Macroscopic behavior and random-walk particle tracking of kinetically sorbing solutes

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Abstract. Analytical expressions are derived for the zeroth, first, and second spatial moments of sorbing solutes that follow a linear reversible kinetic mass transfer model. We determine phase-transition probabilities and closed-form expressions for the spatial moments of a plume in both the sorbed and aqueous phases resulting from an arbitrary initial distribution of solute between the phases. This allows for the evaluation of the effective velocity and dispersion coefficient for a homogeneous domain without resorting to numerical modeling. The equations for the spatial moments and the phase-transition probabilities are used for the development of a new random-walk particle-tracking method. The method is tested against three alternate formulations and is found to be computationally efficient without sacrificing accuracy. We apply the new random-walk method to investigate the possibility of a double peak in the aqueous solute concentration resulting from kinetic sorption. The occurrence of a double peak is found to be dependent on the value of the Damköhler number, and the timing of its appearance is controlled by the mass transfer rate and the retardation factor. Two ranges of the Damköhler number leading to double peaking are identified. In the first range ($Da_1 < 1$), double peaking occurs for all retardation factors, while in the second range ($1 < Da_1 < 3$), this behavior is most significant for $R > 12$.

1. Introduction

A thorough understanding of sorption processes is necessary for accurate groundwater transport predictions. Sorption in porous media is often described by assuming local equilibrium. The local-equilibrium assumption is not always valid, however, and sorption rates must be considered in some cases, especially where the adsorption and desorption reactions are slow relative to the seepage velocity [Brusseau and Rao, 1989]. Various multisite and multiprocess models have been proposed to describe kinetic sorption, reviewed by Haggerty and Gorelick [1995]. However, a simple linear reversible mass transfer model has been shown to be an accurate approximation to more complicated nonequilibrium models in many cases [Nkedi-Kizza et al., 1984; van Genuchten, 1985; Parker and Valocchi, 1986; Valocchi, 1990; Sardin et al., 1991].

One of the phenomena that may be attributable to kinetic sorption is the formation of a transient double peak in the aqueous concentration profile. Such behavior has been observed in some reactive solute experiments, such as the ones conducted at the Borden [Mackay et al., 1986; Roberts et al., 1986] and Cape Cod [Garabedian et al., 1988; LeBlanc et al., 1991] field sites, although kinetic sorption has not been considered as a possible causal mechanism for such observations. Quinodoz and Valocchi [1993] suggested that such double peaks appear only for very large retardation factors and discussed no rate limitations on such behavior. Their claim was based on the evolution of the first spatial moment of the solute in the aqueous phase, which indicates that the mean velocity temporarily drops below its asymptotic value for large retardation factors. However, this claim has not been verified numerically. Bellin et al. [1991] investigated the formation of double peaks in the breakthrough curves of column experiments involving solutes undergoing kinetic sorption. The concentration profile was measured as a function of time at the outflow of the column, and a necessary condition for double peaking was found to be

$$\frac{v}{D} \gg \frac{k}{\eta \nu},$$

where $D$ is the dispersion coefficient, $k$ is a mass transfer coefficient, $\eta$ is the mobile phase porosity, and $\nu$ is the seepage velocity. In other words, most of the desorption had to occur after the transport effects ceased to affect the breakthrough curve. Furthermore, double peaking occurred only when $(kL/\eta \nu)$ was "not too large," where $\eta$ is the total porosity and $L$ is the length of the column. Sample runs were performed only for a Peclet number $Pe = vL/D = 10$ and a retardation coefficient $R = 10$, and only point sources were examined.

1.1. Previous Particle-Tracking Methods

A simple and efficient numerical method is needed to investigate the behavior of kinetically sorbing solutes. The particle-tracking method [Ahlstrom and Foote, 1976; Prickett et al., 1981] is a Lagrangian approach in which a large number of particles is tracked in order to simulate conservative-tracer transport. In contrast to Eulerian simulation techniques, negative concentrations cannot occur, concentration profile artificial smoothing and oscillations are greatly reduced, and dispersive fluxes are approximated accurately, provided that the number of particles is high enough. The random-walk method is therefore particularly applicable to groundwater situations, where sharp concentration fronts are common and mixing rates are low relative to surface water and atmospheric applications.
The random-walk method has also been applied to sorption problems. Abulaban et al. [1998] used it to examine cases of linear and nonlinear sorption isotherms, applying an algorithm developed by Tompson [1993]. The experiments of Tompson [1993] focused on four hypothetical constituents, one being inert and the other three independently obeying linear, Freundlich, and Langmuir partitioning relationships. Both Abulaban et al. [1998] and Tompson [1993] used constituents that arise from reversible, equilibrium sorption reactions. Nonequilibrium sorption was not addressed.

Selroos and Cvetkovic [1992] proposed a method for coupling sorption kinetics and solute advection in particle-tracking models. However, their method is efficient only when sorption rate coefficients can be assumed uniform. The solution for an instantaneous injection was derived in the Laplace domain. In the case of uniform rate coefficients the inverse Laplace transformation yields an equation involving a modified first-order Bessel function of the first kind. The mass flux is dependent only on the sorption coefficients and on the intrinsic travel time. If the sorption coefficients are assumed uniform, the mass flux at a given location along a streamline can be readily obtained by evaluating the travel time of a particle from the origin to the given location.

