ELSEVIER

Chemical Engineering Journal 80 (2000) 81–89

Chemical Engineering Journal

www.elsevier.com/locate/cej

Stochastic sedimentation and hydrodynamic diffusion

Elmer M. Tory*

Department of Mathematics, Mount Allison University, Sackville, NB, Canada

Abstract

Molecular collisions with very small particles induce Brownian motion. Consequently, such particles exhibit classical diffusion during their sedimentation. However, identical particles too large to be affected by Brownian motion also change their relative positions. This phenomenon is called hydrodynamic diffusion. Long before this term was coined, the variability of individual particle trajectories had been recognized and a stochastic model had been formulated. In general, stochastic and diffusion approaches are formally equivalent. The convective and diffusive terms in a diffusion equation correspond formally to the drift and diffusion terms of a Fokker–Planck equation (FPE). This FPE can be cast in the form of a stochastic differential equation (SDE) that is much easier to solve numerically. The solution of the associated SDE, via a large number of stochastic paths, yields the solution of the original equation. The three-parameter Markov model, formulated a decade before hydrodynamic diffusion became fashionable, describes one-dimensional sedimentation as a simple SDE for the velocity process $\{V(t)\}$. It predicts correctly that the steady-state distribution of particle velocities is Gaussian and that the autocorrelation of velocities decays exponentially. The corresponding position process $\{X(t)\}$ is not Markov, but the bivariate process $\{X(t),\ V(t)\}$ is both Gaussian and Markov. The SDE pair yields continuous velocities and sample paths. The other approach does not use the diffusion process corresponding to the FPE for the three-parameter model; rather, it uses an analogy to Fickian diffusion of molecules. By focusing on velocity rather than position, the stochastic model has several advantages. It subsumes Kynch's theory as a first approximation, but corresponds to the reality that particle velocities are, in fact, continuous. It also profits from powerful theorems about stochastic processes in general and Markov processes in particular. It allows transient phenomena to be modeled by using parameters determined from the steady-state. It is very simple and efficient to simulate, but the three parameters must be determined experimentally or computationally. Relevant data are still sparse, but recent experimental and computational work is beginning to determine values of the three parameters and even the additional two parameters needed to simulate three-dimensional motion. If the dependence of the parameters on solids concentration is known, this model can simulate the sedimentation of the entire slurry, including the packed bed and the slurry–supernate interface. Simulations using half a million particles are already feasible with a desktop computer.

Keywords: Sedimentation; Hydrodynamic diffusion; Stochastic; Markov

1. Introduction

Kynch's theory [1] is based on the assumption that all particles at the same solids concentration settle with the same velocity. Although this was acknowledged as an approximation, it was widely believed that identical particles would have the same velocity apart from some minor fluctuations [2]. In the colloidal size range (up to 0.1 μm), the bombardment of the particle by solvent molecules produces Brownian motion and the particle motion is no longer deterministic [3]. Such particles exhibit classical diffusion. However, experimental observations of closely sized particles that are much larger also show a great variation in their velocities (see Tory et al. [4] for references to early work). Even identical spheres change their relative positions during sedimentation [5,6]. This process is called hydrodynamic diffusion [7,8]. Although this phenomenon had been described a decade earlier as a stochastic process [5,9], the diffusion approach was much more familiar and rapidly became more widely used. However, the stochastic and diffusion approaches are related and the former has many advantages. Each stochastic trajectory mimics the path of an individual particle in an actual experiment. Collectively, the trajectories illustrate the overall behavior of the dispersion. In particular, the three-parameter Markov model [10–13] is a generalization of Kynch's theory that incorporates all the major features of one-dimensional sedimentation. A five-parameter model describes three-dimensional sedimentation [14].

2. Fokker–Planck equation

Almost all chemical engineering problems are solved within the general framework of the basic laws of mass, momentum, and energy transport. The partial differen-

* Tel.: +1-506-5362426; fax: +1-506-3641183.
E-mail address: sherpa@nbnet.nb.ca (E.M. Tory).

1383-5866/00/$ – see front matter
PII: S1383-5866(00)00079-4

tial equations known as *equations of change* determine how mass, energy, and momentum change within a region of space [15]. These equations are closely related to the Fokker–Planck equation (FPE), which can be written in the general form:

$$\frac{\partial}{\partial t} P(t, \mathbf{x}) = -\frac{\partial}{\partial \mathbf{x}} [\mathbf{A}(t, \mathbf{x}) P(t, \mathbf{x})] + \frac{1}{2} \frac{\partial}{\partial \mathbf{x}} \frac{\partial}{\partial \mathbf{x}} : [\mathbf{D}(t, \mathbf{x}) P(t, \mathbf{x})] \quad (1)$$

where t represents time, $\mathbf{x}$ is a d-dimensional vector of coordinates, P is a probability density, $\mathbf{A}$ is a d-dimensional vector, and $\mathbf{D}$ is a positive-semidefinite symmetric $d \times d$ matrix. The term containing $\mathbf{A}$ is the drift term and the term containing $\mathbf{D}$ is the diffusion term [15]. There are many cases in which a transport equation can be written as an FPE. However, the dependent variable in the transport equation is concentration, temperature, etc. while the dependent variable in the FPE is a probability density. By definition, the integral of the latter over the x-space is unity, so a trivial rescaling is necessary [15].

3. Transformation of an FPE to a stochastic differential equation (SDE)

Assuming that $\mathbf{A}$ and $\mathbf{D}$ satisfy certain conditions, it can be proved that the FPE given by Eq. (1) corresponds to a Markov process that is the solution of the multivariate stochastic differential equation:

$$\mathrm{d}\mathbf{X}_t = \mathbf{A}(t, \mathbf{X}_t)\mathrm{d}t + \mathbf{B}(t, \mathbf{X}_t)\mathrm{d}\mathbf{W}_t \quad (2)$$

where

$$\mathbf{D}(t, \mathbf{x}) = \mathbf{B}(t, \mathbf{x})\mathbf{B}^T(t, \mathbf{x}) \quad (3)$$

and $\mathbf{W}$ is a d-dimensional vector of independent Wiener processes [15,16].

