Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Field-Flow Fractionation: Extensions to Nonspherical Particles and Wall Effects

Lawrence J. Gajdos[ab]; Howard Brenner[ac]
[a] DEPARTMENT OF CHEMICAL, ENGINEERING CARNEGIE-MELLON UNIVERSITY, PITTSBURGH, PENNSYLVANIA [b] Formerly Gaydos. Currently with Carnegie-Mellon Institute of Research., [c] Department of Chemical Engineering, University of Rochester, Rochester, New York

To cite this Article Gajdos, Lawrence J. and Brenner, Howard(1978) 'Field-Flow Fractionation: Extensions to Nonspherical Particles and Wall Effects', Separation Science and Technology, 13: 3, 215 — 240
To link to this Article: DOI: 10.1080/01496397808060221
URL: http://dx.doi.org/10.1080/01496397808060221

SEPARATION SCIENCE AND TECHNOLOGY, 13(3), pp. 215–240, 1978

Field-Flow Fractionation: Extensions to Nonspherical Particles and Wall Effects

LAWRENCE J. GAJDOS* and HOWARD BRENNER†

DEPARTMENT OF CHEMICAL ENGINEERING
CARNEGIE-MELLON UNIVERSITY
PITTSBURGH, PENNSYLVANIA 15213

Abstract

A rigorous analysis of the phenomenon of field-flow fractionation (FFF) is presented for particles which are both nonspherical in shape and of sufficient size (compared with apparatus dimensions) to be significantly influenced by wall effects. Calculations are presented for axially-symmetric particles in an arbitrary flow field. Orienting torques directed along the symmetry axis of the particle are also considered. The theory is compared with the experimental data of Berg, Purcell, and Stewart. Reasonably satisfactory agreement is observed.

INTRODUCTION

This contribution is concerned with the combined diffusive and convective transport of an isolated, arbitrarily shaped Brownian particle immersed in a fluid flowing horizontally above a flat plate. It applies equally well to dilute systems of noninteracting particles. In the presence of conservative external forces and torques normal to the flow direction (such as arise from gravity), which simultaneously influence the particle's position and orientation, the average convective transport of the particle is governed by its buoyant mass. In turn, this determines the *average* particle

*Formerly Gaydos. Currently with Carnegie-Mellon Institute of Research.

†Current address: Department of Chemical Engineering, University of Rochester, Rochester, New York 14627.

position in the potential field. This phenomenon can be used to effect a separation between particles of different size, shape, or density. This separation concept was developed independently by Berg and Purcell (*1–3*) and by Giddings (*4–6*), who termed the method "field-flow fractionation." Here, the theoretical analysis is improved upon and extended to include nonspherical particles in an orienting field.

Our approach, which considers the temporal evolution of the probability density describing both the position and orientation of a single particle, has previously (*7*) been applied to analyze transport of Brownian spheres in fluid-filled circular cylinders. However, in that situation, particle transport is affected by the size of the particle (due to "exclusion effects" and hydrodynamic interactions with the system boundaries). Here, size is primarily of importance only insofar as it determines the particle's buoyant mass. This greatly simplifies the hydrodynamic analysis of the particle's behavior.

Berg and Purcell (*1*) employed an ingenious random-walk analysis to (in effect) obtain the approximate time-evolution of the moments of the particle distribution. Giddings (*5*) used somewhat different, but still heuristic, concepts in his theoretical analysis ("nonequilibrium theory"), as is pointed out by Subramian (*8*), who shows how the Gill and Subramian dispersion theory (*9*) is more suitable for theoretical treatment of these problems.

The analysis to be given here extends the range of problems for which theoretical analysis of field-flow fractionation may be contemplated. Considerations are given to the finite size of the particle in terms of the consequences of the regions close to the system boundaries being inaccessible to the particle. Also, by beginning with the six-space continuity equation, it is possible to extend the applicability to nonspherical particles. Illustrative examples are carried out for special subcases of the general theory to indicate how it can be applied.

A more detailed summary of the developments to be presented now follows.

We begin by presenting the continuity equation governing the particle's six-space probability density. Boundary conditions are incorporated into the continuity equation via a synthetic wall potential, which expresses the fact that the particle surface is unable to penetrate physical barriers. The particle is assumed to be introduced into the flowing fluid at zero time at an arbitrary location and with an arbitrary orientation.

Particle size is assumed relatively small compared with the physical dimensions of the apparatus. For times longer than the characteristic "diffusion time" of the particle, it is then shown that the particle loses all memory of its initial orientation. Consequently, a condition of "orientational equilibrium" obtains instantaneously at each point, wherein the particle's rotary Brownian motion is equilibrated with the orienting effects of the external couple. As a consequence, it becomes possible to average the continuity equation over all orientations of the particle, leading to a closed-form expression for the time-evolution of the marginal probability density of particle-locator position in physical space only. The expression is identical to that describing convective diffusion phenomena in an anisotropic medium.

For illustrative purposes, the physical problem is then specialized. The particle is assumed to be a body of revolution, possessing both fore/aft symmetry and an axisymmetric (but possibly inhomogeneous) distribution of mass. The general theory, however, is not restricted to these assumptions. Further, the external force is assumed to arise from a constant acceleration potential, such that any external torque due to the particle's mass inhomogeneity is constant too. Again, these restrictions lend concreteness but are not essential to the development of the theory. The continuity equation is then simplified to a form specific to these assumptions.

Analysis of the problem is continued by deriving relationships for the asymptotic, first, and second axial moments of particle position in the direction of flow. For these long times, the particle loses all memory of its initial position in the plane perpendicular to the flow. It is shown that a "positional equilibrium" develops wherein translational diffusion is balanced by the deterministic influences of the external field. The moments are given in terms of the physical parameters of the problem as well-defined integrals of the local undisturbed fluid velocity profile. These integrals are weighted by an appropriate factor dependent on the strength of the external field.

The transport moment integrals are then evaluated for an arbitrary, power-series velocity profile. The integrals are reduced to finite sums involving the incomplete gamma function. Numerical results are given for two of the more common velocity profiles, namely flow between two parallel flat plates (full parabola) and flow with an upper free surface (half parabola). These results are parameterized by a dimensionless grouping proportional to the strength of the external field.

Following this, the results for an appropriate limiting case are shown to be comparable to those of Berg and Purcell (*1*). Our computations are more accurate at extreme values of the field strength grouping. We then show how our results may be applied to nonspherical particles, taking the dimers observed by Berg and Purcell as a prototype shape. Next, the results are extended to incorporate first-order effects of particle size (for spheres only) on the rate of particle transport. The modification appears able to account for most of the observed deviation between theory and experiment. Lastly, we indicate how the appropriate corrections can be calculated for nonspherical particles.

PROBLEM DESCRIPTION

Consider a single Brownian particle inserted into an otherwise unidirectional horizontal fluid motion taking place in the z direction. The fluid extends to infinity in all horizontal directions being bounded vertically, below and above, by planes $y = 0$ and $y = h$, respectively. With $\hat{z}$ a unit vector in the direction of flow, the undisturbed fluid velocity field is assumed to be of the form

$$\mathbf{V}_f = \hat{z} V_f(y) \tag{1}$$

This automatically satisfies the continuity equation

$$\nabla \cdot \mathbf{V}_f = 0 \tag{2}$$

for any choice of $V_f(y)$.

