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A Stochastic Model of Transport in Three-Dimensional Porous Media¹

Cyril Fleurant² and Jan van der Lee²

Modeling of solute transport remains a key issue in the area of groundwater contamination. The fundamental processes of solute transport are advection and dispersion and an accurate description is needed for all modeling studies. The most common approach (advection-dispersion equation) considers an average advective flow rate and a Fickian-like dispersion. Here we propose a more accurate approach: advection is a function of the dispersive behavior of the solute and of medium characteristics. This method provides useful insight for the dispersion process in general. The aim of this article is to present the mathematical background of the random walk model and a simple numerical application.

KEY WORDS: modeling, mass transport, non-Fickian dispersion, random walk, stochastic processes.

INTRODUCTION

Solute transport model has been the subject of an intense research effort in recent years and remains a key research area in hydrogeology. The motivations are problems of aquifers contamination and particularly migration of radionuclides from repository sites.

The movement of solute in porous media is commonly described by the advection-dispersion equation:

$$\nabla \cdot (\mathbf{D}\nabla C - C\mathbf{U}) = \frac{\partial C}{\partial t} \quad (1)$$

where C is the concentration (M/L^3), t is the time (T), \mathbf{U} is the average velocity (L/T), \mathbf{D} is the dispersion tensor (L^2/T), and ∇ is the operator divergence or gradient.

This classical approach considers the dispersive mass flux equal to the Fick's first law. If the dispersion tensor is expressed in its principal directions of anisotropy,

it is limited to three components: D_X is the longitudinal dispersion coefficient (in the direction of the flow), D_Y and D_Z are the transverse dispersion coefficients.

In the domain of typical groundwater velocities, the following relations are admitted:

$$\begin{aligned} D_X &= D_m + \alpha_X U \\ D_Y &= D_Z = D_m + \alpha_Y U \end{aligned} \quad (2)$$

where α_X and α_Y are the longitudinal and transverse dispersivities respectively (L), D_m is the molecular diffusion coefficient in porous media (L^2/T) and U is the modulus of the average velocity (L/T).

Two different methods are commonly used to solve the advection-dispersion equation numerically:

- Finite difference and finite element methods are fast and can be used for a variety of scales. But they are inflexible when other processes have to be added (such as sorption, dual-porosity, etc.). Their results are not precise for a high Peclet number, i.e., when advection is predominant, resulting in an alteration by the numerical dispersion. This is due to the double nature of the advection-dispersion equation, advection forming the parabolic and dispersion the hyperbolic part. The solution of this problem is to refine the mesh and so to increase the calculation time.
- Methods using particles. These methods come from stochastic physics in order to solve diffusion and dispersion problems. A deterministic description of the pollutant transfer in porous media is impossible, consequently the best approach is to consider all possible movements (Scheidtger, 1953). Many models exist to solve the advection-dispersion equation in this way (Ackerer and Kinzelbach, 1985; Uffink, 1988; Wen and Kung, 1995; Delay and others, 1996; Banton, Delay, and Porel, 1997). These methods are generally less efficient than the other methods, in terms of calculation time, but they are more flexible and can be used for many different situations such as particle interactions, volume exclusion, and non-Fickian dispersion.

The most important drawbacks of the advection-dispersion Equation (1) to simulate solute transport can be attributed to the non-Fickian behavior of the dispersive transport as well as the apparent scale dependence of the dispersivity (Matheron and de Marsily, 1980; Neuman and Zhang, 1990; Dagan, 1990; Gelhar, 1993).

Fitting of experimental data by the advection-dispersion Equation (1) sometimes fails because of non-Fickian behavior leading to long tails in breakthrough curves and skewness in the spatial dissemination of solute (Carrera, 1993). If the dispersion of solute was Fickian, the rate of increase in size of a plume should be

constant. This has been demonstrated experimentally at the Borden site (Ontario, Canada) where the rate of longitudinal growth increased with time and reaches a constant value only after 3 years (Freyberg, 1986).

Most difficulties in simulating solute transport arise from the manner in which dispersion is treated. The advection rate (defined by the ratio of the system length and breakthrough time) must be a consequence of the average pathway length, and therefore depends on dispersion. With the advection-dispersion Equation (1), advection is independant of dispersion.

The classical random walk approach generally aims at solving the following equation:

$$X(t + \Delta t) = X(t) + U \Delta t + \Omega \sqrt{2D\Delta t} \tag{3}$$

where Ω is a random number from a Gaussian distribution with 0 mean and a standard deviation equal to unity. This formula does not give any useful solution either, because it is still based on the assumption of an average flow velocity and some random noise factor that represents the dispersive effect. Therefore, Equation (3) is another formulation of Equation (1). A more mechanistic description of the dispersion requires a different random walk approach.

Different theories have been proposed to explain and to express hydrodynamic dispersion in porous media. The mathematical basis of this paper's theory is inspired to the statistical theory utilizing microscopic pore structure parameters, brought forward by, e.g., Scheidegger (1953), de Jong (1958), and Saffman (1959).

These authors provided mathematical descriptions of displacement and dispersion of particles in a porous medium. The medium is regarded as an assemblage of small, randomly orientated straight tubes of eventually variable length, denoted by ℓ . Each time a particle reaches a junction, a new direction is randomly chosen according to a uniform distribution of probability density functions for θ and ϕ (Fig. 1).

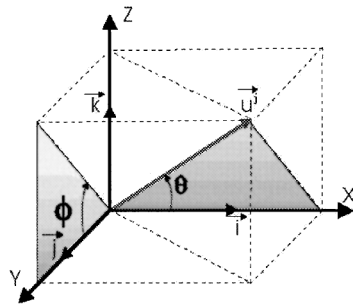


Figure 1. Geometrical principles and general notation of the approach.

Accordingly, the spatial coordinates X , Y , and Z after n steps are given by:

$$\begin{cases} X_n = \sum_i^n (\ell_i \cos \theta_i) \\ Y_n = \sum_i^n (\ell_i \sin \theta_i \cos \phi_i) \\ Z_n = \sum_i^n (\ell_i \sin \theta_i \sin \phi_i) \end{cases}$$

The actual flow velocity (u) depends on the direction, in such a way that the flow velocity tends to zero when the direction is perpendicular to the mean flow direction, hence for $\theta \rightarrow \pi/2$. The total residence time is then given by:

$$T_n = \sum_i^n (\ell_i, u_i)$$

The assumption of straight capillary tubes was introduced in order to establish simplified mathematical relationships for macroscopic quantities, such as the advection rate as well as the longitudinal and transverse dispersion.

This theory has led to one of the first comprehensive demonstrations of the behavior of longitudinal and transverse dispersion as a function of time, distance, and average flow velocity. At present, it also seems an appropriate basis for comprehensive modeling of solute transfer and dispersion.

PRINCIPLES OF THE THREE-DIMENSIONAL MODEL

Mathematical Background

Transport of matter in a porous medium is a function of the flow velocity vector \vec{u}^j with pore velocity as the scalar value. Its random nature leads to an average flow velocity U but also to a noise that leads to spatial dispersion. Increasing the spatial scale increases the noise (for the number of movements is increased): hence dispersion is scale dependent as expected and desired.