Since the hydrodynamic diffusion of sedimenting particles is deemed to be analogous to the Fickian diffusion of molecules [7,8], it is useful to begin with a well-known diffusion problem. In sedimentation, the value of the diffusion coefficient will be a function of the solids concentration. Bargiel and Tory [17] used the stochastic approach to solve the simple (but non-trivial) PDE:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial \mathbf{x}} \left[\alpha(\theta) \frac{\partial \theta}{\partial \mathbf{x}} \right] \quad (4)$$

that describes one-dimensional diffusion with a diffusion coefficient α that depends on θ where θ is the dependent variable (concentration, temperature, etc.). To convert this to an SDE, they noted that:

$$\frac{\partial^2}{\partial x^2} [\alpha(\theta)\theta] = \frac{\partial}{\partial x} \left[\alpha(\theta) \frac{\partial \theta}{\partial x} + \frac{\mathrm{d}\alpha}{\mathrm{d}\theta} \frac{\partial \theta}{\partial x} \theta \right] \quad (5)$$

and hence

$$\frac{\partial}{\partial x} \left[\alpha(\theta) \frac{\partial \theta}{\partial x} \right] = -\frac{\partial}{\partial x} \left[\frac{\mathrm{d}\alpha}{\mathrm{d}\theta} \frac{\partial \theta}{\partial x} \theta \right] + \frac{\partial^2}{\partial x^2} [\alpha(\theta)\theta] \quad (6)$$

When Eq. (6) is substituted in Eq. (4) the latter has the form of Eq. (1) with:

$$A(t, x) = \frac{\mathrm{d}\alpha}{\mathrm{d}\theta} \frac{\partial \theta}{\partial x} \quad (7)$$

Thus, the corresponding SDE is:

$$\mathrm{d}X(t) = \frac{\mathrm{d}\alpha}{\mathrm{d}\theta} \frac{\partial \theta}{\partial x} \mathrm{d}t + (2\alpha(\theta))^{1/2} \mathrm{d}W(t) \quad (8)$$

Note that Eq. (6) is not an FPE because θ is not a probability density. Since θ is proportional to P this affects only the details of the normalization. If Eq. (4) describes molecular diffusion, each solution of Eq. (8) represents the (one-dimensional) path of a single molecule.

An SDE is solved by discretizing the space and time variables and generating many sample paths [15] (the spatial subdivisions are called bins). As in scientific polling, a fairly small representative sample closely approximates the entire population. Bargiel and Tory [17] solved Eq. (8) with the boundary condition $\theta(0, t) = 1, \quad t > 0$ and the initial condition $\theta(x, 0) = 0, \quad x > 0$, (for which an analytical solution is available). It is easy to scale the SDE results to satisfy the boundary condition. N_0 is the number of particles (in a bin) corresponding to $\theta = 1$. Then, for each bin, $\theta_j = N_j / N_0$. The discrete approximation of Eq. (8) is:

$$X_i(t + \triangle t) = x_i(t) + \left(\frac{\theta_{j+1} - \theta_{j-1}}{2\triangle x} \right) \frac{\mathrm{d}\alpha}{\mathrm{d}\theta}\Big|_{\theta_j} \triangle t + (2\alpha_j \triangle t)^{1/2} \psi_i \quad (9)$$

where ψ_i is a random number from the standard normal distribution and α_j and θ_j are the values of α and θ for the bin in which the ith particle is located. The only limitation of the method is that $\triangle t$ must be very small to ensure that the last term in Eq. (9) is not too large. Thus, it is only fairly recently that this method has become a practical alternative. Fig. 1, which compares the stochastic and analytical solutions, shows that the stochastic method is very accurate with a modest number of solutions. Fig. 1(a) indicates that the individual values from each run cluster around the line representing the analytical solution. Fig. 1(b) shows that the average values fall almost exactly on that line. A different, but similar, example is shown in the paper by Bargiel and Tory [17]. Of course, the hydrodynamic diffusion description of sedimentation will contain a drift term which was not part of the molecular diffusion problem.

A special feature of their solution is that many paths are generated in parallel and non-linear diffusion is solved as a *Pickard–Tory process* [12]. The number of particles in each space interval at a given time provides an estimate of the value of θ and hence α. Given α, the trajectories are independent. Each particle moves, in each time step, according to