In addition to the hydrodynamic surface force exerted on the particle by this fluid motion, an external body force is assumed to act upon the particle in the vertical direction. This force may also give rise to a torque on the particle, tending to align the latter in a particular orientation with respect to the direction of the external force field. This would occur, for example, if the particle's mass were inhomogeneously distributed.

As a result of the diffusive, random Brownian forces superimposed on the above, the net motion of the particle is a stochastic process whose statistical properties may be described by the temporal evolution of the probability density function describing the particle's instantaneous position.

The "position" of an arbitrarily shaped, rigid particle of finite size is described by six coordinates, three to fix the location of the particle in space and three to describe its orientation. In this paper, the configuration-space representation of Brenner and Condiff (*10*) shall be used. Particle location is given by the vector $\mathbf{R}$ from a point fixed in space to an arbitrary "locator point" rigidly attached to (but not necessarily lying within) the particle. $\mathbf{R}$ will be given the Cartesian coordinates (x, y, z) delimiting the apparatus. Particle orientation is specified by the set of Euler angles (*10, 11*) $\boldsymbol{\phi}$ which relate the orientation of axes fixed in the particle (body-fixed axes) to a set of axes fixed in space.

The particle's position $(\mathbf{R}, \boldsymbol{\phi})$ is a stochastic process with given initial condition $(\mathbf{R}', \boldsymbol{\phi}')$ at time $t = 0$. As is discussed later, for sufficiently long times the statistics of this process become independent of this initial condition—whence the particle loses all "memory" of its initial state. The probability density function describing this motion will be denoted by $\sigma = \sigma(\mathbf{R}, \boldsymbol{\phi}, t \mid \mathbf{R}', \boldsymbol{\phi}')$. That is, $\sigma d^3\mathbf{R} d^3\boldsymbol{\phi}$ is the probability that the particle's position at time t lies in the six-space volume element $d^3\mathbf{R} d^3\boldsymbol{\phi}$ centered at $(\mathbf{R}, \boldsymbol{\phi})$. By definition, the integral of this function over the entire domain must be unity:*

$$\iint \sigma d^3\mathbf{R} d^3\boldsymbol{\phi} = 1 \qquad (\text{for all } t) \tag{3}$$

Conservation and continuity of probability density require that σ satisfy the continuity equation (*7, 10, 12–15*)

$$\frac{\partial \sigma}{\partial t} + \frac{\partial}{\partial \mathbf{R}} \cdot {}^t\mathbf{J} + \frac{\partial}{\partial \boldsymbol{\phi}} \cdot {}^r\mathbf{J} = \delta(t)\delta(\mathbf{R} - \mathbf{R}')\delta(\boldsymbol{\phi} - \boldsymbol{\phi}') \qquad (\text{for } t \geq 0) \tag{4}$$

$$\sigma = 0 \qquad (\text{for } t < 0) \tag{5}$$

In the above, δ is the Dirac delta function, defined for vector arguments such that it is normalized when integrated over the appropriate vector space:

$$\int \delta(\mathbf{R} - \mathbf{R}') d^3\mathbf{R} = 1 \tag{6}$$

$$\int \delta(\boldsymbol{\phi} - \boldsymbol{\phi}') d^3\boldsymbol{\phi} = 1 \tag{7}$$

$\partial/\partial\mathbf{R}$ and $\partial/\partial\boldsymbol{\phi}$ represent gradient operators in physical and orientation space, respectively, while the quantities ${}^t\mathbf{J}$ and ${}^r\mathbf{J}$, respectively, are the vector fluxes of probability due to translation and rotation of the particle. These quantities, which contain contributions arising from all three sources of particle motion (fluid convection, external forces and torques, and Brownian motion) can be related to the density function σ (*10*).

The motion of the particle is constrained such that every point in the

*The notation $\int \cdots$ indicates integration over the entire domain of either physical space, $\mathbf{R}$, or orientation space, $\boldsymbol{\Phi}$.

particle necessarily lies between $y = 0$ and $y = h$ at all times. Taking account of the finite size of the nonspherical particle is mathematically nontrivial as regards the impenetrability of the wall to the particle. In general, for a given set of locations **R**, only certain orientations $\boldsymbol{\phi}$ of the particle will meet this restriction. The description of the boundary condition will also depend on the particular choice made for the locator point.* Gajdos (*16*) discusses a technique for incorporating this boundary condition directly into the continuity equation, by recognizing that penetration of the boundaries by the particle is prevented by very short-range, intermolecular, repulsive forces. These forces may be most simply modeled by assuming that they give rise to a potential which is everywhere zero, except when particle-boundary penetration occurs, in which event the potential assumes a value of infinity. Such a potential could still be a complicated switching-type function of location and orientation. Nevertheless, it eliminates and/or postpones many conceptual problems associated with the boundary condition.

When size effects are irrelevant, as will be true here, the wall potential "switching function" takes an especially simple form, independent of orientation. If we specify that the particle-locator point be "somewhere near" the particle—for example, within it or not too far from some point on its surface—we may take as the wall potential E_w, a function which is infinite whenever the vertical y coordinate of the particle's location vector **R** lies outside the vertical boundaries of the system:

$$E_w = \begin{cases} 0, & 0 < y < h \\ \infty, & y \leq 0; y \geq h \end{cases} \tag{8}$$

This ignores any considerations of the finite size of the particle. Simply stated, the difference between the true cutoff values, which vary with particle orientation, and those used above (0 and h) is much smaller than the distance scale of interest. Hence, to a certain order of approximation (consistent with other assumptions to be invoked), Eq. (8) allows a valid representation of the boundary condition.

Thus, if the other forces and torques on the particle can also be expressed

*For example, if the particle is a sphere, any choice of locator point other than the sphere center implies that the boundary condition must involve a complicated interconnection between location and orientation. For other particle shapes, no locator point proves to eliminate this interdependence—although some choices may prove better than others.

as a potential, the net force **F** and torque **T** on the particle are given by

$$\mathbf{F}/kT = -\partial E/\partial \mathbf{R} \tag{9}$$

$$\mathbf{T}/kT = -\partial E/\partial \boldsymbol{\phi} \tag{10}$$

with k the Boltzmann constant and T the absolute temperature. This definition of the net potential* E, which incorporates the mean thermal particle energy kT, renders it dimensionless. The potential arises from both the physical origins previously discussed as well as from the synthetic considerations of the boundary condition.

Equations (4) and (5) describe the evolution of the probability density function of the stochastic process $(\mathbf{R}, \boldsymbol{\phi})$ from its initial value $\sigma(\mathbf{R}, \boldsymbol{\phi}, 0 \mid \mathbf{R}', \boldsymbol{\phi}') = \delta(\mathbf{R} - \mathbf{R}')\delta(\boldsymbol{\phi} - \boldsymbol{\phi}')$. This evolution is governed by the convective velocity field, Eq. (1), the potential field E, Eqs. (9) and (10), and the random Brownian motion of the particle. These influences are linked into Eq. (4) via the vector probability fluxes ${}^t\mathbf{J}$ and ${}^r\mathbf{J}$ according to known constitutive relationships (*10*).

ORIENTATIONAL EQUILIBRIUM

The assumption of orientational equilibrium constitutes a major simplification of the problem. Here, the particle orientation is determined solely by a balance between the deterministic, orienting effects of the external field and the stochastic effects of rotary Brownian movement. The orienting effect of fluid shear is assumed to be negligible.