Notations are introduced in an orthonormal coordination system (\vec{i} , \vec{j} , and \vec{k}) such that \vec{i} points to X , the direction of the average flow velocity. As shown schematically in Figure 1, vector \vec{u}^j can be expressed relative to the basis (\vec{i} , \vec{j} , \vec{k}) in terms of the angles θ and ϕ :

$$\begin{cases} \delta X^j = u^j dt \cos \theta \\ \delta Y^j = u^j dt \sin \theta \cos \phi \\ \delta Z^j = u^j dt \sin \theta \sin \phi \end{cases}$$

where u^j is the velocity of the particle j , dt is the time step and δX^j , δY^j , and δZ^j are the elementary displacements of the particle j during a time step in the X , Y , and Z directions, respectively. We assume a pure Markovian process, i.e., a stochastic process in which the prediction of the probability distribution of a random variable at time t depends only on that given distribution at the previous time. The Markovian process can be written for the particle j :

$$\begin{cases} X_n^j = \sum_{i=1}^n (u^j dt \cos \theta_i) \\ Y_n^j = \sum_{i=1}^n (u^j dt \sin \theta_i \cos \phi_i) \\ Z_n^j = \sum_{i=1}^n (u^j dt \sin \theta_i \sin \phi_i) \end{cases} \quad (4)$$

Stochastic Parameters

Deviation Parameters

Equation (4) is the schematization of the particle trajectory in porous media. A particle runs through a porous medium bypassing the grains. The orientation of the trajectories are random, according to the angles θ and ϕ , which are random variables. This is the principle of the stochastic models described by the de Jong (1958) and Saffman (1959), but these authors considered a random porous medium (with a random channels system); here we consider random trajectories of the solute. The stochastic behavior of angles θ and ϕ represents the spatial variance of the vector \vec{u}^j . We make the assumption (also made by de Jong, 1958, and Saffman, 1959) of random perpendicular directions uniformly distributed, then the azimuthal angle ϕ is distributed within $[0, \pi]$ according to a uniform probability density function (noted pdf):

$$\text{pdf}(\phi) = \frac{1}{\pi} \quad \text{for } 0 \leq \phi \leq \pi \quad (5)$$

The polar angle θ is the randomness of the static medium properties and the hydrodynamic. We make the assumption of a laminar flow between the grains of the medium, then the probability of a particle to have a straight trajectory (direction of the main flow) is large while the probability to have a trajectory perpendicular to the main flow is not realistic. These informations impose mathematical criteria on the pdf of θ : a symmetrical function with $P(0) = 1$ and $P(-\pi/2) = P(\pi/2) = 0$ (where $P(\theta)$ denotes the probability of θ). This physical argument of laminar flow

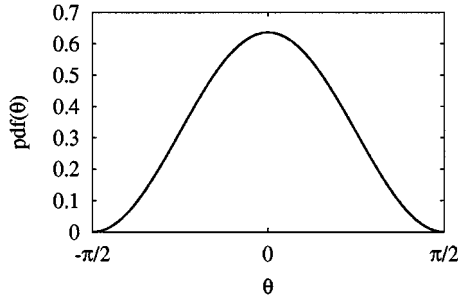


Figure 2. Probability density functions of θ .

leads to many possible functions that allow those mathematical properties, then we have to choose arbitrarily (because of lack of informations). Then we chose a square cosine function (Fig. 2) for its continuity and derivative properties:

$$\text{pdf}(\theta) = \frac{2}{\pi} \cos^2 \theta \quad \text{for } -\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2} \tag{6}$$

Diffusion Parameter

The diffusion is added on the convective transport using a Gaussian function. At each coordinate of the particle, a random variable is added where the probability density function is (Fig. 3):

$$\text{pdf}(\xi) = \frac{1}{\sigma_d \sqrt{2\pi}} \exp\left(-\frac{\xi^2}{2\sigma_d^2}\right) \quad \sigma_d = \sqrt{2D_m dt} \tag{7}$$

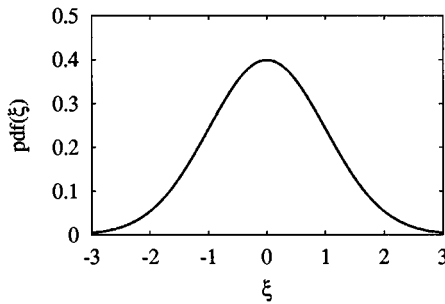


Figure 3. Probability density function of ξ .

where dt is the time step and D_m the molecular diffusion coefficient in porous media:

$$D_m = \tau d_0$$

where d_0 is molecular diffusion coefficient in free water and τ the tortuosity.

Convection Parameter

Even for a homogeneous porous medium, porosity is distributed according to some statistical distribution that leads to a random behaviour of velocities at pore scale. We make the assumption (as de Jong, 1958, made) that a particle j keeps a constant value of its velocity u^j at each time step; that means a particle runs through a capillary that has constant velocities in its cross section. Then particles velocities are initially (before transport simulation) randomized according to a pdf. A lognormal pdf was chosen, because of several criteria:

- if particles are trapped in dead-end pores or slow down in stagnant zones, velocities have to be very small or nil;
- if we make the assumption of a parabolic velocities profile between two grains of the medium, then particles could not have velocities faster than $3U/2$ or $2U$.

These two facts imply a nonsymmetrical function. A lognormal probability density function allows such properties (Fig. 4):

$$fdp(u^j) = \frac{1}{(u_{max} - u^j)\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln((u_{max} - u^j)/U))^2}{2\sigma^2}\right) \quad (8)$$

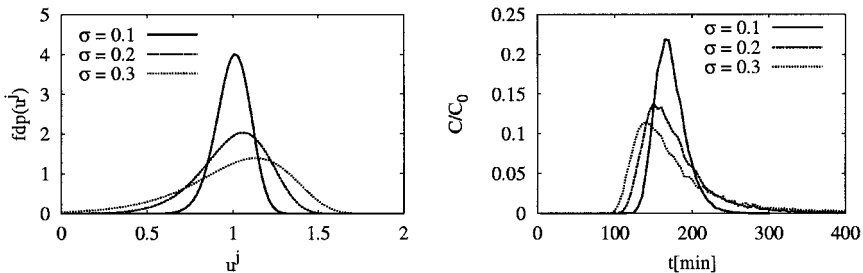


Figure 4. Probability density function of u^j vs. the parameters σ and the impacts on the breakthrough curves.

Table 1. Simulation Data

| | | |
|------------------|--------------------|-----|
| Column length | 10 | cm |
| Column diameter | 5 | cm |
| Average velocity | 1×10^{-5} | m/s |
| Injection time | 8 | min |
| Time step | 8 | min |

where u_{\max} is a parameter that controls the maximum velocity. U is the macroscopic average velocity and σ the standard deviation of the pdf. When σ is lower than 0.1, the probability density function of the velocities is approaches a Gaussian shape. To keep a constant velocity of the function (8), u_{\max} has to be related to U and σ by the following relation (see Appendix A):

$$u_{\max} = U(1 + e^{(\sigma^2/2)}) \tag{9}$$

The standard deviation σ controls the spatial distribution of the particle cloud. It is interesting to study the sensitivity of this parameter to understand its impact. According to Equation (8) and Figure 4, when σ is close to zero, the greatest velocity is close to the average velocity and the distribution is effectively Gaussian. Figure 4 also shows the impact of the parameter σ on the resulting breakthrough curves. The simulation data is given in Table 1. When σ increases, interval of velocities increases then dispersion increases (Fig. 5).