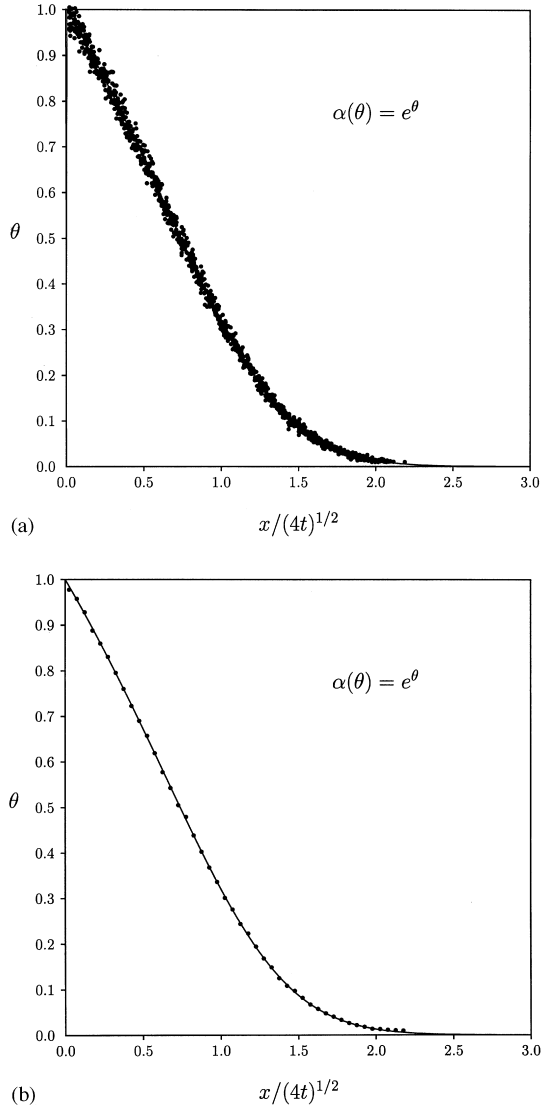

Fig. 1. Non-linear diffusion. (a) Each point represents a simulated value of θ in a bin centered at x at time t. (b) Points represent values averaged over 0.05 on the abscissa. The solid line is the analytical solution.

the value corresponding to its position. However, α is also a random variable, being determined by the empirical estimate of θ which is itself evolving. This process was first encountered in modelling sedimentation and is discussed in more detail in Section 8. Eq. (9) shows the limitations of the hydrodynamic diffusion approach. Since $\lim_{\Delta\to 0}(\Delta t)^{-1/2} = \infty$, the square-root in the last term implies that $X(t)$ is continuous everywhere, but differentiable nowhere.

4. The three-parameter Markov model

Despite its theoretical limitations, Kynch's theory has been very successful in explaining the behavior of incompressible slurries [18]. However, there are two features of sedimentation that it cannot describe. Not only do identical particles in a suspension settle with different velocities, but also the velocity of each particle changes with time. These features are incorporated in a Markov model [5,19,20]. The Markov property reflects the well-known result that the velocity of a particle in creeping flow depends only on the current configuration of the system and not on any previous configuration. Solids concentration is used as a proxy for configuration. Since a given concentration represents many different configurations (and hence many different velocities), the deterministic effect of this variability (of configurations on particle velocity) is replaced by a random process. The assumption that particle velocity depended only on the local solids concentration was crucial to the success of Kynch's theory. However, the spatial and temporal variability of identical particles at the same solids concentration shows that (at least) two additional parameters are necessary for a complete description. In contrast to Kynch's assumption, the three parameters are assumed to be functions of a weighted-average of local solids concentrations. This assumption is supported by computational evidence [4,21,22].

The three-parameter Markov model [10–12] can be written as:

$$\mathrm{d}V(t) = -\beta(V-\mu)\mathrm{d}t + \sigma\,\mathrm{d}W \tag{10}$$

$$\mathrm{d}X(t) = V(t)\mathrm{d}t \tag{11}$$

where V is the velocity of an individual particle, X is its position, and β, μ and σ are the three parameters; σ controls the variation of velocity *increments*, while $\beta(V-\mu)\mathrm{d}t$ describes the strength with which individual velocities are shifted to the steady-state ensemble value μ [12]. From Eqs. (1)–(3) with v replacing x, the Fokker–Planck equation (also known as the (Kolmogorov) forward equation [16,23]) corresponding to Eq. (10) is:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial v}\left[\beta(v-\mu)P\right] + \frac{1}{2}\frac{\partial^2}{\partial v^2}(\sigma^2 P) \tag{12}$$

The three-parameter model differs from the well-known Ornstein–Uhlenbeck model only in the presence of μ [24]. Consequently [12,25], its principal features are easily obtained. Velocity, $V(t)$ is an Ornstein–Uhlenbeck process with parameters μ, β and σ; position is the corresponding integrated Ornstein–Uhlenbeck process:

$$X(t) = X(0) + \int_0^t V(\tau)\mathrm{d}\tau \tag{13}$$

Both $V(t)$ and $X(t)$ have continuous sample paths. Given a standard Wiener process $W(t)$ starting from $W(0) = w_0$ then:

$$V(t) = e^{-\beta t}\,W\left[\sigma_v^2\left(e^{-2\beta t}-1\right)\right] + \mu \tag{14}$$

is a solution of Eq. (10) with $\sigma_v^2 = \sigma^2/(2\beta)$ and $V(0) = w_0 + \mu$ [25].

When the solids concentration remains essentially constant, any initial distribution of particle velocities evolves toward a steady-state (in practice, of course, the particles may

reach the bottom of the settling tank before the steady-state can be reached). This approach to a steady-state distribution of velocities is a general feature of Markov models for sedimentation [5,20]. For the three-parameter model, the steady-state velocity distribution is normal with mean μ and variance σ_v^2. Velocity autocorrelations are given by $\rho(t) = e^{-\beta t}$.

The velocity process $\{V(t)\}$ is both Gaussian and Markov. The corresponding position process $\{X(t)\}$ is Gaussian, but obviously not Markov. However, the bivariate process $\{X(t), V(t)\}$ is both Gaussian and Markov. Its transition structure is bivariate normal with the following moments [12,25]:

$$E(V(t)|X(0)=x_0,\ V(0)=v_0) = \mu + (v_0-\mu)e^{-\beta t} \quad (15)$$

$$E(X(t)|X(0)=x_0,\ V(0)=v_0) = x_0 + \mu t + (1-e^{-\beta t})(v_0-\mu)/\beta \quad (16)$$

$$\mathrm{Var}(V(t)|X(0)=x_0,\ V(0)=v_0) = (1-e^{-2\beta t})\sigma_v^2 \quad (17)$$

$$\mathrm{Var}(X(t)|X(0)=x_0,\ V(0)=v_0) = (2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t})\sigma_v^2/\beta^2 \quad (18)$$

$$\mathrm{Cov}(X(t),\ V(t)|X(0)=x_0,\ V(0)=v_0) = (1-e^{-bt})^2\sigma_v^2/\beta \quad (19)$$