Brenner and Condiff (*10*) have derived criteria prescribing conditions for the validity of this assumption. First, times must be longer than the diffusion time,† τ_D, characteristic of the particle. In such circumstances the particle will have lost all memory of its initial orientation. Second, the particle must be small compared with apparatus size. With a a charac-

*If the wall potential is a true step function, care must be taken in applying Eqs. (8) and (9). Physically, of course, the potential becomes infinite over a finite distance, rather than abruptly; it is only because of the scale of distance that will be treated that we make the step function approximation. For example, the potential only resembles a step function due to the scaling that will ultimately be of concern to us.

†For a spherical particle of radius a immersed in a fluid of viscosity μ, $\tau_D \simeq 8\pi\mu a^3/kT = 1/D_r$, where D_r is the rotary diffusion coefficient. In the two systems studied by Berg and Purcell, $\tau_D \simeq 0.6$ sec and $\tau_D \simeq 0.8 \times 10^{-4}$ sec in the studies dealing with ~1 μm latex spheres (*2*) and *E. coli* bacteriophage (*3*), respectively. Since the total times for their experiments ran into hours, the condition $t \gg \tau_D$ is certainly true in their work.

teristic particle size, this condition may be stated as

$$\lambda \overset{\text{def}}{=} a/h \tag{11}$$

where

$$\lambda \ll 1 \tag{12}$$

By suitably scaling Eq. (4) and by expanding σ in a perturbation series in the parameter λ, Brenner and Condiff (*10*) have determined that orientational equilibrium represents a zeroth order (in λ) solution of the continuity equation. That is, they found that

$$\sigma = \psi e^{-E} + O(\lambda) \qquad (\text{for } t \gg \tau_D) \tag{13}$$

where $\psi = \psi(\mathbf{R}, t \mid \mathbf{R}')$ is an arbitrary function, independent of orientation. The utility of expressing the "no penetration" boundary condition as part of the potential is immediately apparent from Eq. (13). Equation (3) guarantees that $\psi(\mathbf{R}, t \mid \mathbf{R}')$ be finite for all times greater than zero. Thus, Eq. (13), the mathematical statement of orientation equilibrium, implies that σ be zero whenever E is infinite. Thus the boundary condition has most simply been incorporated into the partial solution of Eq. (4).

Substitution of Eq. (13) into the continuity Eq. (4), and integration over all orientations, yields

$$\frac{\partial}{\partial t}\psi e^{-\bar{E}} + O(\lambda) + \frac{\partial}{\partial \mathbf{R}}\cdot\bar{\mathbf{J}} = \delta(t)\delta(\mathbf{R} - \mathbf{R}') \tag{14}$$

where the integrated potential $\bar{E}$ is defined by

$$e^{-\bar{E}} \overset{\text{def}}{=} \int e^{-E} d^3\boldsymbol{\phi} \tag{15}$$

$\bar{\mathbf{J}}$ is the orientation-averaged translational flux vector,

$$\bar{\mathbf{J}} \overset{\text{def}}{=} \int {}^t\mathbf{J}\, d^3\boldsymbol{\phi} \tag{16}$$

The orientation-averaged divergence of the rotary flux is identically zero, as a consequence (*5*) of $\boldsymbol{\phi}$ being a closed space and of the single-valuedness of ${}^r\mathbf{J}$:

$$\int \frac{\partial}{\partial \boldsymbol{\phi}}\cdot {}^r\mathbf{J}\, d^3\boldsymbol{\phi} = 0 \tag{17}$$

The constitutive relation for the translational flux vector is (*10*)

$$^{t}\mathbf{J} = \sigma\mathbf{V} - e^{-E}\left({}^{t}\mathbf{D}\cdot\frac{\partial}{\partial\mathbf{R}} + {}^{c}\mathbf{D}^{\dagger}\cdot\frac{\partial}{\partial\boldsymbol{\phi}}\right)\sigma e^{E} \tag{18}$$

Here,* $^{t}\mathbf{D}$ and $^{c}\mathbf{D}$ are, respectively, the translational and coupling diffusion dyadics, and $\mathbf{V}$ is the purely hydrodynamic convective velocity of the particle locator point in the absence of Brownian movement and external forces. In general, each are functions of particle and boundary sizes and shapes, fluid properties, and of particle location and orientation relative to the boundaries. However, to zeroth order (in λ), these diffusivity dyadics are "almost everywhere"** those which obtain in the absence of boundaries. Moreover, the translational convective velocity is identical to the value of the undisturbed fluid velocity at the locator point,

$$\mathbf{V} = \mathbf{V}_f + O(\lambda) \tag{19}$$

In applying Eqs. (13) and (18) to Eq. (16) for the orientation-averaged translational flux, explicit recognition must be given to the fact that the last term of Eq. (18), involving the coupling dyadic, is of higher order than the other terms. Thus, although Eq. (13) seems to imply the vanishing of this term when proper scaling is applied, the order λ term in the perturbation expansion (13) for σ must be included (for this last term only). Thus, omitting details (*10*),

$$\bar{\mathbf{J}} = \psi e^{-\bar{E}}\mathbf{V}_f - (kT/\mu)\left(\int {}^{t}\mathbf{K}^{-1}e^{-E}d^{3}\boldsymbol{\phi}\right)\cdot\frac{\partial\psi}{\partial\mathbf{R}} \tag{20}$$

wherein the inverse of the translational resistance dyadic, $^{t}\mathbf{K}$, appears, rather than the translational diffusion dyadic, $^{t}\mathbf{D}$, related by the generalized Stokes-Einstein relation,

$$(kT/\mu)^{t}\mathbf{K}^{-1} = {}^{t}\mathbf{D} - {}^{c}\mathbf{D}^{\dagger}\cdot{}^{r}\mathbf{D}^{-1}\cdot{}^{c}\mathbf{D} \tag{21}$$

with $^{r}\mathbf{D}$ the rotatary diffusion dyadic. In the absence of boundaries, the coupling dyadic is identically zero for centrally-symmetric particles when

*Note that "†" indicates transposition, e.g., $(\mathbf{ab})^{\dagger} = \mathbf{ba}$.

**Gajdos (*16*) has treated the mathematical formalities of this assertion. It is always true that a region exists near the boundary—say, within 10 particle lengths of the boundary—where hydrodynamic interaction occurs between the particle and the boundary. However, for very small particles (in Berg and Purcell's experiments, $\lambda \simeq 0.0001$), this region is such a small portion of the total domain of the particles that phenomena occurring in the boundary region can be neglected.

the locator point lies at the body's "center of reaction" (*14*). Under these conditions, which obtain in the following, the distinction is of no consequence.