Valocchi and Quinodoz [1989] compared three methods for dealing with kinetic sorption assuming a linear driving force. The arbitrary time step method (ATSM) uses a three-step process to determine the fraction of time that each particle spends in the aqueous phase during each time step. The continuous time history method (CTHM) simulates the history of phase changes for each particle during each time step. The small time step method (STSM) is an operator-splitting approach that was originally introduced by Kinzelbach [1987] and Kinzelbach and Uffink [1991]. The method is based on the premise that the probability of having more than one phase change in a small time step is negligible, and a particle can therefore be assumed to remain in its initial state for the entire time step. Valocchi and Quinodoz [1989] concluded that the ATSM is a more efficient and accurate method relative to the CTHM and STSM.

Andricevic and Foufoula-Georgiou [1990, 1991] developed a method similar to the ATSM [Valocchi and Quinodoz, 1989]. However, they proposed a different approximate approach for determining the fraction of time that each particle spends in the aqueous phase during each time step, based on the first two moments of the total time spent by each particle in the aqueous phase.

Delay et al. [1996] developed a method for kinetic sorption with a linear isotherm assuming that for a given time step, the advective-dispersive jump is instantaneous at the beginning of the time step. By analytically integrating the phase-transfer (or transition) equation, the number of particles in the mobile and immobile phases in a cell after a given time step are determined based on the number of particles in the mobile and immobile phases before that time step. This method is similar to that introduced by Kinzelbach [1987] and Kinzelbach and Uffink [1991].

Mishra et al. [1999] developed a recursion formulation for the transport of linearly sorbing solutes undergoing kinetic sorption. The method is based on a Markov process model of sorption-desorption. However, the method is based on discretizing time and space as \( \Delta x = v \Delta t \), where \( \Delta x \) is the grid size, \( \Delta t \) is the time step, and \( v \) is the seepage velocity, and either advecting a solute particle by \( \Delta x \) or by \( 0 \) in a given time step. Therefore the applicability of this method to heterogeneous media is limited. Furthermore, the method does not incorporate local-scale dispersion, which can be important in some applications.

1.2. Scope of Paper

In this work, we apply the method of moments [Aris, 1956] to the problem of kinetic sorption with a linear driving-force kinetics model. We derive analytical expressions for the zeroth, first, and second spatial moments of the sorbed and aqueous solute distributions for solute starting in either the aqueous or sorbed phase. The original method of moments was derived for conservative solutes [Aris, 1956]. Goltz [1986] and Goltz and Roberts [1987] derived the analytical solution for the zeroth and first spatial moments of a kinetically sorbing solute injected into the aqueous phase. The second moment was derived only for a solute starting and ending in the aqueous phase. Solutions for a solute starting in the sorbed phase were not presented.

On the basis of analytical moment expressions we derive analytical expressions for the first and second moments of the solute distribution resulting from an arbitrary initial distribution between the aqueous and sorbed phases. This allows for a general description of the solute distribution without resorting to numerical modeling, as would have been necessary in the past.

Furthermore, spatial moments can be used to define advective and dispersive steps for particle-tracking models [Kitanidis, 1994]. We therefore develop a highly efficient random-walk method based on the spatial moment expressions. This method is shown to be at least as accurate as, and more efficient than, any of the methods suggested by Valocchi and Quinodoz [1989].

Finally, we apply our new numerical method to the problem of double peaking in the aqueous concentration profile and show that double peaking caused by kinetic sorption is controlled by the relative magnitude of the reaction rate as compared to the advection rate for the case of a linear driving-force sorption model and that such double peaking can therefore occur for any retardation factor.

2. Mathematical Conceptualization of the Problem

2.1. General Development

The basic equations governing the transport of kinetically sorbing solutes are the advection-dispersion equation for the aqueous (or mobile) phase,

\[
\eta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = -\eta v \frac{\partial C}{\partial x} + \eta \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right),
\]

and a phase-transition (or mass transfer) equation, which is, for a linear driving force,

\[
\frac{\partial S}{\partial t} = k(K_a C - S),
\]

where \( C \) is the aqueous concentration \( [M/L^3_{\text{solution}}] \), \( \eta \) is the porosity, \( S \) is the contaminant mass sorbed per mass of aquifer solids \( [M/M] \), \( \rho \) is the bulk solids density (mass of aquifer solids per total volume) \( [M/L^3] \), \( v \) is the velocity \( [L/T] \), \( D \) is the dispersion coefficient \( [L^2/T] \), \( t \) is the time variable \( [T] \), \( x \) is the space variable \( [L] \), \( K_a \) is the distribution coefficient...
[\eta \frac{\partial C}{\partial t} + \rho \frac{\partial S}{\partial t} = -\eta v_i \frac{\partial C}{\partial x_i} + \eta D \frac{\partial^2 C}{\partial x_i^2}].\tag{4}

The dimensionless retardation coefficient is defined as

\[ R = 1 + \frac{\rho K_d}{\eta} .\tag{5}\]

We derive analytical solutions for the zeroth, first, and second spatial moments based on the advection-dispersion equation for the aqueous phase (equation (4)), and the phase-transition equation (equation (3)). All analytical expressions are derived for spatially uniform and temporally constant coefficients. Each type of moment is derived for four separate base cases: (1) aqueous distribution for solute originating in the aqueous phase; (2) aqueous distribution for solute originating in the sorbed phase; (3) sorbed distribution for solute originating in the aqueous phase; and (4) sorbed distribution for solute originating in the sorbed phase.