Note that the last three values are independent of the initial conditions. Also, for $t_1 \le t_2$ the relationship between the velocities at two different times is:

$$\mathrm{Cov}(V(t_1),\ V(t_2)) = \sigma_v^2\left[e^{2\beta t_1}-1\right]\left[e^{-\beta(t_1+t_2)}\right] \quad (20)$$

Similarly, that for the distances travelled is:

$$\mathrm{Cov}(X(t_1),\ X(t_2)) = \left[\sigma_v^2/\beta^2\right]\left[2\beta t_1 - 2 + 2e^{-\beta t_1} + 2e^{-\beta t_2} - e^{-\beta t_2}(e^{\beta t_1}+e^{-\beta t_1})\right] \quad (21)$$

Eqs. (15)–(19) form the basis for simulating sedimentation; Eqs. (20) and (21) have been used for interpolation in the determination of crossing velocities [26] and transit times [13], respectively.

Let $t_1 = t'$ and $t_2 = t' + t$ in Eq. (20). Then:

$$C(t) = \mathrm{Cov}(V(t'),\ V(t'+t)) = \sigma_v^2\, e^{-\beta t}(1-e^{-2\beta t'}) \quad (22)$$

plays an important role in the diffusion approach.

5. Simulation of transit times

Experiments to determine settling velocity as a function of solids concentration have used the rate of fall of the slurry–supernate interface, the time for marker particles to traverse a fixed distance, the distance travelled by particles in a fixed time, and the determination of the instantaneous velocities. Even when the values of the three parameters are not known precisely, simulations can be useful in determining the validity of some of these methods.

Measuring the time for marker particles to traverse a fixed distance has been a popular method of determining mean velocity [7,26–32]. Since both downward and upward velocities occur in dispersions, starting and finishing the journey with a downward velocity might be expected to bias the results toward a value greater than μ [10]. Later work [11,13,26] showed that total time divided by total distance provides an unbiased and strongly consistent estimate of μ^{-1} i.e.:

$$E\left[\sum_{i=1}^{n} t_i/(nx)\right] = \mu^{-1} \quad (23)$$

and

$$\lim_{n\to\infty}\sum_{i=1}^{n} t_i/(nx) = \mu^{-1} \quad (24)$$

These results have been proven rigorously for dispersions in which all particles move downward. Simulations have demonstrated that these equations hold even for coefficients of variation ($\lambda = \sigma_v/\mu$) far larger those obtained experimentally. Simulations have also shown that these equations hold even when the distance traversed is very small [32]. It remains, however, to prove that they hold as $x \to 0$.

The variability of the times to traverse a fixed distance indicates that particle velocities vary, but it is not immediately clear what is being measured. Pickard et al. [11] clarified the fundamental structure of the model by defining the dimensionless variables:

$$v_* = v/\mu \qquad t_* = \beta t \qquad \mathbf{x}_* = \beta x/\mu \quad (25)$$

whence

$$\mu_* = \beta_* = 1 \qquad \sigma_* = \sigma/\mu = \lambda$$

The coefficient of variation, λ, then becomes the only remaining parameter, the other two being absorbed in the scaling process. In this dimensionless form, t_* is measured in correlation times and x_* in correlation lengths. This simplification shows that λ is the fundamental parameter that determines the nature of sedimentation at steady-state; the other two parameters (β and μ) simply determine the time and distance over which the phenomena occur.

For moderately large values of x_* transit times, $T_*(x_*)$, are distributed according to a log-normal distribution [11,13]. Tory et al. [26] determined the distribution of crossing velocities and first-crossing velocities and clarified the distinction between them. Simulations [11,13] also established that:

$$\mathrm{Var}\,[T_*(x_*)] = 2\lambda^2 x_* \quad (27)$$

As $x_* \to \infty$, $T_*(x_*)$ is given approximately by the first-passage time in the Wiener process with drift μ_* [11]. This yields the asymptotic value of 2, but the fit is also

excellent at small values of $\lambda^2 x_*$ In terms of the original variables, Eq. (27) is:

$$\mathrm{Var}\,[T(x)] = 2\sigma_v^2 x/(\beta\mu^3) \tag{28}$$

In many experiments to determine the times to traverse a fixed distance, x, only Var[$T(x)$] and μ are determined. This leaves σ_v^2 and β inextricably intertwined.

6. Distribution and autocorrelation of velocities

Assuming a Poisson distribution of sphere centers in a very dilute dispersion, Tory and Kamel [33] calculated the variance of the velocity of a sphere in a spherical container. When the test sphere is momentarily concentric with the container, the mobility tensor assumes a particularly simple form [34] and the mean and variance are easily calculated. Tory et al. [35] extended these theoretical calculations to the third and fourth central moments of velocity, thereby determining the skewness and kurtosis of the distribution. They proved that the distribution quickly approaches normality as the size of the container (relative to the particle size) increases. More generally, Caflisch and Luke [36] had stated earlier that the initial distribution of velocities is asymptotically normal. In dilute dispersions, however, rapid "demixing" of the dispersion occurs and cluster formation is extensive [37,38]. Tory and Pickard [10] found that velocities in the second minute of sedimentation [4] were highly variable; the largest downward and upward velocities both occurred in this interval. A Kolmogorov–Smirnov test [39] shows that this distribution was not normal. Rather, it is skewed to large downward values. From the fifth minute on, however, the distribution of velocities was normal, as noted below.