Equations (14) and (20) show that the vertical domain, y, of $\mathbf{R}$ is limited by the wall potential defined in Eq. (8). Outside of the region $0 \le y \le h$, the coefficients of each term in Eqs. (14) and (20) vanish. With this in mind, define the marginal probability density, $c = c(\mathbf{R}, t \mid \mathbf{R}')$,

$$c = \int \sigma d^3\boldsymbol{\phi} = \psi e^{-\tilde{E}} + O(\lambda) \qquad (t \gg \tau_D) \tag{22}$$

The latter equality follows from Eqs. (13) and (15). Since c is a probability density,

$$\int c d^3\mathbf{R} = 1 \qquad \text{(for all } t\text{)} \tag{23}$$

which also follows independently from Eq. (3). Thus, utilizing Eqs. (20), (22), and (2), the orientation-averaged continuity Eq. (14) becomes, for $t \gg \tau_D$,

$$\frac{\partial c}{\partial t} + \mathbf{V}_f \cdot \nabla c - \nabla \cdot e^{-\tilde{E}} \tilde{\mathbf{D}} \cdot \nabla c e^{\tilde{E}} = \delta(t)\delta(\mathbf{R} - \mathbf{R}') + O(\lambda)$$

$$(0 \le y \le h) \tag{24}$$

$$c = 0 \qquad (y < 0; y > h) \tag{25}$$

The average diffusivity $\tilde{\mathbf{D}}$ has been defined as

$$\tilde{\mathbf{D}} \stackrel{\text{def}}{=} (kT/\mu)\langle {}^t\mathbf{K}^{-1} \rangle \tag{26}$$

Moreover, ∇ has replaced the physical space gradient operator,

$$\nabla \stackrel{\text{def}}{=} \partial/\partial \mathbf{R} \tag{27}$$

The orientation-averaging operator is given by

$$\langle \cdots \rangle \stackrel{\text{def}}{=} \int (\cdots)\, e^{-E} d^3\boldsymbol{\phi} \Big/ \int e^{-E} d^3\boldsymbol{\phi} \tag{28}$$

Note that Eq. (25) follows from Eqs. (8), (15), and (22).*

Equations (24) and (25) represent the final result of carrying through,

*In addition to (25), observe from (26) and (28) that the product $e^{-\tilde{E}}\tilde{D}$ must vanish at $y = 0$ and $y = h$, whereas the product $e^{\tilde{E}}c$ is everywhere equal to ψ (Eq. 22). This consideration implies that the flux $e^{-\tilde{E}}\tilde{D} \cdot \nabla c e^{\tilde{E}}$ must also vanish at $y = 0$ and $y = h$.

to zeroth order in λ, the consequences of orientational equilibrium. The residue is a conventional physical-space convective-diffusion equation. Under the dual assumptions of $t \gg \tau_D$ and $\lambda \to 0$, this equation applies to particles of arbitrary shape in the presence of orienting external fields.

SPECIALIZATION OF PROBLEM

The preceding results will now be specialized to axisymmetric, centrally-symmetric particles. Further, the external field will be assumed to arise solely from a gravitational force acting downward on the particle. The latter is allowed to possess a nonuniform, but axisymmetric, mass distribution, such that if the centers of mass and of buoyancy are distinct, they both lie along the axis of symmetry. Failure of these centers to coincide results in the existence of a permanent, embedded dipole—creating a gravitational torque tending to align the particle's symmetry axis in the vertical direction, with the heavier end of the particle pointing vertically downward.

Brenner and Condiff (*10*) have derived the general form of the potential resulting from such circumstances. Their result may be expressed as

$$E = y/h_s + \chi \mathbf{e} \cdot \hat{\mathbf{g}} \tag{29}$$

In the above

$$h_s \overset{\text{def}}{=} kT/m_b g \tag{30}$$

is the "scale height" (*1*), and

$$\chi \overset{\text{def}}{=} m_p g r_{mb}/kT \tag{31}$$

the Langevin parameter, with m_b and m_p, respectively, the buoyant and actual particle masses, g the acceleration of gravity, and r_{mb} the distance between the centers of mass and buoyancy. The assumed geometric symmetry of the particle is such that (*17*)

$$^c\mathbf{D} = \mathbf{0} \tag{32}$$

$$^t\mathbf{D} = \mathbf{ee}\,^tD_\parallel + (\mathbf{U} - \mathbf{ee})\,^tD_\perp \tag{33}$$

with the locator point chosen to lie at its centroid, which is also its center of reaction. The unit vector $\mathbf{e}$ along the particle's symmetry axis is a function of orientation, i.e., $\mathbf{e} = \mathbf{e}(\phi)$. $\mathbf{U}$ is the idemfactor, while $^tD_\parallel$ and $^tD_\perp$ are intrinsic scalars depending only on the size and shape of the particle, representing, respectively, the translational particle diffusivities in directions parallel and perpendicular to the symmetry axis. Equations (32), (33), (21), and (26) thus give

$$\tilde{\mathbf{D}} = \mathbf{U}{}^{t}D_{\perp} + \langle \mathbf{ee} \rangle ({}^{t}D_{\parallel} - {}^{t}D_{\perp}) \tag{34}$$

Given the potential (29), the orientation average (27) of the dyad **ee** is *(10)*

$$\langle \mathbf{ee} \rangle = \hat{y}\hat{y} + (\mathbf{U} - 3\hat{y}\hat{y})\chi^{-1}L(\chi) \tag{35}$$

with $L(\chi)$ the Langevin function

$$L(\chi) = -\chi^{-1} + \operatorname{ctnh} \chi \tag{36}$$

Hence

$$\tilde{\mathbf{D}} = (\mathbf{U} - \hat{y}\hat{y})D + \hat{y}\hat{y}D' \tag{37}$$

where the scalars D and D' are defined by

$$D = {}^{t}D_{\perp} + \chi^{-1}L(\chi)({}^{t}D_{\parallel} - {}^{t}D_{\perp}) \tag{38}$$

$$D' = {}^{t}D_{\parallel} - 2\chi^{-1}L(\chi)({}^{t}D_{\parallel} - {}^{t}D_{\perp}) \tag{39}$$

Introduction of (29) and (37) into the orientation-averaged continuity Eq. (24) yields

$$\frac{\partial c}{\partial t} + V_f(y)\frac{\partial c}{\partial z} - D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2}\right) - D'\frac{\partial}{\partial y}\left[e^{-y/h_s}\frac{\partial}{\partial y}(ce^{y/h_s})\right]$$
$$= \delta(t)\delta(x - x')\delta(y - y')\delta(z - z') + O(\lambda) \tag{40}$$

The comments in the footnote on page 224 lead to the boundary conditions

$$\partial(ce^{y/h_s})/\partial y = 0, \qquad \text{at} \quad y = 0, h \tag{41}$$

Two further simplifications are now easily made. The form of (40) shows the initial z-coordinate of the particle to be inconsequential, whence z' may be arbitrarily chosen. The obvious choice is

$$z' = 0 \tag{42}$$

In addition, no interest attaches to particle transport in the x-direction, across the width of the apparatus. This leads to the introduction of marginal density, f, of c, defined by

$$f = f(y, z, t \mid y') \stackrel{\text{def}}{=} \int_{-\infty}^{\infty} c\,dx \tag{43}$$

Hence integration of (40) and (41) over the range $-\infty < x < \infty$ gives, with the use of (42),

$$\frac{\partial f}{\partial t} + V_f(y)\frac{\partial f}{\partial z} - D\frac{\partial^2 f}{\partial z^2} - D'\frac{\partial}{\partial y}\left[e^{-y/h_s}\frac{\partial}{\partial y}(fe^{y/h_s})\right] = \delta(t)\delta(y - y')\delta(z) + O(\lambda) \tag{44}$$

$$\partial(fe^{y/h_s})/\partial y = 0, \qquad \text{at} \quad y = 0, h \tag{45}$$

since the probability flux, $\partial c/\partial x$, must vanish at $x = \pm\infty$.

PARTICLE TRANSPORT MOMENTS

Our main concern is with particle transport in the z direction. Moment techniques of the Taylor, Aris, and Gill and Subramanian genre (*9*, *18–20*) can therefore be applied to extract the macroscopic manifestations of such transport without necessity for a complete solution of the pertinent differential equation governing the probability density. Specifically, knowledge of the time variation of the first and second axial moments (of the horizontal position z of the particle) will prove sufficient.