The complete Markovian process including advection-diffusion-dispersion is then

$$\left\{ \begin{aligned} X_n^j &= \sum_{i=1}^n (\xi_i^X + u^j dt \cos \theta_i) \\ Y_n^j &= \sum_{i=1}^n (\xi_i^Y + u^j dt \sin \theta_i \cos \phi_i) \\ Z_n^j &= \sum_{i=1}^n (\xi_i^Z + u^j dt \sin \theta_i \sin \phi_i) \end{aligned} \right. \tag{10}$$

Here we have the position of a particle j after n steps.

RULES OF THE RANDOM WALK PROCESS

The aim of this section is to find, from the equation of the random walk (10), some mathematical relations between the microscopic parameters of the random walk model presented here and the macroscopic parameters of the classical

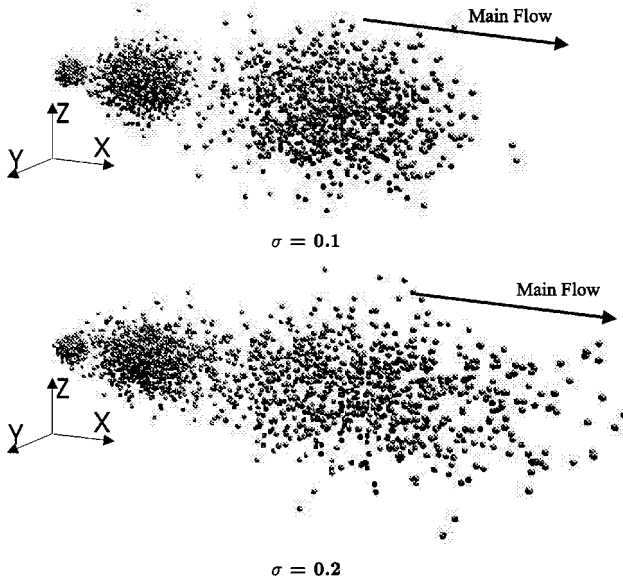


Figure 5. Tridimensional perspective view of the influence of σ on the structure cloud, at three different times.

transport model such as average velocity and dispersivity. First, statistical properties of the displacement of a single particle are studied.

Rules for a Particle

Here we consider a single particle j , so the velocity u^j is keeps as a constant value. According to the Lindeberg–Lévy theorem (Kaufmann, 1965), mean displacements of a single particle after n steps along the axes are given by

$$\langle \delta X_n^j \rangle = n \langle \delta X^j \rangle \quad \langle \delta Y_n^j \rangle = n \langle \delta Y^j \rangle \quad \langle \delta Z_n^j \rangle = n \langle \delta Z^j \rangle$$

and the variances of these displacements are

$$\sigma_{\delta X_n^j}^2 = n \sigma_{\delta X^j}^2 \quad \sigma_{\delta Y_n^j}^2 = n \sigma_{\delta Y^j}^2 \quad \sigma_{\delta Z_n^j}^2 = n \sigma_{\delta Z^j}^2$$

where $\langle \rangle$ denote an ensemble average and σ^2 the variance of the displacement.

After performed means and variances (see Appendix B), one obtains

$$\begin{aligned}\langle \delta X_n^j \rangle &= \frac{8u^j dt}{3\pi} \\ \langle \delta Y_n^j \rangle &= \langle \delta Z_n^j \rangle = 0 \\ \sigma_{\delta X_n^j}^2 &= 2Ddt + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) (u^j dt)^2 \\ \sigma_{\delta Y_n^j}^2 &= \sigma_{\delta Z_n^j}^2 = 2Ddt + \frac{(u^j dt)^2}{8}\end{aligned}$$

Then according to the Lindeberg–Lévy theorem, the pdf of the longitudinal and transverse displacements are, after many steps,

$$\begin{aligned}\text{fdp}(\delta X_n^j) &= \frac{1}{\sqrt{2n\pi \left(2Ddt + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) (u^j dt)^2 \right)}} \\ &\quad \times \exp \left(- \frac{\left(\delta X_n^j - \frac{8u^j dt}{3\pi} \right)^2}{2n \left(2Ddt + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) (u^j dt)^2 \right)} \right) \\ \text{fdp}(\delta Y_n^j) &= \frac{1}{\sqrt{2n\pi \left(2Ddt + \frac{(u^j dt)^2}{8} \right)}} \exp \left(- \frac{(\delta Y_n^j)^2}{2n \left(2Ddt + \frac{(u^j dt)^2}{8} \right)} \right) \\ \text{fdp}(\delta Z_n^j) &= \frac{1}{\sqrt{2n\pi \left(2Ddt + \frac{(u^j dt)^2}{8} \right)}} \exp \left(- \frac{(\delta Z_n^j)^2}{2n \left(2Ddt + \frac{(u^j dt)^2}{8} \right)} \right)\end{aligned}$$

Figure 6 illustrates that after $n > 10$ the Lindeberg–Lévy theorem is true and even more accurate when the diffusion coefficient increases.

Here we have demonstrated that for a quite large number of steps, the displacement of a single particle is a diffusive model.

Now, looking at a cloud of particles, one must consider the distribution of the velocity of all the particles.

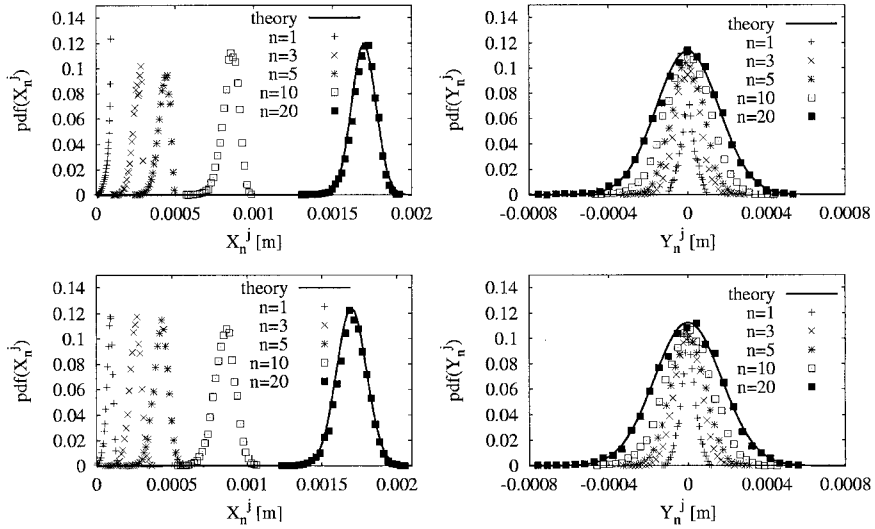


Figure 6. Evolution of δX_n^j and δY_n^j pdf vs. n . No diffusion (up) and $D_m = 1 \times 10^{-10} \text{ m}^2/\text{s}$ (down).