Tory and Pickard [10] measured the distances travelled by marker spheres in consecutive one-minute intervals and determined the values of the three parameters from 32 pairs of data. Subsequent analyses [4,40] of their data refined and strengthened their results. Bürger and Tory [40] showed that the solids concentration near the top changed from that in the bulk of the dispersion to a considerably lower value. Tory et al. [4] found that steady-state values in the lower part of the dispersion were similar to those higher up. The net result of these studies was to eliminate a few pairs from the original analysis [10] and to add many others to bring the total to 68 pairs. Using the first member of each pair, we conducted a Kolmogorov–Smirnov test [39] for normality. The value of 0.718 is close to the size typically found under the null hypothesis (i.e. $KS \in [0.6,\ 0.7]$. The critical values for the 15 and 5% levels of significance are 0.775 and 0.895, respectively, so these values are completely compatible with normality. Since the theoretical distribution of distances travelled is also normal, this suggests that the experimental distribution of instantaneous velocities is normal. However, it is possible that the averaging effect [41] could produce a normal distribution of distances travelled from a non-normal distribution of velocities.

Nicolai et al. [42] measured changes in vertical and horizontal positions during very short time periods to obtain essentially instantaneous velocities. Histograms of these velocities were found to be very smooth and approximately Gaussian. Ladd [43] used a method for computing the hydrodynamic interactions among spherical particles as the basis for a small-scale simulation of sedimentation of spheres. He found that non-Gaussian effects were small at low concentrations, but increased with concentration, becoming large at high concentrations. The small size of the simulation may have magnified the non-Gaussian effects. In any case, his results support the view that the distribution of velocities is approximately normal in dilute dispersions. Höfler also found that computed velocities were approximately Gaussian.

We have already noted that a normal distribution of velocities gives rise to a distribution of transit times that is approximately log-normal. Koglin [31,45] measured transit times and found that they followed a log-normal distribution. This provides additional support for a normal distribution.

Ladd [43] also found that correlations in the translational velocities parallel to the sedimentation axis decayed as a single exponential in time, i.e. $\rho(t) = e^{-\beta t}$ in our notation. Nicolai et al. [42] found the same relationship. Koglin [31,45,46] measured the times for a particle to traverse a succession of fixed distances and calculated the mean velocity for each interval. He found that the correlation coefficient between these mean velocities was satisfactorily represented by an exponential decrease with increasing distance between the centers of the distance segments. The three-parameter model predicts an exponential decay of correlations between the distances travelled in fixed time intervals [10,25,47]. Intuition suggests and simulations confirm that this should hold approximately for mean velocities over fixed space intervals [25]. Tory et al. [13] showed that correlation coefficients of simulated transit times for successive space intervals decayed exponentially and that the value of β was the same as for the decay of the correlations of the instantaneous velocity. After a few intervals, however, random fluctuations overwhelm the relationship.

7. Parameter values

In order to compare experimental values of the three parameters, we need to express them in a suitable dimensionless form. We use:

$$\mu^* = \mu/u_0 \qquad \sigma^* = \sigma_v/u_0 \qquad \beta^* = \beta l/u_0 \tag{29}$$

where u_0 is the Stokes velocity of the particle and l is its characteristic dimension. An alternative is to use a relaxation time, t^*, which is expressed in terms of t_0, the time for a particle moving at its Stokes velocity to traverse a distance equal to its characteristic dimension l. Then, $t_0 = l/u_0$ and $t^* = 1/\beta^*$. For spheres, it is usual to choose the radius, a, as

the characteristic dimension. These parameters are functions of the solids concentration, φ.

In their reanalysis of the data of Tory and Pickard [10], Bürger and Tory [40] obtained $\mu^*(0.02) = 0.959$ and $\sigma^*(0.02) = 0.587$. They also obtained values of 0.819 and 0.209, respectively, for these parameters in a dilute region with a gradient in which φ appeared to vary between roughly 0.0064 and 0.0095 from top to bottom. Kaye and Boardman [27,28], Johne [30], and Koglin [31,48] also found that μ^* and σ^* increased with φ in this range of concentrations. In very dilute dispersions, the mean velocity varies with the size of the container relative to the particles. Thus, the range over which μ^* increases with φ depends on the size ratio. The variance increases with the relative size of the container and with φ. Consequently, the upper levels become depleted [10,40,48]. Thus, values of these parameters cannot be compared directly, but they are consistent [4,48]. In one study [48], the interface was sharp only for $\varphi \geq 0.2$. Then, the upper levels were no longer depleted and the rate of fall of the interface was given fairly accurately by the Richardson–Zaki equation [49]. When the relative size of the container is smaller, depletion is less and the interface becomes sharp at much smaller values of φ [27,28]. Then, the mean velocity is given fairly accurately by the rate of fall of the interface for $\varphi \geq 0.05$. Values of $\sigma^*$for $\varphi \geq 0.05$ are controversial; theory [4,33,36] and simulations [50,51] predict an increase with container size that was not found experimentally by Nicolai and Guazzelli [52]. However, their values may have been affected by the presence of a small concentration gradient (see Section 9).

Until recently, most experimenters paid little attention to determining the values of β^* or, equivalently, t^*. Prior to the formulation of the three-parameter model [10], t^* was not measured, although Koglin [31,46] determined a related parameter. Bürger and Tory [40] found that $\beta^*(0.02) = 0.0149$ and hence $t^* = 67.1$. The latter is higher than the value cited by Tory and Hesse [22] because the reanalysis used additional data and because the value of u_0 is less at 24.0° than at 25.1°. Bürger and Tory determined that β^* in the gradient was 0.0350 (t^*=28.6). Ladd [43] obtained values of t^* between 25 and 50 with a minimum at $\varphi = 0.25$. More recently [51], he found that $t^* = 10$ for $\varphi = 0.1$. The difference between his values may be due to the fact that his first simulation involved fewer spheres and, consequently, there was less opportunity for spheres to slide past one another without interference. Nicolai et al. [42] found that t^* varied between 16 and 26. It increased slightly with φ from 0.15 to 0.40. There may be a minimum between 0.10 and 0.15, but the difference in values is within experimental error. Höfler [44] obtained a value of $t^* \approx 18$ for $\varphi = 0.3$. Hesse and Ramos [47] found that t^* was essentially constant at 387 in very dilute dispersions of cylinders. This is much higher than values for spheres, but part of the variation in the velocities of cylinders arises from differences in orientation [47,53]. It is plausible that orientation changes slowly at these values of φ.