To this end, define the moment generation functions, $\mu_n(y, t \mid y')$:

$$\mu_n \overset{\text{def}}{=} \int_{-\infty}^{\infty} z^n f\, dz \qquad (\text{for } n \geq 0) \tag{46}$$

In terms of these, the desired moments are given by

$$m_n = m_n(t) = \overline{z^n} = \int_0^h \mu_n\, dy \qquad (n \geq 0) \tag{47}$$

The differential equations and boundary conditions governing the μ_n can be obtained by multiplying (44) and (45) by z^n, and integrating over the domain of z, to obtain

$$\frac{\partial \mu_n}{\partial t} - L\mu_n = nV_f\mu_{n-1} + n(n-1)D\mu_{n-2} + \begin{cases}\delta(t)\delta(y - y') & (n = 0)\\ 0 & (n > 0)\end{cases} \tag{48}$$

and

$$\partial(\mu_n e^{y/h_s})/\partial y = 0, \qquad \text{at} \quad y = 0, h \text{ (for all } n) \tag{49}$$

where the operator L is defined by

$$L\mu = D\frac{\partial}{\partial y}\left[e^{-y/h_s}\frac{\partial}{\partial y}(\mu e^{y/h_s})\right] \tag{50}$$

Integration of (48) over the domain of y, and application of (49), yields, according to (47),

$$\frac{dm_n}{dt} = n\overline{V_f \mu_{n-1}} + n(n-1)Dm_{n-2} + \begin{cases} \delta(t) & (n = 0) \\ 0 & (n > 0) \end{cases} \tag{51}$$

The overbar denotes integration over the entire domain of y:

$$\overline{(\cdots)} = \int_0^h (\cdots)\, dy \tag{52}$$

Equations (51) and (48) offer a recursive procedure for obtaining moments of any order. In the applications to follow, only the moments of orders $n = 0$, 1, and 2 are required.

With $n = 0$, Eq. (51) yields

$$m_0 = 1 \tag{53}$$

This is merely a restatement of (3). The form of m_0 suggests that μ_0 possesses an asymptotic solution of the form

$$\mu_0 = a\mathrm{e}^{-y/h_s} + \exp \tag{54}$$

where "exp" denotes terms that are exponentially small for large times t. Appendix A quantifies the criterion for "long times." It is readily verified that Eq. (54) satisfies (48) and (49) for an arbitrary constant a. The value of a is determined by noting that $\bar{\mu}_0 = m_0$ (see Eqs. 47 and 52), so that

$$\mu_0 = \mathrm{e}^{-y/h_s}/\overline{\mathrm{e}^{-y/h_s}} + \exp \tag{55}$$

With $n = 1$, Eq. (51) leads to

$$\frac{dm_1}{dt} = \overline{V_f \mu_0} + \exp \tag{56}$$

Hence, employing (55), and neglecting exponentially small terms, yields

$$m_1 = \bar{\mu}_1 = \bar{U}t \tag{57}$$

where

$$\bar{U} \overset{\text{def}}{=} \overline{V_f \mathrm{e}^{-y/h_s}}/\overline{\mathrm{e}^{-y/h_s}} \tag{58}$$

The form of (57) suggests a trial solution for μ_1 of the form

$$\mu_1 = (\mathrm{e}^{-y/h_s}/\overline{\mathrm{e}^{-y/h_s}})(\bar{U}t + b) + \exp \tag{59}$$

The latter is consistent with (57) for b any function of y, satisfying

$$\overline{\mathrm{e}^{-y/h_s} b(y)} = 0 \tag{60}$$

Substitution of (59) and (55) into (48) provides the necessary differential equation satisfied by b:

$$\frac{d}{dy}\left(e^{-y/h_s}\frac{db}{dy}\right) = \frac{1}{D'}e^{-y/h_s}(\overline{U} - V_f) \tag{61}$$

Furthermore, from (49),

$$\frac{db}{dy} = 0, \qquad \text{at} \quad y = 0, h \tag{62}$$

A first integral of (61) is

$$\frac{db}{dy} = \frac{e^{y/h_s}}{D'}\int_0^y e^{-y'/h_s}(\overline{U} - V_f)\,dy' \tag{63}$$

It is unnecessary to obtain b itself in order to calculate the moments. Rather, the above equations suffice.

Continuing to the last step of the procedure, Eq. (51) requires that the second moment be given by the solution of the equation,

$$\frac{dm_2}{dt} = 2\overline{V_f\mu_1} + 2D \tag{64}$$

By using Eq. (59), the term involving μ_1 can be written as

$$\overline{V_f\mu_1} = \overline{U}^2 t + I/\overline{e^{-y/h_s}} \tag{65}$$

with I defined as

$$I = \int_0^h b(y)V_f e^{-y/h_s}\,dy \tag{66}$$

The following manipulations obviate the need for an explicit expression for $b(y)$ for use in (66). Multiply (61) by $b(y)$ and integrate from $y = 0$ to $y = h$. Next, integrate the resulting left-hand side by parts and use (62). Also recognize that the first term on the right-hand side integrates to zero because of (60). The remaining terms can then be rearranged to give an expression for I that is easier to evaluate, namely.

$$I = D'\int_0^h e^{-y/h_s}\left(\frac{db}{dy}\right)^2 dy \tag{67}$$

This result substantiates the claim that $b(y)$ itself need not be obtained.

Equation (67) can be simplified greatly. First, substitute in (63) and integrate the result by parts. One obtains, using the definition (58) of $\overline{U}$,

$$I = -\frac{2h_s}{D'}\int_0^h (\overline{U} - V_f)\int_0^y e^{-y'/h_s}(\overline{U} - V_f')\,dy'\,dy \tag{68}$$

where $V'_f \equiv V_f(y')$. Lastly, as a result of (62) and (63), it is easy to show* that an equivalent expression is

$$I = \frac{2h_s}{D'} \int_0^h e^{-y/h_s} (\bar{U} - V_f) \int_0^y (\bar{U} - V'_f)\, dy'\, dy \tag{69}$$

Hence, integration of (64) gives

$$m_2 = (\bar{U}t)^2 + 2t(D + I/\overline{e^{-y/h_s}}) \tag{70}$$

Consequently, the standard deviation, or second central moment, is

$$\begin{aligned} \overline{(z - \bar{z})^2} &= m_2 - m_1^2 \\ &= 2t\left[D + \frac{2h_s}{D'\overline{e^{-y/h_s}}} \int_0^h e^{-y/h_s} (\bar{U} - V_f) \int_0^y (\bar{U} - V'_f)\, dy'\, dy\right] \end{aligned} \tag{71}$$

Equations (57) and (71), which constitute the desired relationships, express the average rate of travel of the particle through the system and the deviation about this rate. Given the physical constants for the system (h, χ, h_s, ${}^tD_\perp$, ${}^tD_\parallel$), and a specific velocity profile $V_f(y)$, one can calculate $\bar{z}$ and $\overline{(z - \bar{z})^2}$ using (57) and (71) in conjunction with the defining relationships (38), (39), (36), and (58).

The principal results may be cast in dimensionless form. To this end, define

$$\xi \equiv y/h_s \tag{72}$$

The upper limit on ξ, corresponding to h, is then given by

$$\beta = h/h_s \tag{73}$$

or

$$\beta \equiv m_b g h/kT \tag{74}$$

such that β can be thought of as the "relative field strength" characterizing the experiment.