Rules for a Cloud of Particles

The particle cloud is a numerical analogy of a plume of solute. Now we want to calculate the two first moments of the cloud: the center of mass variance of the plume.

Calculation of the first moments is straightforward and the coordinates of the center of mass is

$$\begin{aligned} \langle X_n^j \rangle &= \frac{8n \langle u^j \rangle dt}{3\pi} \\ \langle Y_n^j \rangle &= 0 \\ \langle Z_n^j \rangle &= 0 \end{aligned}$$

The variances of the particles cloud in the X direction and Y, Z directions are (see Appendix C):

$$\begin{aligned} \sigma_{X_n^j}^2 &= 2nDdt + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) \langle (u^j)^2 \rangle n dt^2 + \frac{64}{9\pi^2} (\sigma_{u^j}^2) n^2 dt^2 \\ \sigma_{Y_n^j}^2 &= \sigma_{Z_n^j}^2 = 2nDdt + \frac{\langle (u^j)^2 \rangle n dt^2}{8} \end{aligned}$$

$(\langle X_n^j \rangle, \langle Y_n^j \rangle, \langle Z_n^j \rangle)$ is the center of mass of the particle cloud and $\sigma_{X_n^j}^2, \sigma_{Y_n^j}^2, \sigma_{Z_n^j}^2$ are the variances of the cloud, i.e., the spread of the cloud relative to its center of mass. To calculate $\langle u^j \rangle$, $\langle (u^j)^2 \rangle$, and $\sigma^2 u^j$ we use Equation (8). By definition, the probability density function of u^j is a Gaussian function with the following variable changing:

$$Y = \frac{\ln(u_{\max} - u^j) - \ln(U)}{\sigma} \quad (11)$$

where Y is a random variable from a normal law with 0 mean and 1 standard deviation. If u_{\max} is replaced by its value [Eq. (25)],

$$u^j = U(1 + e^{\sigma^2/2} - e^{\sigma Y})$$

then:

$$\langle (u^j)^2 \rangle = U^2 \langle (1 + e^{\sigma^2/2} - e^{\sigma Y})^2 \rangle$$

with:

$$\langle e^{(\sigma Y)} \rangle = e^{(\sigma^2/2)}$$

$$\langle e^{(2\sigma Y)} \rangle = e^{(2\sigma^2)}$$

$$\langle (u^j)^2 \rangle = U^2(1 - e^{\sigma^2} + e^{2\sigma^2})$$

The final expression is

$$\begin{aligned} \sigma_{u^j}^2 &= \langle (u^j)^2 \rangle - \langle u^j \rangle^2 \\ &= U^2(e^{2\sigma^2} - e^{\sigma^2}) \end{aligned}$$

The mean positions and the variances of the cloud are then ($t = ndt$)

$$\langle X_n^j \rangle = \frac{8}{3\pi} U t \quad (12)$$

$$\langle Y_n^j \rangle = 0 \quad (13)$$

$$\langle Z_n^j \rangle = 0 \quad (14)$$

$$\sigma_{X_n^j}^2 = 2D_m t + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) (1 - e^{\sigma^2} + e^{2\sigma^2}) U^2 t dt + \frac{64}{9\pi^2} (e^{2\sigma^2} - e^{\sigma^2}) U^2 t^2 \quad (15)$$

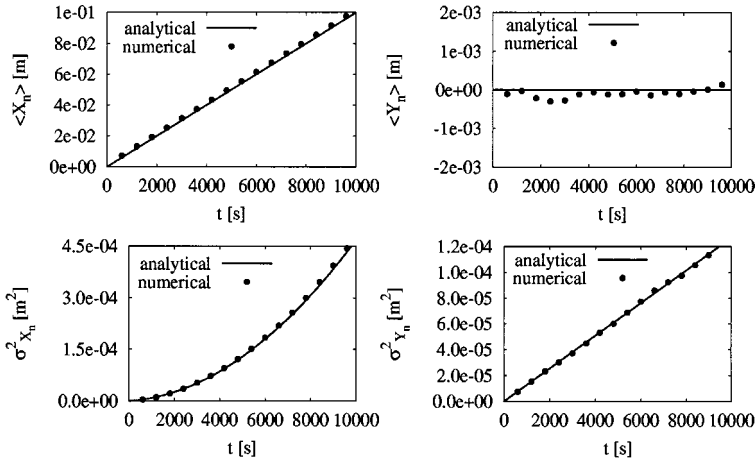


Figure 7. Evolution of the centers of mass and the variances of the particles cloud vs. time.

$$\sigma_{Y_n}^2 = 2D_m t + \frac{(1 - e^{\sigma^2} + e^{2\sigma^2})U^2 t dt}{8} \tag{16}$$

$$\sigma_{Z_n}^2 = 2D_m t + \frac{(1 - e^{\sigma^2} + e^{2\sigma^2})U^2 t dt}{8} \tag{17}$$

Figure 7 shows the evolution of coordinates of the center of mass and of the variances of the plume. A numerical simulation was carried out with parameters presented in Table 1, theoretical curves are the plotted Equations (17), and numerical results are those given by the random walk model after a statistical analysis of the particle coordinates. The displacement of the center of mass of the cloud increases linearly with time, which is confirmed by experimental results of a nonreactive solute (Freyberg, 1986; Brusseau, 1998). Comments on the variances will be given in the next section, which is concerned with the dispersion.

Dispersion Coefficients

The dispersion mechanisms differ from one scale to another. At the molecular scale, diffusion causes mixing. At microscopic scale, mixing is caused by the velocity distribution resulting from porous medium characteristics, such as porosity, tortuosity and dead-end pores. At a macroscopic scale, mixing is caused by the velocity distribution resulting from the variability of hydraulic conductivity. A distinction is generally made between Fickian and non-Fickian dispersion (Sahimi, 1993). If the transport is called Fickian, the longitudinal variance of the cloud

grows linearly with time. For non-Fickian transport, the longitudinal variance of the cloud does not grow linearly with time and is related to the heterogeneous porous media (Matheron and de Marsily, 1980; Dieulin, 1980; Simmons, 1982; Neuman and Zhang, 1990; Cvetkovic, Cheng, and Wen, 1996; Fiori, 1998). Non-Fickian transport can be classified as subdiffusive transport (fractal dispersion) and superdiffusive transport (the case of hydrodynamic dispersion in multilayered media without transverse dispersion). In mathematical terms,

$$\begin{aligned} \sigma^2 &\propto t^\alpha \\ D &\propto t^{\alpha-1} \end{aligned}$$

where σ^2 is the longitudinal variance of the cloud, D is the longitudinal dispersion coefficient, t is the time, and α the value describing the transport regime. If $\alpha = 1$, dispersion is Fickian. If $\alpha < 1$, dispersion is subdiffusive, and if $\alpha > 1$, dispersion is superdiffusive.