Pickard and Tory [12] conjectured that t^* reaches a maximum at $\varphi = 0.02$ (where cluster settling is extensive) and decreases thereafter. The decrease in t^* with decreasing φ found by Bürger and Tory [40] together with the values found by Ladd [43] suggests that there is indeed a local maximum (at least) at some low value of φ. Also supporting this view is the fact that an isolated sphere quickly attains its steady-state value, implying a very small value of t^*. On the other hand, the type of motion observed at very high concentrations by Ladd suggests that relaxation times should be long and this is supported by his values. The best guess at the moment appears to be an initial increase to a maximum or local maximum followed by a decrease to a local minimum and a subsequent increase with φ. There is a great need for good experimental data over a wide range of concentrations.

8. Comparison of the stochastic and diffusion approaches

The formal equivalence between the three-parameter Markov model and a hydrodynamic diffusion approach is through Eq. (12), the FPE, to an equation of change that describes the diffusion of *velocity*. From its beginning, however, the hydrodynamic diffusion approach assumed that 'the random positions of the particles and a large number of interactions are expected to cause the details of individual interactions to be lost and an individual particle to execute a random walk through the suspension. Such a random walk process leads naturally to a description of particle migrations as a Fickian process. Once an analogy to Fickian diffusion is made, the associated dispersion coefficient, D, can be described in terms of the long-time behavior of the '*distribution of particle positions* (our emphasis)...' [7]. Then D is given by [42].

$$D = \int_0^\infty C(t)\mathrm{d}t \tag{30}$$

where C is defined by Eq. (22). Also:

$$C(t) = C(0)\, e^{-t/t^*} \tag{31}$$

whence

$$t^* = [1/C(0)] \int_0^\infty C(t)\mathrm{d}t \tag{32}$$

Note that Eqs. (17) and (22) imply that:

$$C(0) = \mathrm{Var}\left[V(t')\right] \tag{33}$$

and

$$\rho(t) = C(t)/C(0) = e^{-\beta t} \tag{34}$$

as noted in the section on the three-parameter model.

Thus, the principal difference between the two approaches is that hydrodynamic diffusion focuses on position while

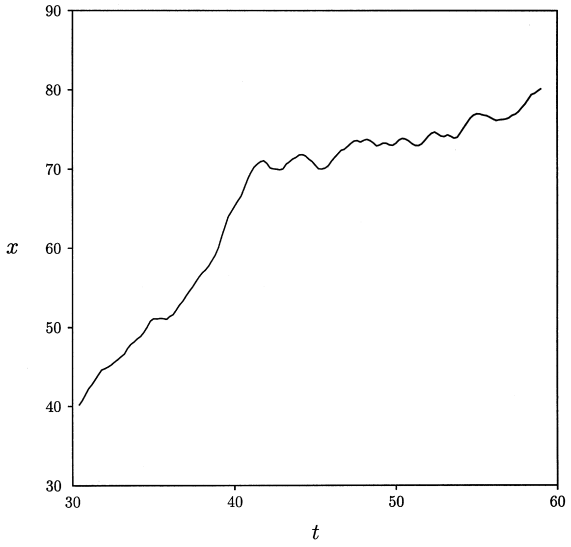

Fig. 2. Simulated trajectory of a sedimenting sphere. x is the distance travelled in the downward direction (from Tory et al. [13]).

the Markov model focuses on velocity. In this respect, the latter has an advantage. In Fickian diffusion, particle paths are continuous, but velocity is not. In the Markov model, both velocity and sample paths are continuous [11,12,25] and interpolated paths are piecewise smooth [11,13]. Fig. 2 shows a typical one-dimensional path. The diffusion model emphasizes the long-run behavior of the particles. While the Markov model also makes predictions about long-term behavior, it can also handle situations in which particles pass through regions in which the solids concentration changes rapidly. By emphasizing velocity, the Markov model subsumes Kynch's theory as a first approximation [19]. Most importantly, the three-parameter Markov model is ideally suited for simulations [11,12,25,54]. Where changes are gradual and fluctuations in velocity are relatively small, the simulations will closely follow Kynch's theory [19] (in the Markov model, however, there are no discontinuities in velocity). In other situations, the model predicts phenomena that would not be possible if Kynch's theory were strictly true [40].

The three-parameter model makes specific predictions about the behavior of slurries. In particular, it predicts that particle velocities will evolve to a steady-state distribution and that this distribution will be normal. It also predicts the exponential decay of the autocorrelation of velocities. These predictions have been verified experimentally. More generally, however, sedimentation is a Pickard–Tory process [12]. This approach uses a parametrized (by environment) family of independent processes to define a single complex process for the ensemble of all particles. Then, sedimentation is characterized by the following fundamental principle: Identical particles in the same environment are governed, *independently*, by the same stochastic process.

At each time, each particle moves according to the family member describing its current environment. Moreover, the particles act *independently*, given their parameter values (i.e. environments). However, these parameters are also random variables, being determined by the *configuration of the entire system*, which is itself evolving. Sedimentation proceeds incrementally as follows:

Particles (simultaneously) consult their current environments and move (simultaneously) with Markov velocities, yielding new velocities and positions, and hence new environments.