Since the governing equations (3) and (4) are linear, superposition is applicable, and all cases are covered by the analytic moment solutions for the four base cases. Therefore moments can be evaluated for any initial distribution between the aqueous and sorbed phases by linear combination of the four base cases.

In random-walk models, solute concentrations are equivalent to particle densities, when a sufficient number of particles is used. Furthermore, owing to the linearity of the problem, the probability distribution of a single particle in both space and phase is independent of other particles. When the spatial moments of concentrations are interpreted as those of particles, the spatial-moment behavior of any particle is known as a function of time, regardless of its original or final phase. The phase-transition probabilities, which are a function of the specific transport parameters as well as the chosen time step, are derived based on the analytical solutions for the zeroth moments.

For the particle-tracking model developed in this work, the initial and final phase of each particle is determined with a Bernoulli trial on the appropriate phase-transition probability at each time step. The particle is advected according to the displacement mandated by the corresponding analytical first-moment equation, and the random dispersive redistribution of particles is based on the corresponding analytical second-moment equation.

2.2. Development of Moment Equations

Although the spatial moments of the aqueous and sorbed distributions (C and S, respectively) are generally defined in three dimensions [Aris, 1956], they are presented here in one dimension for simplicity:

\[ \mu_n = \int_{-\infty}^{\infty} x^n \eta C(t, x) \, dx \quad \nu_n = \int_{-\infty}^{\infty} x^n \rho S(t, x) \, dx,\tag{6} \]

where \( \mu_n \) and \( \nu_n \) are the \( n \)th aqueous and sorbed phase moments, respectively. This formulation results in the zeroth moment being equal to the total mass of solute in each of the phases.

The central spatial moments are

\[ \mu^*_n = \int_{-\infty}^{\infty} (x - \mu) \eta C(t, x) \, dx \tag{7a} \]

\[ \nu^*_n = \int_{-\infty}^{\infty} (x - \nu) \rho S(t, x) \, dx. \tag{7b} \]

Replacing C and S with their Fourier transforms

\[ C(t, x) = \int_{-\infty}^{\infty} \tilde{C}(t, s) \exp(j2\pi xs) \, ds \tag{8a} \]

\[ S(t, x) = \int_{-\infty}^{\infty} \tilde{S}(t, s) \exp(j2\pi xs) \, ds, \tag{8b} \]

where \( j = \sqrt{-1} \), and applying the auxiliary conditions

\[ \lim_{s \to \infty} \tilde{C} = 0 \quad \lim_{s \to \infty} \tilde{S} = 0, \]

\[ \lim_{x \to \infty} \frac{\partial C}{\partial x} = 0 \quad \lim_{x \to \infty} \frac{\partial S}{\partial x} = 0 \]

yields

\[ \eta \frac{\partial \tilde{C}}{\partial t} + \rho \frac{\partial \tilde{S}}{\partial t} + 2\eta v_i \pi s \tilde{C} + 4\eta D \pi^2 s^2 \tilde{C} = 0, \tag{11} \]

where \( \tilde{C} \) and \( \tilde{S} \) are the Fourier transforms of the aqueous and sorbed concentrations, respectively. The same approach for the phase-transition equation yields

\[ \frac{\partial \tilde{S}}{\partial t} - k(K_d \tilde{C} - \tilde{S}) = 0. \tag{12} \]

The spatial moments of the concentration in the real domain can be evaluated from the concentration Fourier coefficients by [Bracewell, 1986; Goltz and Roberts, 1987]

\[ \mu_n = \eta \frac{\partial \tilde{C}}{\partial \delta^n} \bigg|_{s=0} \quad \nu_n = \rho \frac{\partial \tilde{S}}{\partial \delta^n} \bigg|_{s=0}. \tag{13} \]

All spatial moments will be presented for the four possible phase combinations: solute starting and ending in the aqueous phase \( \mu_n^{(A)} \), solute starting in the sorbed phase and ending in the aqueous phase \( \mu_n^{(S)} \), solute starting in the aqueous phase and ending in the sorbed phase \( \nu_n^{(C)} \), and solute starting and ending in the sorbed phase \( \nu_n^{(S)} \).

Additionally, we define spatial moments normalized by their respective zeroth moments:

\[ \mu^*_n = \frac{\mu_n}{\mu_0} \quad \nu^*_n = \frac{\nu_n}{\nu_0}. \tag{14} \]

\[ \mu^*_n = \frac{\mu_n}{\mu_0} \quad \nu^*_n = \frac{\nu_n}{\nu_0}. \tag{15} \]

2.2.1. Zeroth moments. The equations for the zeroth moments in Fourier space are (from (13))

\[ \mu_0 = \eta \tilde{C} \bigg|_{s=0} \quad \nu_0 = \rho \tilde{S} \bigg|_{s=0}. \tag{16} \]

Substituting (16) into (12) and setting \( s = 0 \) yields

\[ \mu_0 = \frac{1}{(R - 1)} \left( \frac{1}{k} \frac{\partial \nu_0}{\partial t} + \nu_0. \right). \tag{17} \]
### Table 1. Longitudinal Moment Equations for Kinetically Sorbing Solutes