The dispersion coefficient has a scale dependent value. The well-known relation between the dispersion coefficient and the variance is the Einstein equation (Dagan, 1986; Gelhar, 1986; Freyberg, 1986):

$$D_i = \frac{1}{2} \frac{d\sigma_i^2}{dt} \tag{18}$$

Using the relation, one can calculate the dispersion coefficients of the random walk model by taking the derivative of the Equations (17):

$$D_x = D_m + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) (1 - e^{\sigma^2} + e^{2\sigma^2}) \frac{U^2 dt}{2} + \frac{64}{9\pi^2} (e^{2\sigma^2} - e^{\sigma^2}) \frac{U^2 t}{2} \tag{19}$$

$$D_y = D_m + \frac{(1 - e^{\sigma^2} + e^{2\sigma^2})U^2 dt}{16} \tag{20}$$

$$D_z = D_m + \frac{(1 - e^{\sigma^2} + e^{2\sigma^2})U^2 dt}{16} \tag{21}$$

Figure 8 shows the evolution of the dispersion coefficients vs. time. Longitudinal dispersion coefficient is superdiffusive ($\alpha > 1$) and transverse dispersion coefficients are diffusive ($\alpha = 1$).

Here we demonstrated that the distribution of the particle velocities introduces non-Fickian behavior. This was the initial aim of the approach: the dispersion has to grow with time.

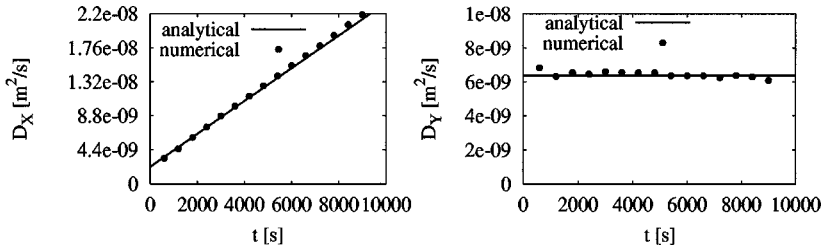


Figure 8. Evolution of the dispersion coefficients vs. time.

MODEL NUMERICAL VALIDATION TEST

In order to validate the mathematical basis of the model, it is useful to compare the numerical calculations with an analytical solution. Because we have no reliable solutions for non-Fickian dispersion, tests have been limited to Fickian transport, i.e. classical one-dimensional (1D) advection-dispersion. The model is tested for a pulse injection with variations in the molecular diffusion coefficient, average velocity, and spatial scale. The transport model is forced to be 1D, i.e., the column length is very long compared to the diameter. In a semiinfinite medium subjected to a uniform flow, the analytical solution of a variable time injection is (Bear, 1972; de Marsily, 1986)

$$\begin{aligned}
 C(X, t) = & \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{X - Ut}{2\sqrt{D_X t}} \right) + \exp \left(\frac{UX}{D_X} \right) \operatorname{erfc} \left(\frac{X + Ut}{2\sqrt{D_X t}} \right) \right] \\
 & - \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{X - U(t - t_0)}{2\sqrt{D_X(t - t_0)}} \right) \right. \\
 & \left. + \exp \left(\frac{UX}{D_X} \right) \operatorname{erfc} \left(\frac{X + U(t - t_0)}{2\sqrt{D_X(t - t_0)}} \right) \right] \quad (22)
 \end{aligned}$$

where C_0 is the initial injected concentration (M/L^3), U is the average velocity (L/T), X is the observation point (L), D_X is the longitudinal dispersion coefficient (L^2/T^2), t is the time (T), and t_0 is the injection time (T); erfc denotes the complementary error function.

Variations in Diffusion Coefficient

Three simulations were carried out with three different values of the diffusion coefficient. For these three simulations, the average velocity is constant ($U = 1 \times 10^{-5}$ m/s) and the dispersion parameter of the random walk model

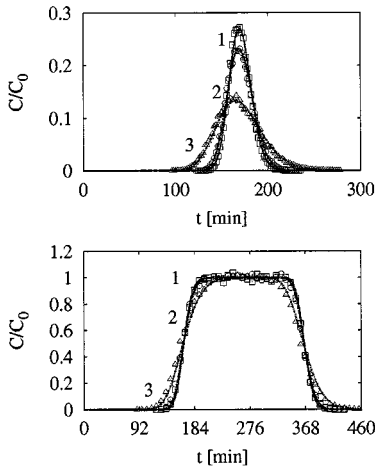


Figure 9. Comparison between simulated curves by the random walk model and analytical solution [Eq. (22)] for different values of the molecular diffusion coefficient. Column length is 10 cm and average velocity is 1×10^{-5} m/s. The dispersivity of the analytical solution is fit to 1.5×10^{-4} m and the random walk model parameter is $\sigma = 0.05$. Diffusion coefficients are 9.3×10^{-10} m²/s (1), 1.86×10^{-9} m²/s (2), and 9.3×10^{-9} m²/s (3).

(σ) is equal to 0.05. The control location (X) is at 10 cm from the injection point. Injection times (t_0) are 8 and 200 min. The dispersivity of the analytical solution is fit ($\alpha_X = 1.5 \times 10^{-4}$ m) and satisfies Equation (2). According to Equation (2), when the diffusion coefficient increases, for a given velocity and dispersivity, transport becomes diffusive. At first, the diffusion coefficient has a value of 9.3×10^{-10} m²/s, which could correspond to the value of tritium diffusion coefficient in a porous medium with a tortuosity of 0.1. Figure 9 confirms that the random walk transport model compares well with the advection-dispersion equation. Equation (19) shows that for small values of the parameters σ , the dispersion coefficient becomes independent of time, which is the case of Fickian transport. With these small values of σ , one can compare the dispersion coefficients according to the random walk model [Eq. (19)] and the analytical solution [Eqs. (22) and (2)], these values are equals.

Variations in Average Velocity

Simulations were carried out with three values of average velocity. The system parameters are the same as those described in the previous section. The diffusion coefficient is constant and equal to 9.3×10^{-10} m²/s. Simulations shown in Figure 10 also confirm the mathematical basis of the random walk model for a weak dispersive porous medium. The fitting value of the dispersivity is the same that in the previous section ($\alpha_X = 1.5 \times 10^{-4}$ m). These two tests are a validation of the numerical model to simulate a Fickian dispersive transport as the classical advection-dispersion equation.

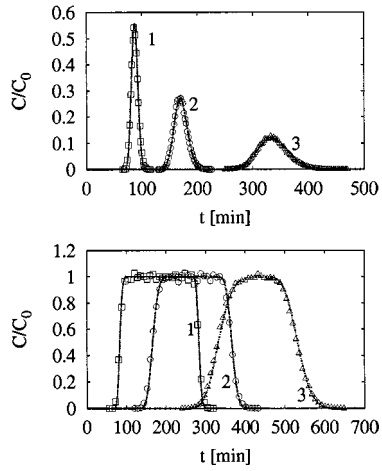


Figure 10. Comparison between simulated curves by the random walk model and analytical solution [Eq. (22)] for different values of the average velocity. Column length is 10 cm and diffusion coefficient is 9.3×10^{-10} m²/s. The dispersivity of the analytical solution is fit to 1.5×10^{-4} m and the random walk model parameter is $\sigma = 0.05$. Average velocities are 2×10^{-5} m/s (1), 1×10^{-5} m/s (2), and 5×10^{-6} m/s (3).