This complex structure was introduced by Pickard and Tory [55] in 1974 and refined by them [12] in 1987. Still later, it was justified for dilute dispersions [4]. However, it does not hold for concentrated dispersions where particles interact directly with their nearest neighbors via lubrication terms [43]. As more information becomes available, it may be possible to refine the Markov model by including such features as different concentration-dependent parameters ϕ_1, ϕ_2 and ϕ_3 for μ, β and σ_v, respectively. Perhaps concentration gradients could be included as a significant feature of the environment (see Section 9).

Unlike molecular diffusion, which involves astronomical numbers of particles, experiments to measure the parameters involve, by necessity [42], a limited number of particles. The exploratory experimental study by Pickard and Tory [10] used roughly 32 000 particles. A simulation of their experiment by Tory and Ford [54] used a comparable number of particles. The experiments by Nicolai et al. [42] with $\varphi = 0.05$ used roughly 1.5 million particles. In both experiments, the positions of a few marked spheres were followed. These experimental trajectories can be compared directly to simulated trajectories. Simulations with half a million particles are already feasible with desktop computers [54]. With relatively small samples, fluctuations in the local solids fraction can influence the settling behavior. Thus it is important to mimic this feature as far as possible. As computers become more powerful and the sedimentation parameters become better known, the advantages of the Markov model will become greater and greater. By incorporating values of σ_v and β for the horizontal component of velocity, we obtain a five-parameter model for three-dimensional sedimentation [14,22]. Simulations have already incorporated this feature, but only for visual effect [12].

9. Discussion

In his report on an international symposium, Davis [56] states that phenomena related to hydrodynamic diffusion have been studied for just under ten years. This statement takes no account of many significant papers that were published long before the field became fashionable. Though the term, hydrodynamic diffusion, is relatively new, evidence for the variability of particle velocities is ancient and abundant. This evidence has been summarized and interpreted by Tory and Pickard [57]. In particular, the Markov model, which can achieve any result obtained from the diffusion

model, preceded the latter by a decade. However, the emphasis on diffusion has led to some excellent work and the steady-state values of the parameters in regions of constant concentrations are slowly being determined. The problem of characterizing these values in regions of rapidly changing concentrations is much more difficult [54].

The major problem for both groups is that theory predicts that the variance of particle velocities in dispersions increases without limit as the dimensions of the dispersion increase [36,50,51]. This increase is found experimentally in very dilute dispersions [4], but not in those with $\varphi \geq 0.05$ [52]. In simulations with periodic boundary conditions [50,51], there is no depletion of the upper levels. In experiments, there is some depletion of the upper levels of dispersions of intermediate concentration even if the particles are identical [20,48]. In one study [48], this depletion occurred for $\varphi < 0.2$. In addition, there will be some segregation by size in dispersions of low to intermediate concentrations. Shannon et al. [58] found that the rise of the packed bed was very non-linear for $\varphi \leq 0.075$ and slightly non-linear for $\varphi \leq 0.1$. The distribution of radii was sharper in the experiments of Nicolai et al. (λ_a=0.043 vs 0.101 for Shannon et al.), but some segregation by size would be expected at $\varphi \leq 0.05$. The segregation by chance and size would produce a concentration gradient and it is possible that this gradient reduces the variance of velocity. In similar experiments by Nicolai et al. [59], the settling speed of a single large particle decreased as it fell through a suspension of smaller particles. This is consistent with the presence of a gradient. If segregation were greatest in the largest containers, the gradients that formed there would be the sharpest. Consequently, the resulting reduction in the variance would also be the greatest. It is also possible that values of t^* are smaller in a gradient because it impedes the downward movement of clusters. In very concentrated dispersions, lubrication effects, which are very short range, dominate the long-range multiparticle effects [43] and the size effect should no longer be a problem.

Acknowledgements

I thank M. Bargiel for preparing Fig. 1.