In these terms, the average particle velocity $\bar{U}$, defined by Eq. (58), can be written as

$$\bar{U} = \int_0^\beta V_f e^{-\xi}\, d\xi \Big/ \int_0^\beta e^{-\xi}\, d\xi \tag{75}$$

*Equations (62) and (63) show that the inner integral of (68) is zero when its upper limit, y, is equal to h. Hence, after reversing the sign of the expression, the inner integral may also be expressed as the integral from $y' = y$ to $y' = h$. Equation (69) then follows by reversing the order of the two integrations and switching dummy indices, y and y'.

Morevoer, in place of (71), the "spread" of particle positions may be written as

$$\overline{(z - \bar{z})^2} = 2[D + k_v(h^2 V_m^2/D')]t \tag{76}$$

where V_m is the mean fluid velocity,

$$V_m = (1/h)\int_0^h V_f(y)\,dy \tag{77}$$

The dispersion parameter,

$$k_v = (2/\beta^2)\int_0^\beta e^{-\xi}\Delta v \int_0^\xi \Delta v'\,d\xi'\,d\xi \Big/ \int_0^\beta e^{-\xi}\,d\xi \tag{78}$$

is a dimensionless function of both the relative field strength β and the fluid velocity profile. Here,

$$\Delta v = (\bar{U} - V_f)/V_m \tag{79}$$

is the normalized velocity deviation function.

EVALUATION OF THE TRANSPORT MOMENTS FOR AN ARBITRARY POWER-SERIES VELOCITY PROFILE

It is especially easy to evaluate the transport moment integrals, (75) and (78), when the fluid velocity is expressed as a power series in the vertical distance variable ξ. Thus, let V_f be given by

$$V_f = V_m \sum_{n=0}^{N} a_n \xi^n \tag{80}$$

For example, the parabolic profile for pressure-driven flow between two flat plates is given by

$$V_f = 6V_m(y/h)(1 - y/h) \tag{81}$$

so that, corresponding to (80), $N = 2$, $a_0 = 0$, $a_1 = 6/\beta$, and $a_2 = -6/\beta^2$.

Substitution of (80) into (75) yields

$$\bar{U} = V_m \sum_{n=0}^{N} a_n \gamma(n + 1, \beta)/\gamma(1, \beta) \tag{82}$$

where $\gamma(n + 1, \beta)$ is the incomplete gamma function (*21*),

$$\gamma(n + 1, \beta) = \int_0^\beta \xi^n e^{-\xi}\,d\xi \tag{83}$$

such that

$$\gamma(1, \beta) = 1 - e^{-\beta} \tag{84}$$

From Eqs. (82) and (79), the velocity deviation function is thus

$$\Delta v = -\sum_{n=0}^{N} a_n' \xi^n \tag{85}$$

with coefficients

$$a_n' = a_n \qquad (n > 0) \tag{86}$$

$$a_0' = a_0 - \bar{U}/V_m = -\sum_{m=1}^{N} a_m \gamma(m+1, \beta)/\gamma(1, \beta) \tag{87}$$

Substitution of (85) into expression (78) for the dispersion parameter k_v permits the double integration to be performed readily, due to (83). After collecting like terms, there results

$$k_v = \sum_{k=1}^{2N+1} A_k \gamma(k+1, \beta)/\gamma(1, \beta) \tag{88}$$

with constants A_k defined by

$$A_k = (2/\beta^2) \sum_{j=1}^{k} a_{j-1}' a_{k-j}'/j \tag{89}$$

Computations were performed with a digital computer to obtain values of $\bar{U}/V_m$ and k_v over a wide range of field strengths. Two velocity profiles were used: the parabolic field of Eq. (81), and the half parabola resulting when the upper plate is replaced by a free surface, namely

$$V_f = 3V_m[(y/h) - 1/2(y/h)^2] \tag{90}$$

The results of these calculations appear in Table 1. Note that the weak field limit results ($\beta = 0$) required further development, as discussed in Appendix B.

Table 1 also lists the parameters $\bar{y}/h$ and $f/2$, the average particle height and the Berg-Purcell (*1*) "width-factor," respectively. The latter parameter is related to the transport parameters utilized herein by the expression

$$f/2 = \sqrt{k_v(D/D')}/(\bar{U}/V_m)(\bar{y}/h) \tag{91}$$

The average particle height parameter may be derived as follows. By

TABLE 1

Variation of Transport Parameters with Relative Field Strength

		Full parabola (81)			Half-parabola (90)		
β	$\bar{y}/h$	$\bar{U}/V_m$	k_v^{-1}	$f/2$[b]	$\bar{U}/V_m$	k_v^{-1}	$f/2$[b]
0.0[a]	0.5	1.0	210	0.138 . . .	1.0	52.5	0.276 . . .
0.1	0.492	—	—	—	0.988	51.9	0.286
0.2	0.484	0.999	209	0.143	0.975	51.6	0.295
0.5	0.459	0.996	204	0.153	0.937	50.9	0.326
1.0	0.418	0.984	190	0.176	0.873	51.4	0.382
2.0	0.344	0.939	159	0.246	0.750	58.4	0.508
2.5	0.311	0.909	149	0.290	0.693	65.2	0.575
$3\frac{1}{3}$	0.263	0.853	143	0.373	0.608	82.7	0.688
4.0	0.231	0.806	146	0.444	—	—	—
5.0	0.193	0.736	163	0.550	0.474	151	0.889
$6\frac{2}{3}$	0.149	0.632	223	0.712	—	—	—
10.0	0.100	0.480	495	0.936	0.270	984	1.182
20.0	0.050	0.270	3901	1.186	0.142	11,670	1.304

[a] See Appendix B for derivation of weak field limits. These results (at $\beta = 0$) are exact.

[b] Assuming $D = D'$ (the case for spheres, or when there is no external torque, such that the Langevin parameter, $\chi = 0$). If this is not the case, the quantity tabulated is actually $(f/2)\sqrt{D'/D}$.

definition, from the marginal density of Eq. (43), we have*

$$\bar{y} = \int_{-\infty}^{\infty} \int_0^h y f(y, z, t\,|\,y')\, dy\, dz \tag{92}$$

This may be expressed alternatively in terms of the moment generating function $\mu_0(y, t \mid y')$, defined by Eq. (46):

$$\bar{y} = \int_0^h y\mu_0(y, t\,|\,y')\, dy \tag{93}$$

Thus, from (55) and the definition (52) of the overbar operator,

$$\bar{y} = \int_0^h y e^{-y/h_s}\, dy \Big/ \int_0^h e^{-y/h_s}\, dy + \exp \tag{94}$$

*Note that the symbol f is employed for both the width-factor and the marginal density. No confusion should result, however, since the former always appears in the form $f/2$.

or, neglecting transients, and utilizing (72) and (73),

$$\bar{y}/h = \int_0^\beta \xi e^{-\xi}\, d\xi \Big/ \beta \int_0^\beta e^{-\xi}\, d\xi \tag{95}$$

Equivalently, in terms of the incomplete gamma function,

$$\bar{y}/h = \gamma(2, \beta)/\beta\gamma(1, \beta) \tag{96}$$

For both cases tabulated in Table 1, the dispersion parameter k_v exhibits a maximum at some intermediate value of the field strength. This effect is most pronounced in the case of the full parabolic velocity profile. Presumably, this behavior may be interpreted by realizing that the dispersion will not decrease until it is less probable that the particle is in the general vicinity of the maximum fluid velocity. Thus, if the fluid velocity is a maximum at the upper boundary (the half-parabola case), the dispersion increases at relatively low field strengths, whereas in the full-parabola case the average particle height must move below the center ($h/2$) of the apparatus.