Scale Variations

One simulation was carried out at constant velocity ($U = 1 \times 10^{-5}$ m/s) and at constant value of the dispersion parameter of the random walk model ($\sigma = 0.05$). (Fig. 11). Control planes were set at $X = 5, 10, 15,$ and 20 cm. This test is of significance to the random walk model behavior: even though σ is constant, the values of the dispersivity have to be increased with the distance from the injected point to fit the model (Table 2). The intrinsic dispersion of the random walk model allows to have a nonscale-dependent nature of the parameter σ .

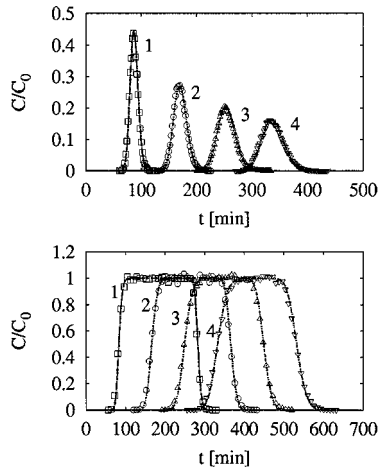


Figure 11. Comparison between simulated curves by the random walk model and analytical solution [Eq. (22)] for different transport scale. Results are summed up in the Table 2. Distance locations are 5 cm (1), 10 cm (2), 15 cm (3), and 20 cm (4).

Table 2. Comparison Between Values of Analytical Dispersivities and the Dispersion Parameters Values of the model^a

| X (m) | σ_X (m) | σ |
|---------|----------------------|----------|
| 0.05 | 1.5×10^{-5} | 0.05 |
| 0.10 | 4.5×10^{-5} | 0.05 |
| 0.15 | 5.5×10^{-5} | 0.05 |
| 0.20 | 6.5×10^{-5} | 0.05 |

^aAverage velocity is 1×10^{-3} m/s and diffusion coefficient is 9.3×10^{-10} m²/s.

CONCLUSIONS

The random walk model presented is based on a mechanistic description of the solute dispersion in porous medium. First, we exposed the mathematical background of the random walk model with the three transport functions: advection, diffusion, and dispersion. Trajectories of solute particles are described in three dimensions by a random walk equation. The random pathways of a particle is determined by two random angles whose probability density functions follow from some assumptions we made. Heterogeneity of the porous medium is described by a law of the velocities; randomness of the particles velocity is actually a representation of the heterogeneities distribution (porosity or permeability). These heterogeneities are described by a parameter (σ) that is the variance of the microscopic velocities around the average velocity.

In a second example, we performed calculations to determine the relationship between the random walk microscopic parameters and the commonly used macroscopic parameters such as average velocity and dispersivity. For small values of the dispersion parameter of the random walk model, i.e., when the model is forced to be Fickian, one can compare the dispersion coefficient of an analytical solution of the advection-dispersion equation and those of the random walk model, calculated in this paper. The dispersion coefficients are equal, which is a kind of validation of the random walk model in a particular case of Fickian transport.

Then simulations were carried out to validate the random walk model with a 1D analytical solution in case of Fickian transport and for a small dispersive medium. It is important to note that breakthrough curves are obtained without any numerical method that could introduce numerical dispersion. Indeed, particles are just counted when they go through a virtual plane that corresponds to the distance location of the concentration control. The analytical solution and breakthrough curves of the random walk model were in good agreement for the three kinds of test made: variation of the diffusion coefficient, variation of the average velocity, and variation of transport scale. This last test is significant of the random walk

model behavior and shows that when advection and dispersion are dependent, dispersion of a solute increases with distance from its injection point. This allows the use of scale-constant dispersion parameters.

This model is an interesting tool to study more complex systems such as, e.g., transport of colloidal suspensions including the volume and charge exclusions effects and the porosity occlusion by particles filtration.

Actually, colloidal transport lends itself to this kind of model because it is very easy to distinguish precisely the dispersive behavior of the colloids on one hand, and on the other, the dispersive behavior of the solute.

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REFERENCES

- Ackerer, P., and Kinzelbach, W., 1985, Modélisation du transport de contaminant par la méthode de marche au hasard: Influence des variations du champ d'écoulement au cours du temps sur la dispersion, *in* de G. Marsily, ed., *The stochastic approach to subsurface flow*: Montvillargenne, p. 517–529.
- Banton, O., Delay, F., and Porel, G., 1997, A new time domain random walk method for solute transport 1-D heterogeneous media: *Groundwater*, v. 35, no. 6, p. 1008–1013.
- Bear, J., 1972, *Dynamics of fluids in porous media*: Elsevier, New York, 640 p.
- Brusseau, M., 1998, Non-ideal transport of reactive solutes in heterogeneous porous media: Model testing and data analysis using calibration versus prediction: *Jour. Hydrology*, v. 209, p. 147–165.
- Carrera, J., 1993, An overview of uncertainties in modelling groundwater solute transport: *Jour. Contam. Hydrology*, v. 13, p. 23–48.
- Cvetkovic, V., Cheng, H., and Wen, X., 1996, Analysis of non-linear effect on tracer migration in heterogeneous aquifers using lagrangian travel time statistics: *Water Resources Res.*, v. 32, no. 6, p. 1671–1680.
- Dagan, G., 1986, Statistical theory of groundwater flow and transport: Pore to laboratory, laboratory to formation, and formation to regional scale: *Water Resources Res.*, v. 22, no. 9, p. 120S–134S.
- Dagan, G., 1990, Transport in heterogeneous porous formation: spatial moments, ergodicity and effective dispersion: *Water Resources Res.*, v. 26, no. 6, p. 1281–1290.
- de Jong, G. J., 1958, Longitudinal and transverse diffusion in granular deposits: *Transactions, American Geophysical Union*, v. 39, no. 1, p. 64–74.
- de Marsily, G., 1986, *Quantitative hydrology*: Academic Press, London, 250 p.
- Delay, F., Housset-Resche, H., Porel, G., and de Marsily, G., 1996, Transport in 2-D saturated porous medium: A new method for particle tracking: *Math. Geology*, v. 28, no. 1, p. 45–71.
- Dieulin, A., 1980, Propagation de pollution dans un aquifère alluvial, l'effet de parcours: Unpubl. doctoral dissertation, École des Mines de Paris, 180 p.