References

[1] G.J. Kynch, Trans. Faraday Soc. 48 (1952) 166.
[2] S. Mirza, J.F. Richardson, Chem. Eng. Sci. 34 (1979) 447.
[3] S. Kim, S.J. Karrila, Microhydrodynamics: Principles and Selected Applications, Butterworth Heinemann, Stoneham, 1991.
[4] E.M. Tory, M.T. Kamel, C.F. Chan Man Fong, Powder Technol. 73 (1992) 219.
[5] D.K. Pickard, E.M. Tory, J. Math. Anal. Appl. 60 (1977) 349.
[6] E.M. Tory, M.T. Kamel, Powder Technol. 93 (1997) 199.
[7] J.M. Ham, G.M. Homsy, Int. J. Multiphase Flow 14 (1988) 533.
[8] R.H. Davis, in: E.M. Tory (Ed.), Sedimentation of Small Particles in a Viscous Fluid, Computational Mechanics, Southampton, 1996 (chapter 6).
[9] D.K. Pickard, E.M. Tory, Settling of Slurries — A Stochastic Approach, 22nd Canadian Chemical Engineering Conference, Toronto, September 17–20, 1972.
[10] E.M. Tory, D.K. Pickard, Can. J. Chem. Eng. 55 (1977) 655.
[11] D.K. Pickard, E.M. Tory, B.A. Tuckman, Powder Technol. 49 (1987) 227.
[12] D.K. Pickard, E.M. Tory, in: I.B. MacNeill, G.J. Umphrey (Eds.), Advances in the Statistical Sciences, vol. 4, D. Reidel, Dordrecht, 1987 (chapter 1).
[13] E.M. Tory, M. Bargiel, R.L. Honeycutt, Powder Technol. 80 (1994) 133.
[14] E.M. Tory, in: E.M. Tory (Ed.), Sedimentation of Small Particles in a Viscous Fluid, Computational Mechanics, 1996 (chapter 1).
[15] M. Laso, AIChE J. 40 (1994) 1297.
[16] P.E. Kloeden, E. Platen, Numerical Solution of Stochastic Differential Equations, Springer-Verlag, Berlin, 1992, p. 37.
[17] M. Bargiel, E.M. Tory, AIChE J. 42 (1996) 889.
[18] M.C. Bustos, F. Concha, R. Bürger, E.M. Tory, Sedimentation and Thickening (1999) Kluwer.
[19] D.K. Pickard, E.M. Tory, J. Math. Anal. Appl. 72 (1979) 150.
[20] E.M. Tory, D.K. Pickard, J. Math. Anal. Appl. 86 (1982) 442.
[21] E.M. Tory, M.T. Kamel, Powder Technol. 55 (1988) 51.
[22] E.M. Tory, C.H. Hesse, in: E.M. Tory (Ed.), Sedimentation of Small Particles in a Viscous Fluid, Computational Mechanics, 1996 (chapter 8).
[23] R. Iranpour, P. Chacon, Basic Stochastic Processes. The Mark Kac Lectures, MacMillan, New York, 1988, p. 19.
[24] S. Karlin, H.M. Taylor, A Second Course in Stochastic Processes, Academic Press, San Diego, 1981.
[25] C.H. Hesse, E.M. Tory, in: E.M. Tory (Ed.), Sedimentation of Small Particles in a Viscous Fluid, Computational Mechanics, 1996 (chapter 7).
[26] E.M. Tory, R.J. Hughes, M. Bargiel, Powder Technol. 84 (1995) 259.
[27] B.H. Kaye, R.P. Boardman, in: Proceedings of the Symposium on Interactions between Fluids and Particles, London, 20–22 June 1962.
[28] R.P. Boardman, The Terminal Velocity of a Particle Settling in the Presence of Other Particles, M.Sc. thesis, London University, 1961.
[29] J. Verhoeven, Prediction of Batch Settling Behaviour, B.Eng. Thesis, McMaster University, April 1963.
[30] R. Johne, D.Ing. Dissertation, Universität Karlsruhe, 1965.
[31] B. Koglin, D.Ing. Dissertation, Universität Karlsruhe, 1971.
[32] E.M. Tory, R.J. Hughes, M. Bargiel, Atlantic Math Days 1994, Acadia University, Wolfville, Nova Scotia.
[33] E.M. Tory, M.T. Kamel, Powder Technol. 55 (1988) 187.
[34] C.W.J. Beenakker, P. Mazur, Phys. Fluids 28 (1985) 3203.
[35] E.M. Tory, M. Bargiel, M.T. Kamel, Powder Technol. 74 (1993) 159.
[36] R.E. Caflisch, J.H.C. Luke, Phys. Fluids. 28 (1985) 759.
[37] B. Koglin, Proceedings of the 1st International Congress on Particle Technology, Chicago, 1973, pp. 265.
[38] M.T. Kamel, E.M. Tory, W.S. Jodrey, Powder Technol. 24 (1979) 18.
[39] M.A. Stephens, J. Am. Stat. Assoc. 69 (1974) 730.
[40] R. Bürger, E.M. Tory, Powder Technol. 108 (2000) 74.
[41] W. Mendenhall, R.J. Beaver, Introduction to Probability and Statistics, PWS-Kent, Boston, 1991.
[42] H. Nicolai, B. Herzhaft, E.J. Hinch, L. Oger, E. Guazzelli, Phys. Fluids 7 (1995) 12.
[43] A.J.C. Ladd, Phys. Fluids A 5 (1993) 299.
[44] K. Höfler, Diplomarbeit, Institut für Computeranwendungen I, Universität Stuttgart, 1997.
[45] B. Koglin, Chem.-Ing.-Tech. 43 (1971) 761.
[46] B. Koglin, in: M.J. Groves, J.L. Wyatt-Sargent (Eds.), Particle Size Analysis 1970, The Society for Analytical Chemistry, London, 1972, p. 223.
[47] C.H. Hesse, E. Ramos, Appl. Math. Model. 18 (1994) 437.
[48] B. Koglin, 1st European Symposium on Particle Size Measurement, Nuremburg, 1975, Dechema Monographs, no. 1589–1615, Vol. 79, part B, Verlag Chemie, GmbH, Weinheim Bergstrasse, 1976, pp. 235.

[49] J.R. Richardson, W.N. Zaki, Trans. Inst. Chem. Eng. 32 (1954) 35.
[50] A.J.C. Ladd, Phys. Rev. Lett. 76 (1996) 1392.
[51] A.J.C. Ladd, Phys. Fluids 9 (1997) 491.
[52] H. Nicolai, E. Guazzelli, Phys. Fluids 7 (1995) 3.
[53] J. Happel, H. Brenner, Low Reynolds Number Hydrodynamics, Nijhoff, Dordrecht, 1983.
[54] E.M. Tory, R.A. Ford, Minisymposium on Sedimentation, ICIAM 99, Edinburgh, July 5–9, 1999.
[55] D.K. Pickard, E.M. Tory, 24th Canadian Chemical Engineering Conference, Ottawa, October 20–23, 1974.
[56] R.H. Davis, J. Fluid Mech. 310 (1996) 325.
[57] E.M. Tory, D.K. Pickard, in: B.M. Moudgil, P. Somasundaran (Eds.), Flocculation, Sedimentation and Consolidation, AIChE, New York, 1986, p. 297.
[58] P.T. Shannon, E. Stroupe, E.M. Tory, I. EC Fund 2 (1963) 203.
[59] H. Nicolai, Y. Peysson, E. Guazzelli, Phys. Fluids 8 (1996) 855.