DISCUSSION

The results derived here are directly comparable to the theoretical results of Berg and Purcell (*1*). They are in substantial agreement—differing slightly only in the values of the width-factor (91) at high and low field strengths. Numerical values derived here are believed to be the more accurate of the two. Berg and Purcell's computational procedure, although ingenious, was based on a random-walk analysis using a finite grid spacing. To obtain the width-factor, it was necessary for them to truncate a complicated infinite summation of transition probabilities, dependent on these grid points. Based on their qualitative discussion of this procedure, it does not seem unreasonable to assume that their results are only accurate to, say, 5%. This conclusion is further supported by the failure of their calculated width-factors (for the full and half parabolas) to approach the weak field limit (Appendix B). In this limit, Table 1 indicates that the width-factor for the half-parabola should become exactly twice that for the full-parabola. Berg and Purcell's results do not quite meet this criterion, although their error is small.

In the middle range of field strengths, agreement between the width-factors calculated here and those obtained by Berg and Purcell is excellent. However, at high field strengths, the two methods once again give slightly different results, Berg and Purcell's being lower by about 5%.

In their experiments with latex spheres, Berg et al. (*2*) discovered that a significant portion of the spheres had stuck together, forming "dimers" and "trimers." The theory presented here is capable of describing the transport of any body of revolution possessing fore-aft symmetry. Thus it can be applied to a dimer and also to a trimer, if the latter is configured as a straight chain.

Our theory shows that, for small particles, the transport rate is independent of shape. However, the spread (76) about this mean rate is seen to depend on the two orientation-averaged diffusivities, D and D'. These scalars, representing the orientation-averaged diffusivities in the direction of the flow and the direction of the field, respectively, are determined from the body's intrinsic diffusivities, ${}^tD_\perp$ and ${}^tD_\parallel$, as functions of the Langevin parameter χ, via Eqs. (31, (38), (39), and (36). This parameter measures the strength of the dipole interaction with the acceleration field. For example, if the dipole interaction is zero, then (*10*)

$$\chi^{-1}L(\chi) = 1/3 \qquad (\chi = 0) \tag{97}$$

so that

$$D = D' = (1/3)\,{}^tD_\parallel + (2/3)\,{}^tD_\perp \equiv (1/3)\mathbf{U}:{}^t\mathbf{D} \tag{98}$$

that is, the orientation-averaged diffusivity is isotropic in the absence of an external couple, the scalar diffusivity being equal to the arithmetic average of the translational diffusivities along the principal axes of the particle. These scalars can be obtained from the translational resistance of the particle via the Stokes-Einstein relationship (21). Hence, with use of (32) and (33), there obtains

$${}^tD_\parallel = (kT/\mu)\,{}^tK_\parallel^{-1} \tag{99}$$

$${}^tD_\perp = (kT/\mu)\,{}^tK_\perp^{-1} \tag{100}$$

The translational resistance scalars, for motion parallel to and perendicular to the axis of revolution, have been denoted ${}^tK_\parallel$, ${}^tK_\perp$, respectively.

Goldman et al. (*22*) show, for two touching, nonrotating spheres, each of radius a, that the resistance coefficient of each sphere is reduced from its Stokes law value of $6\pi a$ by a factor of either 0.645 or 0.725 according as the spheres are moving parallel or perpendicular, respectively, to their line of centers. The translational resistances of the two-sphere particle are thus given by

$${}^tK_\parallel = 1.29(6\pi a) \tag{101}$$

$${}^tK_\perp = 1.45(6\pi a) \tag{102}$$

Hence, from (99) and (100),

$$'D_{\parallel} = 0.775 D_* \tag{103}$$

$$'D_{\perp} = 0.690 D_* \tag{104}$$

where

$$D_* = kT/6\pi\mu a \tag{105}$$

is the diffusivity of the single sphere.

Finally, via Eq. (98), the orientation-averaged diffusivities become

$$D = D' = 0.718 D_* \tag{106}$$

in the absence of an external couple. Had the diffusivity been calculated on the basis of a single sphere possessing the same volume as the dimer, the result would have been

$$D = D' = 0.794 D_*$$

Equation (106) enables the spread in transport times to be calculated for the dimers via (76). Given the appropriate resistance coefficients, $'K_{\parallel}$ and $'K_{\perp}$, for three colinear, touching spheres, analogous results could be obtained for the trimers. Unfortunately, the data of Berg et al. (*2*) are insufficient to confirm these shape-dependent results.

Our last comment pertaining to the work of Berg et al. (*2*) concerns their speculations on the effect of finite particle size. They found that their experimental values of $\bar{U}$ were higher than the predicted values; further, the deviation increased monotonically with particle size. From our work (*7*) with finite-sized spheres in cylindrical tubes, it is seen that (to first order in particle size) the effect of size on average transport velocity is effectively to reduce the domain of y to that region truly occupied by the sphere center, namely,

$$a \leq y \leq h - a \tag{107}$$

This is so because the particle/fluid slip velocity is "almost everywhere" (see the last footnote on page 223) of a still smaller order, whereupon hydrodynamic considerations may be neglected. Thus, in place of (75), we may write

$$\bar{U} = \int_{\varepsilon}^{\beta-\varepsilon} V_f e^{-\xi}\, d\xi \Big/ \int_{\varepsilon}^{\beta-\varepsilon} e^{-\xi}\, d\xi \tag{108}$$

with

$$\varepsilon = a/h_s \tag{109}$$

The power-series velocity profile (80) then gives,

$$\bar{U}/V_m = \sum_{n=0}^{N} a_n[\gamma(n+1, \beta-\varepsilon) - \gamma(n+1, \varepsilon)/(\gamma(1, \beta-\varepsilon) - \gamma(1, \varepsilon)] \quad (110)$$

However, for small values of ε there obtains,

$$\gamma(n+1, \beta-\varepsilon) = \gamma(n+1, \beta) - \varepsilon\beta^n e^{-\beta} + O(\varepsilon^2) \quad (111)$$

$$\gamma(n+1, \varepsilon) = \varepsilon^{n+1}/(n+1) + O(\varepsilon^{n+2}) \quad (112)$$

The former derives from a Taylor series expansion of (83) about β, while the latter is derived by expanding the exponential in (83) and integrating the result term-by-term.

A bit of algebra now yields the corrected expression for $\bar{U}$ in terms of its value calculated by assuming $\varepsilon = 0$. In the case of the full-parabola (81),

$$\bar{U}_{\text{corr}}/\bar{U}_{\varepsilon=0} = 1 + \varepsilon \operatorname{ctnh}(\beta/2) \quad (113)$$

If $h \gg h_s$, as is the case in the Berg et al. (*2*) experiments with latex spheres, this simplifies to

$$\bar{U}_{\text{corr}}/\bar{U}_{\varepsilon=0} \approx 1 + \varepsilon \qquad (\beta \gg 1) \quad (114)$$

Table 2 compares the predicted deviation with that observed by Berg et al. Results for the smaller size particles are clearly inconclusive. Within experimental error, no deviation exists. For the larger size particles, the present theory cannot account for all of the observed deviation. It is unlikely that higher order terms would improve this situation. For example, the next term in the formula (114) is negative, and of order ε^2. [The sign will be negative since this term primarily accounts for the particle speed being slightly less than that of the fluid at any given point due to hydrodynamic wall effects (*7*, *23*).] Nevertheless, these calculations do support the contention of Berg et al. (*2*) that particle size effects were a major contributor to the deviation between theory and experiment.