- Fiori, A., 1998, On the influence of pore-scale dispersion in non-ergodic transport in heterogeneous formations: *Transp. Porous Media*, v. 30, p. 57–73.
- Freyberg, D. L., 1986, A natural gradient experiment on solute transport in a sand aquifer: Spatial moments and the advection and dispersion of non-reactive tracers: *Water Resources Res.*, v. 22, no. 13, p. 2031–2046.
- Gelhar, L., 1986, Stochastic subsurface hydrology from theory to application: *Water Resources Res.*, v. 22, no. 9, p. 135S–145S.
- Gelhar, L., 1993, *Stochastic subsurface hydrology*: Prentice-Hall, New York, 270 p.
- Kauffman, A., 1965, *Cours moderne de calcul des probabilités*: Albin Michel, Paris, 350 p.
- Matheron, G., and de Marsily, G., 1980, Is transport always diffusive? A counterexample: *Water Resources Res.* v. 16, no. 5, p. 901–917.
- Newman, S., and Zhang, Y., 1990, A quasi linear theory of non-Fickian and Fickian subsurface dispersion: Theoretical analysis with application to isotopic media: *Water Resources Res.*, v. 26, no. 5, p. 887–902.
- Saffman, P., 1959, A theory of dispersion in porous medium: *Jour. Fluid Mech.*, v. 6, no. 21, p. 321–349.
- Sahimi, M., 1993, Fractal and superdiffusive transport and hydrodynamic dispersion in heterogeneous porous media: *Transp. Porous Media*, v. 13, no. 1, p. 3–40.
- Scheidegger, A., 1953, Statistical hydrodynamics in porous media: *Jour. Appl. Phys.*, v. 25, no. 8, p. 994–1001.
- Simmons, C., 1982, A stochastic-convective transport representation of dispersion in one-dimensionnal porous media system: *Water Ressources Res.*, v. 18, no. 4, p. 1193–1214.
- Uffink, G., 1988, Modelling of solute transport with the random-walk method: *in* E. Custodio, ed., *Groundwater flow and quality modelling*: The Netherlands, p. 247–265.
- Wen, X., and Kung, C., 1995, A Q-BASIC program for modelling advective mass transport with retardation and radioactive decay by particle tracking: *Computer Geosciences*, v. 13, p. 250–265.

APPENDIX A

The probability density function of u^j is a Gaussian with the following variable change:

$$Y = \frac{\ln(u_{\max} - u^j) - \ln(U)}{\sigma}$$

Then the relationship between u^j and Y is

$$u^j = u_{\max} - Ue^{(\sigma Y)} \quad (23)$$

By taking the average,

$$\langle u^j \rangle = u_{\max} - Ue^{(\sigma Y)} \quad (24)$$

with the following result,

$$\langle e^{(\sigma Y)} \rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{(\sigma x)} e^{(-x^2/2)} dx = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{(-x^2/2 + \sigma x)} dx = e^{(\sigma^2/2)}$$

Equation (24) is then

$$\langle u^j \rangle = u_{\max} - U e^{(\sigma^2/2)}$$

We assume the following relationship: $\langle u^j \rangle = U$, then,

$$u_{\max} = U(1 + e^{(\sigma^2/2)}) \tag{25}$$

APPENDIX B

Mean Position of the Longitudinal Component

The mean position of the longitudinal displacement is

$$\langle \delta X^j \rangle = \langle \xi_i^X \rangle + u^j dt \langle \cos \theta_i \rangle$$

According to Equations (7) for the diffusion distribution and Equation (6) for the pdf of θ ,

$$\begin{aligned} \langle \xi_i^X \rangle &= 0 \quad \text{by definition} \\ \langle \cos \theta_i \rangle &= \frac{2}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^3(x) dx = \frac{8}{3\pi} \end{aligned}$$

then:

$$\langle \delta X^j \rangle = \frac{8u^j dt}{3\pi}$$

Mean Position of the Transverse Component

The mean position of the transverse displacement is:

$$\langle \delta Y^j \rangle = \langle \xi_i^Y \rangle + \langle u^j dt \sin \theta_i \cos \phi_i \rangle$$

According to Equation (7) for the diffusion distribution, Equation (6) for the pdf of θ and Equation (5) for the pdf of ϕ :

$$\begin{aligned} \langle \xi_i^Y \rangle &= 0 \quad \text{by definition} \\ \langle \sin \theta_i \cos \phi_i \rangle &= \langle \sin \theta_i \rangle \langle \cos \phi_i \rangle \quad \text{because } \theta \text{ and } \phi \text{ are independent} \\ &= \left(\frac{2}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin(x) \cos^2(x) dx \right) \left(\frac{1}{\pi} \int_0^\pi \cos(x) dx \right) = 0 \end{aligned}$$

An identical mathematical approach can be used for $\langle \delta Z^j \rangle$ —hence, the mean position of the transverse displacements are

$$\begin{aligned} \langle \delta Y^j \rangle &= 0 \\ \langle \delta Z^j \rangle &= 0 \end{aligned}$$

Mean Variance of the Longitudinal Displacement

The mean variance of the longitudinal displacement is defined by

$$\begin{aligned} \sigma_{\delta X^j}^2 &= \langle (\delta X^j - \langle \delta X^j \rangle)^2 \rangle \\ &= \langle (\delta X^j)^2 \rangle - \langle \delta X^j \rangle^2 \end{aligned}$$

$$\begin{aligned} \langle (\delta X^j)^2 \rangle &= \langle (\xi_i^X + u^j dt \cos \theta_i)^2 \rangle \\ &= \langle (\xi_i^X)^2 \rangle + (u^j dt)^2 \langle (\cos \theta_i)^2 \rangle + 2u^j dt \underbrace{\langle \xi_i^X \rangle}_{=0} \langle \cos \theta_i \rangle \end{aligned}$$

$$\langle (\xi_i^X)^2 \rangle = 2D_m dt \quad \text{by definition}$$

$$\langle \cos^2 \theta_i \rangle = \frac{2}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^4(x) dx = \frac{3}{4}$$

then

$$\sigma_{\delta X^j}^2 = 2D_m dt + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) (u^j dt)^2$$

Mean Variances of the Transverses Displacement

$$\begin{aligned} \sigma_{\delta Y^j}^2 &= \langle (\delta Y^j - \langle \delta Y^j \rangle)^2 \rangle \\ &= \langle (\delta Y^j)^2 \rangle \quad \text{because } \langle \delta Y^j \rangle = 0 \end{aligned}$$

$$\begin{aligned} \langle (\delta Y^j)^2 \rangle &= \langle (\xi_i^Y + u^j dt \sin \theta_i \cos \phi_i)^2 \rangle \\ &= \langle (\xi_i^Y)^2 \rangle + (u^j dt)^2 \langle (\sin \theta_i \cos \phi_i)^2 \rangle + 2u^j dt \underbrace{\langle \xi_i^Y \rangle}_{=0} \langle \sin \theta_i \cos \phi_i \rangle \\ \langle (\xi_i^Y)^2 \rangle &= 2D_m dt \quad \text{by definition} \end{aligned}$$

$$\langle \sin^2 \theta_i \cos^2 \phi_i \rangle = \left(\frac{2}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin^2(x) \cos^2(x) dx \right) \left(\frac{1}{\pi} \int_0^\pi \cos^2(x) dx \right) = \frac{1}{8}$$

thus,

$$\sigma_{\delta Y^j}^2 = 2D_m dt + \frac{(u^j dt)^2}{8}$$

and similarly,

$$\sigma_{\delta Z^j}^2 = 2D_m dt + \frac{(u^j dt)^2}{8}$$

APPENDIX C

Variance in the X direction of a particle j around the center of mass is expressed by

$$\begin{aligned} \sigma_{X_n^j}^2 &= \langle (X_n^j - \langle X_n^j \rangle)^2 \rangle \\ &= \langle (X_n^j)^2 \rangle - \langle X_n^j \rangle^2 \\ \langle (X_n^j)^2 \rangle &= \left\langle \left(\sum_{i=1}^n (\xi_i^X + u^j dt \cos \theta_i) \right)^2 \right\rangle \end{aligned}$$