<table>
<thead>
<tr>
<th>Phase Originating</th>
<th>Zeroth Moment Normalized</th>
<th>First Moment Normalized</th>
<th>Second Central Moment Normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous phase originating in aqueous phase ($\mu_0 = M$, $v_0 = 0$)</td>
<td>$\mu_0(t) = \frac{M(1 + \beta A)}{(\beta + 1)}$</td>
<td>$\nu_1(t) = \frac{v}{\beta + 1} + 4(\beta(1 - A))$</td>
<td>$\nu_2(t) = \frac{v^2(1 - A)^2}{(\beta + 1)(1 + 4\beta(1 - A))}$</td>
</tr>
<tr>
<td>Aqueous phase originating in sorbed phase ($\mu_0 = 0$, $v_0 = M$)</td>
<td>$\mu_0(t) = \frac{M(1 - A)}{(\beta + 1)}$</td>
<td>$\nu_1(t) = \frac{v}{\beta + 1} + 4(\beta(1 - A))$</td>
<td>$\nu_2(t) = \frac{v^2(1 - A)^2}{(\beta + 1)(1 + 4\beta(1 - A))}$</td>
</tr>
<tr>
<td>Sorbed phase originating in sorbed phase ($\mu_0 = 0$, $v_0 = M$)</td>
<td>$\nu_1(t) = \frac{v}{\beta + 1} + 4(\beta(1 - A))$</td>
<td>$\nu_2(t) = \frac{v^2(1 - A)^2}{(\beta + 1)(1 + 4\beta(1 - A))}$</td>
<td></td>
</tr>
<tr>
<td>Sorbed phase originating in aqueous phase ($\mu_0 = M$, $v_0 = 0$)</td>
<td>$\nu_1(t) = \frac{v}{\beta + 1} + 4(\beta(1 - A))$</td>
<td>$\nu_2(t) = \frac{v^2(1 - A)^2}{(\beta + 1)(1 + 4\beta(1 - A))}$</td>
<td></td>
</tr>
</tbody>
</table>

Substituting (16) into (11) and setting $s = 0$ yields

$$\frac{d\mu_0}{dt} + \frac{\beta v_0}{dt} = 0. \quad (18)$$

Letting the initial conditions for the zeroth moment be

$$\mu_0(0) = M_1, \quad v_0(0) = M_2, \quad (19)$$

where $M_1$ and $M_2$ are the initial mass in the aqueous and sorbed phases, respectively, and the total mass is $M = M_1 + M_2$, the solutions to (17) and (18) are

$$\mu_0(t) = \frac{M_1(1 + \beta A)}{(\beta + 1)} + \frac{M_2(1 - A)}{(\beta + 1)} \quad (20)$$

$$v_0(t) = \frac{M_1\beta(1 - A)}{(\beta + 1)} + \frac{M_2(\beta + A)}{(\beta + 1)} \quad (21)$$

where $A = \exp(-Rkt)$ and $\beta = R - 1$.

The examination of the spatial moments of solute distributions allows for the identification of characteristic timescales. According to the definition of the term $A$, $1/kR$ is the characteristic time for the zeroth moments approaching their steady state values. This characteristic time will also apply for the first- and second-moment expressions. The simplified zeroth-moment equations resulting from the initial solute source being entirely in a single phase are presented in Table 1, and the zeroth-moment behavior is illustrated in Figure 1 for the case of $R = 1.5$ for the four possible phase combinations. These moments will also be interpreted, in section 3.3, as phase-transfer probabilities for particles starting and ending in the specified phases. For the cases for which analytical expressions were already available, the zeroth-moment equations derived in this work match those presented in the literature [Goltz, 1986; Goltz and Roberts, 1987]. The same is true for first- and second-moment expressions.

#### 2.2.2. First moments

The derivation of the first moments is similar to that of the zeroth moments and is outlined in Appendix A. The first-moment expressions normalized by their corresponding zeroth moments are presented in Table 1. First-moment behavior and rates of change are presented in Figure 2 for the case of $R = 1.5$ for the four possible phase combinations. The values of the first moments can be interpreted as the total displacement of the centroid of fractions of a solute plume starting and ending in the specified phases. The
rates of change of the first moments correspond to the instantaneous advective velocity of fractions of a solute plume starting and ending in the specified phases. Note that the evolution of the first moment is the same for all solute ending in a phase opposite from its initial phase. Whether a fraction of solute starts in the aqueous phase and is known to end in the sorbed phase or vice versa, the mean amount of time spent in each phase is the same, and the evolution of the first moment is therefore identical. The same will be seen to hold true for the evolution of the second moments. The weighted mean presented in Figure 2a corresponds to the overall first-moment behavior resulting from an initial solute distribution in which the total solute mass is distributed between the phases according to the equilibrium distribution, that is, a $1/R$ fraction in the aqueous phase and a $(R-1)/R$ fraction in the sorbed phase. The plume is then left to evolve according to the sorption kinetics specified.

Since there is no advective transport in the transverse direction(s) in a homogeneous field, the transverse first moments equal zero for both the aqueous and sorbed phases. The transverse moments are presented in Table 2.

