L = 0.1$ cm $\times$ 5 cm $\times$ 250 cm. Near the bottom plate the particles' velocity, owing to Poiseuille flow, can be approximated by Eq. (46) that the residence time of particles is $t \approx Ld/(6Ua)$. To minimize this residence time, the flow rate is chosen as the largest value which permits laminar flow ($\rho Ud/\mu \leq 1000$) and which corresponds to a residence time that is much larger than the relaxation time needed to establish steady Poiseuille flow [say $Ld/(6Ua) \geq 100\ \rho d^2/\mu$]. For large particles ($a \geq 4\ \mu$m) in this particular column, the relaxation time provides the tighter constraint; the largest allowable flow rate corresponds to

$$U = 4\mu/\rho a \tag{57}$$

where μ and ρ are the fluid's viscosity and density. Substituting these values together with $D = kT/(6\pi\mu a)$ and $T = 300$ K into Eq. (41), and neglecting $d^2\Phi/dy^2$, yields

$$\mathscr{L}^2 \gg (3.7 \times 10^{-16}\ \text{g}\cdot\text{cm}^4/\text{s}^2)\ \frac{\rho}{\mu^2 a} \tag{58}$$

where $\mathscr{L} \equiv |dy/d\Phi|$. To have less than 10% distortion in the signal caused by Brownian motion of 10 μm particles in water, Eq. (58) requires $\mathscr{L} \geq 1.9$ μm. According to the definition of $\mathscr{L}$, the signal can be interpreted using Eq. (40) up to the instant at which particles are eluted from that position next to the wall where the local force on the particle equals $kT/\mathscr{L}$ or 2.1×10^{-10} dyn.

A less precise but more useful interpretation of $\mathscr{L}$ is the displacement needed to change the potential energy by kT. To measure the most interesting part of the potential profile, the minimum allowable $\mathscr{L}$ should be smaller than the range of the force. Then the $\mathscr{L}$ of 1.9 μm in the above example would not be adequate to measure the double-layer force, whose range is always less than 1 μm in water.

One way to decrease $\mathscr{L}$ is to use a more viscous fluid. In addition, the molecules composing most other fluids do not dissociate into ions like water does, so that lower ion concentrations, and therefore a longer range for the double-layer force, can be obtained. Using $\mu = 10$ g/cm·s, Eq. (58) is satisfied for $\mathscr{L} \geq 0.0019$ μm, which is small enough to allow measurement of double-layer forces. Actually, Eq. (58) gives a conservative estimate of $\mathscr{L}$ since it does not consider that a particle's diffusion coefficient D may be orders of magnitude smaller than the bulk value D_∞ when it is near the wall (a lower diffusion coefficient yields a lower $\mathscr{L}$).

With this same set of approximations, constraint (42) becomes $l \ll \mathscr{L}L/a = 2.5 \times 10^5\ \mathscr{L}$. Substituting the smaller $\mathscr{L}$ found above, this corresponds to an injection of $dWl \ll 25$ μL. Such small injections are not unusual in liquid chromatography. Thus Eq. (42) is not a severe constraint.

Other sources of error include additional dispersion of the slug owing to shear-induced collisions or to a distribution in the size of particles. Shear-induced collisions may deflect particles off their original streamline by as much as one diameter. Since the frequency of such collisions is proportional to the square of particle concentration, their effect can be minimized by injecting fewer particles, provided the detector is sensitive enough. A variation in size of the injected particles can also contribute to dispersion since the most probable velocity of any particle depends on its size [recall $v(a) \approx 6Ua/d$]. To neglect this effect, the standard deviation in particle size should be smaller than the desired spatial resolution of $\phi(y)$. In practice, this may require further refinement of available standards. Surface roughness in the bottom plate will also have to be small compared to the spatial resolution desired for measuring $\phi(y)$. This might be achieved by lining the bottom wall with a sheet of molecularly-smooth mica. Finally, Caldwell et al. (*15*) observe a flow-rate dependent "lift" force which appears to act on low-density particles during steric FFF. This might be a minifestation of inertial migration of particles across streamlines which has been the subject of many other studies (*16, 17*). If this force is inertial in origin, then it can be made negligible by keeping the flow rate small, although this might make it impossible to meet the requirement of short retention time.

Instead of using a chromatography column and detector to measure the residence-time distribution of an ensemble of particles, one could directly observe under a microscope the distribution of velocities assumed by a single sphere at different instants as it is translated horizontally by linear shear flow near a flat plate. This experiment would provide much greater flexibility in meeting the constraints imposed by the mathematical analysis and would completely avoid the ambiguities arising from the standard deviation in properties of an ensemble. We are currently attempting such an experiment with a single sphere.

If successful, such an experiment would provide the first measurement of the potential profile between a colloidal particle and a plate. The result could be compared with theoretical predictions of the double-layer and van der Waals interactions. Even if only very long-range forces could be probed, this experiment may provide a valuable new tool for the study of colloids.

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REFERENCES

1. H. Small, *J. Colloid Interface Sci.*, *48*, 147 (1974).
2. J. C. Giddings, *Anal. Chem.*, *53*, 1170 (1981).
3. R. S. Subramanian, *J. Colloid Interface Sci.*, *63*, 49 (1978).
4. E. Ruckenstein and D. C. Prieve, *AIChE J.*, *22*, 276 (1976).
5. D. C. Prieve and P. M. Hoysan, *J. Colloid Interface Sci.*, *64*, 201 (1978).
6. G. Taylor, *Proc. R. Soc.*, *A219*, 186 (1953); *A223*, 446 (1954); *A225*, 473 (1954).
7. R. Aris, *Ibid.*, *A235*, 67 (1956).
8. W. N. Gill and R. Sankarasubramanian, *Ibid.*, *A316*, 341 (1970); *A322*, 101 (1971); *A327*, 191 (1972); *A329*, 479 (1972).
9. H. Brenner and L. J. Gaydos, *J. Colloid Interface Sci*, *58*, 312 (1977).
10. A. J. Goldman, R. G. Cox, and H. Brenner, *Chem. Eng. Sci.*, *22*, 653 (1967).
11. H. Brenner, *Ibid.*, *16*, 242 (1961).
12. J. C. Giddings, F. J. F. Yang, and M. N. Myers, *Anal. Chem.*, *46*, 1917 (1974).
13. J. C. Giddings and M. N. Myers, *Sep. Sci. Technol.*, *13*, 637 (1978).
14. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, 1948.
15. K. D. Caldwell, T. T. Nguyen, M. N. Myers, and J. C. Giddings, *Sep. Sci. Technol.*, *14*, 935 (1979).
16. H. Brenner, *Adv. Chem. Eng.*, *6*, 267 (1966).
17. B. P. Ho and L. G. Leal, *J. Fluid Mech.*, *65*, 365 (1974).

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