It is also possible to calculate comparable deviations for the nonspherical

TABLE 2

Effect of Sphere Size on Average Particle Velocity

Radius, a	Scale height, h_s	$\varepsilon = a/h_s$	Deviation	
			Predicted	Observed[a]
0.40 μm	29.8 μm	0.013	1.01	0.99 ± 0.04
0.65 μm	6.76 μm	0.096	1.10	1.16 ± 0.03

[a] Average of four separate trials.

dimers and for linear trimers. Gajdos (*16*) [also see Giddings et al. (*24*)] has shown that, in the regions where not all orientations of the body are possible (e.g., for the dimer, $a \leq y \leq 2a$ and $h - 2a \leq y \leq h - a$), the two integrands of (108) should each contain a weighting factor proportional to the total solid angle "accessible" to the particle's axis of revolution. This factor decreases from a value of unity, when the particle is first able to touch the wall, to a value of zero, when the particle is at its minimum approach to the wall. (In this case, at either $y = a$ or $y = h - a$.)

The limited results obtained here for finite particle size indicate that the assumed scaling of distances with apparatus height in the section entitled "Orientational Equilibrium" requires appropriate modification to include the alternate length scale h_s. It is rather obvious that the apparatus height is of no consequence if the field strength is very large. Indeed, h may be taken as infinity with very little error. A more appropriate scaling, valid for all field strengths, would be, say, $h_s \tanh \beta$, which has limits of h and h_s as the field strength β approaches zero and infinity, respectively. The derivation in the section entitled "Orientational Equilibrium" remains the same, subject only to this modification.

APPENDIX A. RELAXATION TIMES

Since only the long-time moments of the particle position were calculated in the section entitled "Particle Transport Moments," it is of interest to estimate the time it takes the system to relax to this long-time solution—i.e., to "forget" about the particle's initial location, y'. The transients for the moment functions are each governed by the eigenvalues associated with Eq. (48).

It is not difficult to derive these eigenvalues by the method of separation of variables, bearing in mind the boundary conditions (49). Sturm-Liouville theory (*25*) then states that the transient portion of the solution will be governed by the eigenvalues τ_n of the operator L, defined in Eq. (50), and the associated homogeneous boundary conditions (49). In this case the eigenvalues are

$$1/\tau_n = (1/4 + n\pi h_s/h)D'/h_s^2 \qquad (n = 1, 2, \ldots) \tag{A-1}$$

such that the corresponding transient components of the solution die out at the rate $\exp(-t/\tau_n)$. The longest lasting transient consequently decays at a rate

$$1/\tau = (1/4 + \pi h_s/h)D'/h_s^2 \tag{A-2}$$

corresponding to $n = 1$ in (A–1). These formal mathematical considerations accord with Berg and Purcell's (*1*) physical reasoning.

APPENDIX B. WEAK-FIELD LIMIT TRANSPORT PARAMETERS

In the limit when the field vanishes (for example, with neutrally buoyant particles), the relative field strength β becomes zero. Simultaneously, the scale height h_s becomes infinite. Aris' method (*20*) may be employed to calculate the particle transport moments. They are also derivable from the equations in this paper.

The average particle velocity $\bar{U}$ becomes unity, which is evident from either (58) or (75). This agrees with intuition. In the absence of any biasing by an external field, the particle is free to sample all vertical positions equally. It thus moves, on average, at the same velocity as the fluid.

To obtain $\lim k_v(\beta)$, $\beta \to 0$, make the transformation to a new distance variable ω, normalized to the apparatus height rather than to the scale height. That is, let

$$\omega = y/h = \xi/\beta \qquad \text{(B–1)}$$

Substitution into (78) then yields

$$k_v = 2\int_0^1 e^{-\beta\omega}\Delta v \int_0^{\omega} \Delta v'\,d\omega'\,d\omega \Big/ \beta \int_0^1 e^{-\beta\omega}\,d\omega \qquad \text{(B–2)}$$

In the limit $\beta \to 0$, the above can be shown to be of the indeterminate form $0 \div 0$, as a consequence of

$$\int_0^1 \Delta v \int_0^{\omega} \Delta v'\,d\omega'\,d\omega = 0 \qquad \text{(B–3)}$$

Application of L'Hopital's rule thereby yields the limiting value,

$$k_v = -2\int_0^1 \omega\Delta v \int_0^{\omega} \Delta v'\,d\omega'\,d\omega \qquad (\beta \to 0) \qquad \text{(B–4)}$$

Straightforward integrations subsequently produce the theoretical values cited in Table 1.

Acknowledgments

This research was supported by the National Science Foundation under grant no. NSF GK–34855. A portion of this work was performed while

Howard Brenner was on sabbatical leave at the California Institute of Technology as a Sherman Mills Fairchild Distinguished Scholar.

REFERENCES

1. H. C. Berg and E. M. Purcell, *Proc. Natl. Acad. Sci. U.S.A.*, *58*, 862 (1967).
2. H. C. Berg, E. M. Purcell, and W. W. Stewart, *Ibid.*, *58*, 1286 (1967).
3. H. C. Berg and E. M. Purcell, *Ibid.*, *58*, 1821 (1967).
4. J. C. Giddings, *Sep. Sci.*, *1*, 123 (1966).
5. J. C. Giddings, *J. Chem. Phys.*, *49*, 81 (1968).
6. J. C. Giddings, F. J. F. Yang, and M. N. Myers, *Anal. Chem.*, *46*, 1917 (1974).
7. H. Brenner and L. J. Gaydos, *J. Colloid Interface Sci.*, *58*, 312 (1977).
8. S. Krishnamurthy and R. S. Subramian, *Sep. Sci.*, *12*, 347 (1977).
9. W. N. Gill and R. Sankarasubramian, *Proc. R. Soc. London, Ser. A*, *327*, 191 (1972).
10. H. Brenner and D. W. Condiff, *J. Colloid Interface Sci.*, *47*, 199 (1974).
11. H. Goldstein, *Classical Mechanics*, Addison-Wesley, Reading, Massachusetts, 1950.
12. H. Brenner, *Adv. Chem. Eng.*, *6*, 287–483 (1966).
13. H. Brenner, *J. Colloid Interface Sci.*, *23*, 407 (1967).
14. H. Brenner and D. W. Condiff, *Ibid.*, *41*, 228 (1972).
15. D. W. Condiff and H. Brenner, *Phys. Fluids*, *12*, 539 (1969).
16. L. J. Gajdos, Ph.D. Thesis, Carnegie-Mellon University, Pittsburgh, 1977.
17. J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics*, Nordoff, Leyden, 1973.
18. G. I. Taylor, *Proc. R. Soc. London, Ser. A*, *219*, 186 (1953).
19. G. I. Taylor, *Ibid.*, *Ser. A*, *225*, 473 (1954).
20. R. Aris, *Ibid.*, *Ser. A*, *235*, 67 (1956).
21. M. Abramowitz and I. A. Stegun (eds.), *Handbook of Mathematical Functions*, Dover, New York, 1965.
22. A. J. Goldman, R. G. Cox, and H. Brenner, *Chem. Eng. Sci.*, *21*, 1151 (1966).
23. R. G. Cox and H. Brenner, *J. Fluid Mech.*, *28*, 319 (1967).
24. J. C. Giddings, E. Kucera, C. P. Russell, and M. N. Myers, *J. Phys. Chem.*, *72*, 4397 (1968).
25. F. B. Hildebrand, *Advanced Calculus for Applications*, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.

Received by editor May 20, 1977