### 2.2.3. Second moments

An outline of the derivation of the second moments is given in Appendix B. Longitudinal second central moment expressions normalized by the corresponding zeroth moments are presented in Table 1. Central second-moment behavior and rates of change are presented in Figure 3 for the case of $R = 1.5$ for the four possible phase combinations. The values of the second moments can be interpreted as the mean spread about the centroid of fractions of a solute plume starting and ending in the specified phases. The rates of change of the second moments represent 2 times the instantaneous dispersion coefficient of fractions of a solute plume starting and ending in the specified phases.

The normalized second central moments are defined as, for the aqueous and sorbed moments, respectively,

$$
\mu_2^* = \frac{\mu_2 - \mu_0^2}{\mu_0}, \quad \nu_2^* = \frac{\nu_2 - \nu_0^2}{\nu_0},
$$

where the asterisk denotes the normalized second central moments.

The weighted mean presented in Figure 3 corresponds to the overall second-moment behavior resulting from an initial solute distribution in which the total solute mass is distributed between the phases according to the equilibrium distribution, that is, a $1/R$ fraction in the aqueous phase and a $(R-1)/R$ fraction in the sorbed phase. The plume is then left to evolve according to the sorption kinetics specified. Note that the overall normalized second central moment grows faster than the moments of the four individual phase combinations. In other words, the overall plume is spread around its center of mass more than the individual distributions resulting from the four possible phase combinations are spread around their individual centers of mass, as would be expected since the individual plume fractions have different centroids.

For the transverse second moments the derivation is identical to that for the longitudinal case, with the exception that the transverse aqueous phase velocities are zero, thereby sim-
Table 2. Transverse Moment Equations for Kinetically Sorbing Solutes

<table>
<thead>
<tr>
<th>Normalized First Moment</th>
<th>Normalized Second Central Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous phase originating in aqueous phase ($\mu_0 = M$, $\nu_0 = 0$)</td>
<td>$\mu_1(t) = 0$</td>
</tr>
<tr>
<td>Aqueous phase originating in sorbed phase ($\mu_0 = M$, $\nu_0 = 0$)</td>
<td>$\mu_2(t) = \frac{2D}{\beta + 1} + \frac{kD(\beta - 1)}{k(\beta + 1)^2}$</td>
</tr>
<tr>
<td>Sorbed phase originating in sorbed phase ($\mu_0 = 0$, $\nu_0 = M$)</td>
<td>$\nu_1(t) = 0$</td>
</tr>
<tr>
<td>Sorbed phase originating in aqueous phase ($\mu_0 = M$, $\nu_0 = 0$)</td>
<td>$\nu_2(t) = \frac{2D}{\beta + 1} + \frac{kD(\beta - 1)}{k(\beta + 1)^2}$</td>
</tr>
</tbody>
</table>

plifying the final moment equations. These expressions are presented in Table 2.

2.3. Phase Transition Probabilities

On the basis of the analytical solutions for the zeroth spatial moments we derive the particle phase-transition probabilities. The total mass in the system is assumed to be $M$. Assuming that at time $t = 0$, all the solute is in the aqueous phase ($\mu_0(0) = M$ and $\nu_0(0) = 0$), (20) and (21) simplify to

\[
\mu_C(t) = M \left(1 + \beta A\right) \left(\beta + 1\right), \quad (23)
\]

\[
\nu_C(t) = M \left(\beta(1 - A)\right) \left(\beta + 1\right), \quad (24)
\]

where the superscript $(C)$ represents solute originating in the aqueous phase. Conversely, assuming that at time $t = 0$, all the solute is in the sorbed phase ($\mu_0(0) = 0$ and $\nu_0(0) = M$), (20) and (21) are

\[
\mu_S(t) = M \left(1 - A\right) \left(\beta + 1\right), \quad (25)
\]

\[
\nu_S(t) = M \left(\beta + A\right) \left(\beta + 1\right), \quad (26)
\]

where the superscript $(S)$ represents solute originating in the sorbed phase.

Normalizing (23) to (26) by the total mass gives the probabilities that a particle starting in a given phase is in a certain phase after time $t$:

\[
P_{C \to S} = \frac{1}{M} \frac{\nu_C(t)}{\mu_C(t)} \quad P_{C \to A} = \frac{1}{M} \frac{\mu_C(t)}{\nu_C(t)} \quad (27)
\]

\[
P_{S \to C} = \frac{1}{M} \frac{\mu_S(t)}{\nu_S(t)} \quad P_{S \to A} = \frac{1}{M} \frac{\nu_S(t)}{\mu_S(t)} \quad (28)
\]

where the subscript $P_1 \to P_2$ refers to a particle starting in phase $P_1$ and ending in phase $P_2$, with $S$ designating the sorbed phase and $C$ designating the aqueous phase. The transition probabilities are plotted in Figure 1. Valocchi and Qui-

Figure 3. Behavior of normalized second central moments for $R = 1.5$ with $v = 1$ [L/T], $k = 0.1$ [1/T], $D = 0$, and $\mu_2^C$ and $\nu_2^C$ as normalized second central spatial moments for solute in the aqueous and sorbed phases, respectively. (a) Normalized second central moments as a function of time. (b) Rates of change of normalized second central moments.
nodoz [1989] derived these expressions by relying on results obtained by Parzen [1962] and on Kolmogorov differential equations. Conversely, the current derivation is obtained directly from expressions for the zeroth moments of the aqueous and sorbed phases.