$$\begin{aligned}
 &= \left\langle \left(\left(\sum_{i=1}^n \xi_i^X \right) + u^j dt \left(\sum_{i=1}^n \cos \theta_i \right) \right)^2 \right\rangle \\
 &= \left\langle \left(\sum_{i=1}^n \xi_i^X \right)^2 + (u^j dt)^2 \left(\sum_{i=1}^n \cos \theta_i \right)^2 \right. \\
 &\quad \left. + 2u^j dt \left(\sum_{i=1}^n \xi_i^X \right) \left(\sum_{i=1}^n \cos \theta_i \right) \right\rangle \\
 &= \left\langle \left(\sum_{i=1}^n \xi_i^X \right)^2 \right\rangle + \langle (u^j)^2 \rangle dt^2 \left\langle \left(\sum_{i=1}^n \cos \theta_i \right)^2 \right\rangle \\
 &\quad + 2 \underbrace{\langle u^j \rangle dt}_{=0} \left(\sum_{i=1}^n \langle \xi_i^X \rangle \right) \left(\sum_{i=1}^n \langle \cos \theta_i \rangle \right)
 \end{aligned}$$

$$\begin{aligned}
 \left\langle \left(\sum_{i=1}^n \xi_i^X \right)^2 \right\rangle &= \left\langle \sum_{i=1}^n \left((\xi_i^X)^2 + 2 \sum_{j<i}^n \xi_i^X \xi_j^X \right) \right\rangle \\
 &= \sum_{i=1}^n \left(\underbrace{\langle (\xi_i^X)^2 \rangle}_{=2D_m dt} + 2 \sum_{j<i}^n \underbrace{\langle \xi_i^X \xi_j^X \rangle}_{=0} \right) \\
 &= 2nD_m dt
 \end{aligned}$$

$$\begin{aligned}
 \left\langle \left(\sum_{i=1}^n \cos \theta_i \right)^2 \right\rangle &= \left\langle \sum_{i=1}^n \left(\cos^2 \theta_i + 2 \sum_{j<i}^n \cos \theta_i \cos \theta_j \right) \right\rangle \\
 &= \sum_{i=1}^n \left(\langle \cos^2 \theta_i \rangle + 2 \sum_{j<i}^n \underbrace{\langle \cos \theta_i \rangle \langle \cos \theta_j \rangle}_{8/3\pi} \right)
 \end{aligned}$$

$$\langle \cos^2 \theta_i \rangle = \frac{2}{\pi} \int_{-\pi/2}^{\pi/2} \cos^4(x) dx = \frac{3}{4}$$

$$\left\langle \left(\sum_{i=1}^n \cos \theta_i \right)^2 \right\rangle = \sum_{i=1}^n \left(\frac{3}{4} + 2 \frac{64}{9\pi^2} \sum_{j<i}^n 1 \right) = \frac{3n}{4} + \frac{64}{9\pi^2} n(n-1)$$

indeed

$$\sum_{i=1}^n \left(\sum_{j<i}^n 1 \right) = \sum_{i=1}^n \sum_{j=i+1}^n 1 = \sum_{i=1}^n (n-i) = \frac{n(n-1)}{2}$$

thus,

$$\sigma_{X_n^j}^2 = 2nD_m dt + \left(\frac{3}{4} - \frac{64}{9\pi^2} \right) \langle (u^j)^2 \rangle n dt^2 + \frac{64}{9\pi^2} (\sigma_{u^j}^2) n^2 dt^2$$

The variance in the Y direction or in the Z direction of a particle j around the center of mass is expressed by

$$\begin{aligned} \sigma_{Y_n^j}^2 &= \langle (Y_n^j - \langle Y_n^j \rangle)^2 \rangle \\ &= \langle (Y_n^j)^2 \rangle \quad \text{because } \langle Y_n^j \rangle = 0 \end{aligned}$$

$$\begin{aligned} \langle (Y_n^j)^2 \rangle &= \left\langle \left(\sum_{i=1}^n (\xi_i^X + u^j dt \sin \theta_i \cos \phi_i) \right)^2 \right\rangle \\ &= \left\langle \left(\left(\sum_{i=1}^n \xi_i^Y \right) + (u^j dt) \left(\sum_{i=1}^n \sin \theta_i \cos \phi_i \right) \right)^2 \right\rangle \\ &= \left\langle \left(\sum_{i=1}^n \xi_i^Y \right)^2 + (u^j dt)^2 \left(\sum_{i=1}^n \sin \theta_i \cos \phi_i \right)^2 \right. \\ &\quad \left. + 2u^j dt \left(\sum_{i=1}^n \xi_i^Y \right) \left(\sum_{i=1}^n \sin \theta_i \cos \phi_i \right) \right\rangle \\ &= \left\langle \left(\sum_{i=1}^n \xi_i^Y \right)^2 \right\rangle + (u^j)^2 dt^2 \left\langle \left(\sum_{i=1}^n \sin \theta_i \cos \phi_i \right)^2 \right\rangle \\ &\quad + 2 \underbrace{\langle u^j \rangle}_{=0} dt \left(\sum_{i=1}^n \langle \xi_i^Y \rangle \right) \left(\sum_{i=1}^n \langle \sin \theta_i \cos \phi_i \rangle \right) \end{aligned}$$

$$\begin{aligned}
 \left\langle \left(\sum_{i=1}^n \xi_i^Y \right)^2 \right\rangle &= \left\langle \sum_{i=1}^n \left((\xi_i^Y)^2 + 2 \sum_{j<i}^n \xi_i^Y \xi_j^Y \right) \right\rangle \\
 &= \sum_{i=1}^n \left(\underbrace{\langle (\xi_i^Y)^2 \rangle}_{=2D_m dt} + 2 \sum_{j<i}^n \underbrace{\langle \xi_i^Y \xi_j^Y \rangle}_{=0} \right) \\
 &= 2nD_m dt
 \end{aligned}$$

$$\begin{aligned}
 &\left\langle \left(\sum_{i=1}^n \sin \theta_i \cos \phi_i \right)^2 \right\rangle \\
 &= \left\langle \sum_{i=1}^n \left(\sin^2 \theta_i \cos^2 \phi_i + 2 \sum_{j<i}^n \sin \theta_i \cos \phi_i \sin \theta_j \cos \phi_j \right) \right\rangle \\
 &= \sum_{i=1}^n \left(\langle \sin^2 \theta_i \cos^2 \phi_i \rangle + 2 \sum_{j<i}^n \underbrace{\langle \sin \theta_i \cos \phi_i \rangle}_{=0} \langle \sin \theta_j \cos \phi_j \rangle \right)
 \end{aligned}$$

$$\langle \sin^2 \theta_i \cos^2 \phi_i \rangle = \frac{2}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin^2(x) \cos^2(x) dx \frac{1}{\pi} \int_0^\pi \cos^2(x) dx = \frac{1}{8}$$

$$\left\langle \left(\sum_{i=1}^n \sin \theta_i \cos \phi_i \right)^2 \right\rangle = \frac{n}{8}$$

so,

$$\sigma_{Y_i}^2 = 2nD_m dt + \frac{\langle (u^j)^2 \rangle n dt^2}{8}$$