3. Overall Moment Behavior: Analytical Results

We use the moment equations (Tables 1 and 2) and the transition probabilities (equations (27) and (28)) in order to define general properties of kinetically sorbing solute transport. Since the two equations governing the problem (equations (3) and (4)) are linear, their moments can be superposed. Therefore, regardless of the initial distribution of the solute between the two phases, the location of the center of mass and the degree of spreading of the solute can now be determined analytically, without resorting to numerical modeling. Even though the first and second moments are explicitly derived only for the cases of all the solute being in either the aqueous or sorbed phase at time \( t = 0 \), the solute distribution can be described for any initial distribution by applying the proper weighting function to the analytical moment equations.

For an initial mass fraction \( \frac{1}{2} \) in the aqueous phase and \( 1 - \frac{1}{2} \) in the sorbed phase, the first moment and second central moment are

\[
m_1^* = \psi P_{C-C} \mu_{1(C)}^* + (1 - \psi) P_{S-C} \mu_{1(S)}^* + \psi P_{C-S} \psi_{1(C)}^* + (1 - \psi) P_{S-S} \psi_{1(S)}^* + \psi P_{C-S} \psi_{1(C)} + (1 - \psi) P_{S-C} \psi_{1(S)} + \psi P_{C-C} (\psi_{1(C)} + (\psi_{1(C)} - m_{1(C)}^2))^2 + (1 - \psi) P_{S-C} (\psi_{1(S)} + (\psi_{1(S)} - m_{1(S)}^2))^2
\]

\[
m_2^* = \psi P_{C-C} [\mu_{2(C)}^* + (\mu_{1(C)}^* - m_{1(C)}^2)] + (1 - \psi) P_{S-C} [\mu_{2(S)}^* + (\mu_{1(S)}^* - m_{1(S)}^2)]
\]

where \( m_1^* and m_2^* are the moments of the overall solute distribution (sorbed and aqueous fractions) and the superscripts \( (C) and (S) \) represent solute originating in the aqueous and sorbed phases, respectively. The aqueous and sorbed moments are

\[
\mu_{1(C)}^* = \frac{1}{\xi_c} \left[ \psi P_{C-C} \mu_{1(C)}^* + (1 - \psi) P_{S-C} \mu_{1(S)}^* \right]
\]

\[
\mu_{1(S)}^* = \frac{1}{\xi_s} \left[ (1 - \psi) P_{S-S} \psi_{1(S)}^* + \psi P_{C-S} \psi_{1(C)}^* \right]
\]

where the superscript \( (C, S) \) represents solute starting in either phase, and the solute fractions present in each phase are defined as

\[
\xi_c = \psi P_{C-C} + (1 - \psi) P_{S-C},
\]

\[
\xi_s = (1 - \psi) P_{S-S} + \psi P_{C-S},
\]

where \( \xi_c and \xi_s are the fractions in the aqueous and sorbed phases, respectively.

On the basis of these analytical relations the first and second moments of any instantaneous point source can be determined. For nonpoint sources the first moment and second central moment can be determined by simply adding the initial moment value to the point source moment value. For noninstantaneous sources a convolution integral must be performed for each moment in order to determine the overall moment behavior.

As an example, the moment behavior for the case of a steady state solute distribution between the aqueous and sorbed phases will be used to develop transport parameters. A steady state is defined herein as one for which the total solute mass is distributed between the phases according to the equilibrium distribution but for which local equilibrium is not satisfied at every point in the medium. In other words, overall, the fractions of solute in the aqueous and sorbed phases are those that would have been predicted by the local-equilibrium assumption, that is, \( 1/R \) and \( (R - 1)/R \), respectively. At steady state a \( 1/R \) fraction of the total solute mass will be in the aqueous phase. Therefore the cumulative rate of change of the overall first moment can be defined as

\[
u_{eff} = \frac{1}{\Delta t} \left[ \frac{P_{C-C}}{(\beta + 1)} \mu_{1(C)}^* + \frac{BP_{S-S}}{(\beta + 1)} \psi_{1(S)}^* \right]
\]

where all moments are calculated at time \( t = \Delta t \). This result is illustrated by the weighted mean in Figure 2b.

The effective dispersion coefficient \( D_{eff} \) can be defined in a similar manner by taking a weighted mean of the average rates of change of the individual plume components (each component corresponding to a given initial and final phase):

\[
D_{eff} = \frac{1}{2\Delta t} \left[ \frac{P_{C-C}}{(\beta + 1)} [\mu_{2(C)}^* + (\mu_{1(C)}^* - m_{1(C)}^2)] + \frac{BP_{S-S}}{(\beta + 1)} [\psi_{1(S)}^* + (\psi_{1(S)} - m_{1(S)}^2)] \right]
\]

\[
+ \frac{P_{C-S}}{(\beta + 1)} [\psi_{1(C)}^* + (\psi_{1(C)} - m_{1(C)}^2)]
\]

\[
+ \frac{BP_{S-C}}{(\beta + 1)} [\mu_{2(S)}^* + (\mu_{1(S)}^* - m_{1(S)}^2)]
\]

where all moments are calculated at time \( t = \Delta t \) and the asterisks indicate that the normalized first moments and second central moments are being used.

4. Particle-Tracking Implementation

On the basis of the analytical solution for the spatial moments and phase-transition probabilities we develop a particle-tracking model, referred to as the semianalytical moment method (SAMM). We compare our approach to the three
4.1. Semianalytical Moment Method (SAMM)

The implementation of the SAMM is based on the analytical expressions for the spatial moments and the phase-transition probabilities. The values of the four first and second moments (Tables 1 and 2) as well as the four phase-transition probabilities (equations (27) and (28)) are calculated for \( t = \Delta t \).

For each time step the final phase of each particle is determined by a Bernoulli trial based on its initial phase and the corresponding phase-transition probability. Each particle is then displaced by the value of the first moment at \( t = \Delta t \) corresponding to the particle's initial and final phase. These moment expressions are plotted in Figure 2a. To account for dispersion, each particle is displaced by a distance proportional to the square root of the value of the normalized second central moment corresponding to each particle's initial and final phase. These distances are weighted using normally distributed random numbers with a mean of zero and a variance of one. The second-moment expressions are plotted in Figure 3a. A flow chart for the method, applied to a single particle, is presented in Figure 4.

Since the analytical results for the zeroth, first, and second moments are applied, and therefore enforced, directly, the method is guaranteed to reproduce these values precisely and accurately if a sufficient number of particles is used.

Although only the lower moments are directly specified, the method reproduces the transient skewness (or tailing) characteristic of solute subjected to kinetic sorption. The accuracy with which the skewness is represented is a function of the time step used. However, although this effect was not quantified, time step limitations were not observed for the examined parameters.

4.2. Continuous Time History Method (CTHM)

The CTHM simulates the history of phase changes for each particle during each time step by generating a sequence of exponentially distributed phase residence times. The process stops when the total time elapsed for a given particle is equal to the specified time step. At that point the waiting times for each state are summed, and the particle is advected and dispersed using a time step equal to the time spent in the aqueous phase [Valocchi and Quinodoz, 1989].

The exponential phase residence times can be expressed as

\[
\begin{align*}
t_C &= -\ln P_{C,C} / k(R-1) \\
t_S &= -\ln P_{S,S} / k 
\end{align*}
\]

(40)

where \( t_C \) and \( t_S \) are the exponential phase residence times for a particle in the aqueous and sorbed phases, respectively. \( P_{C,C} \) and \( P_{S,S} \) can be randomly generated from a uniform distribution in the range [0,1]. Note that the probabilities denoted as \( P_{C\rightarrow C} \) and \( P_{S\rightarrow S} \) in (27) and (28) represent the probability that a particle is in its original phase after a given time, whereas the probabilities represented as \( P_{C,C} \) and \( P_{S,S} \) represent the probability that a particle remains in its original phase throughout an examined period. In short, \( P_{C,C} \) and \( P_{S,S} \) are the zero phase-transition probabilities.

4.3. Small Time Step Method (STSM)

The STSM [Kinzelbach, 1987; Kinzelbach and Uffink, 1991] is based on the fact that for small enough time steps, the transition probabilities become

\[
\begin{align*}
P_{C\rightarrow S} &= k \beta \Delta t \\
P_{S\rightarrow C} &= k \Delta t.
\end{align*}
\]

(41)
Since the number of phase transitions can be considered a Poisson process, the probability of having more than one phase change in a small time step is negligible. Therefore a particle is assumed to remain in its initial state for the entire time step, and its final state is adjusted by a Bernoulli trial, where a value of less than 1 indicates that a phase change occurs. Thus a particle is assumed to remain in its initial state for the entire time step, to eliminate the possibility of zero transfers. Finally, the fraction of time spent in the aqueous phase is determined from the probability density functions of the fraction of time spent in the aqueous phase.

### 4.4. Arbitrary Time Step Method (ATSM)

The ATSM was introduced by Valocchi and Quinodoz [1989]. This method uses a three-step procedure to determine the fraction of each time step spent by each particle in the aqueous phase. The first step involves a Bernoulli trial to determine whether a phase change occurs according to the zero phase-transition probability functions: 

\[
P_{c,c} = \exp (-k(R - 1)\Delta t),
\]

\[
P_{s,s} = \exp (-k\Delta t).
\]

If a phase transfer occurs, the final phase is determined using the transition probabilities (equations (27) and (28)), adjusted to eliminate the possibility of zero transfers. Finally, the fraction of time spent by each particle in the aqueous phase is determined from the probability density functions of the fraction of time spent in the aqueous phase for each of the initial/final phase combinations [Keller and Giddings, 1960]:

\[
f_{c,c}(\gamma) = \frac{ab\gamma}{\sqrt{1 - \gamma}} \exp [-a(1 - \gamma) - b\gamma] I_0(\sqrt{4ab\gamma(1 - \gamma)})
\]

\[
f_{c,s}(\gamma) = a \exp [-a(1 - \gamma) - b\gamma]I_0(\sqrt{4ab\gamma(1 - \gamma)})
\]

\[
f_{s,c}(\gamma) = \frac{a}{b} f_{c,c}(\gamma)
\]

\[
f_{s,s}(\gamma) = \frac{1 - \gamma}{\gamma} f_{c,c}(\gamma)
\]

where \(f_{c,c}, f_{c,s}, f_{s,c}, \) and \(f_{s,s}\) are the probability distribution functions of the fraction of time \(\gamma\) spent by a particle in the aqueous phase, \(a = k\Delta t\), and \(b = k\beta\Delta t\). The initial and final phases of the particle are indicated by the subscripts \(C\) and \(S\), corresponding to the aqueous and sorbed phases, respectively. \(I_0\) and \(I_1\) are modified Bessel functions of the first kind of order 0 and 1, respectively.

These probability distribution functions are numerically integrated over the range \(0 \leq 0 \leq 1\) and normalized by their total integral in order to obtain cumulative probability distribution functions of the fraction of time spent in the aqueous phase. This integration is performed once, before the start of time stepping. For each time step and particle the random number used to determine the fraction of time spent in the aqueous phase is compared to the probabilities of each fraction \(\gamma\), and linear interpolation is performed between the two closest values to obtain an estimate of \(\gamma\) for the given particle.

### 4.5. Model Comparison

The four available models were tested using a method similar to that of Valocchi and Quinodoz [1989]. Each model was run 10 times for each set of parameters in order to obtain an estimate of the mean error in the aqueous solute distribution resulting from each method, relative to the available analytical solutions. In this manner the standard deviation of the error was also estimated. The simulations were performed with the reaction rates and number of particles presented in Table 3. All particles were initially in the aqueous phase. The velocity \(v\) was unity (in arbitrary length over time units), the local dispersion \(D\) was set to zero, and the retardation factor was \(R = 1.5\). The numerical integration required for the ATSM was performed with 100 and 10 discretization points using an adaptive recursive Simpson’s rule [Forsythe et al., 1977].

Each method was implemented in Matlab using both a vectorized algorithm, and a loop-structured algorithm. The algorithm that minimized CPU time was selected individually for each application. A vectorized algorithm is one that uses multiplication by matrices or vectors containing logical operators instead of using a looped if/else structure, where required. Vectorized algorithms were found to be more efficient for all cases except the fine integration discretization runs of the ATSM model, for which a loop-structured algorithm was
found to be more efficient (although, as seen in Table 3, the vectorized algorithm results in significantly higher floating-point operation counts).

The error in the values of the mean position were very small in general, and only results for the aqueous concentration variance are discussed. These results are presented in Table 3.

4.6. Results and Discussion

The examined methods offer different advantages and disadvantages. Although the CTHM is computationally simple, it requires the generation of a large number of waiting times, especially when reaction rates are high, which makes it less efficient at high reaction rates. The STSM is also simple to implement. However, this method requires that the time step be chosen to ensure that $P_{c \rightarrow s}$ and $P_{s \rightarrow c}$ are much smaller than unity. Otherwise, the method overestimates the second moment of the aqueous article distribution. This requirement makes the STSM inefficient for high reaction rates. As mentioned in section 4.4, the ATSM requires numerical integration of the probability density functions and interpolation between the integrated values for each particle for each time step. This requirement makes the method inefficient when the integration is performed with a fine discretization.

Overall, results of comparable quality were obtained with the CTHM, the ATSM (with fine discretization), and the SAMM, while the STSM produced larger errors. As expected, accuracy was found to decrease for all models when the number of particles was reduced.

The computational costs differ among the methods. For a slow reaction rate the relative number of floating-point operations was lowest for the ATSM (fine discretization), followed by the SAMM, the STSM, and the CTHM. For higher reaction rates the CTHM and STSM require much greater computational effort since the number of phase changes in the CTHM and the number of required time steps in the STSM increase dramatically. For the fast reaction rate both these methods require approximately 25 times more floating-point operations than the SAMM. The number of floating-point operations required for the ATSM (fine discretization), however, is below that required for the SAMM for all simulations.

The actual CPU time gives additional insight into the models' performance because the methods differ significantly in the number of relational and logical operations required. The SAMM was faster than all other models for all parameter settings. For the CTHM the ratios of the computational times relative to the SAMM are about double the ratios of the flop counts. For the ATSM, however, the computational time ratios vary from approximately 11 to 55. The difference between the flops and computational time ratios is due to the fact that since the ATSM requires numerical integration, random numbers generated for each particle for each time step must be compared to $n$ numbers, where $n$ is the number of discretization points used for the numerical integration of the cumulative probability distributions.

In order to decrease the CPU time requirements of the ATSM method, the runs were repeated with a coarser discretization of the probability density functions. The relative CPU time decreased but remained an order of magnitude greater than that of the SAMM. Furthermore, for high reaction rates, where the cumulative probability density functions exhibit sharp fronts, the ATSM relative error in the second moment increased significantly.

Therefore the SAMM was found to be at least as accurate as all other available methods and significantly more computationally efficient than these methods. It is important to note that the computational efficiency of the examined methods could potentially be improved. Specifically, for the ATSM a binary search technique could be used for comparing the random number generated for determining $\gamma$ to the values of the discretized cumulative density function. Alternatively, an approximate analytical expression for the density functions could be found. However, such extensions are beyond the scope of this work.

5. Investigation of Double-Peak Behavior

Double peaks in the aqueous concentration distribution are sometimes observed in reactive solute experiments such as the ones conducted at the Borden [Mackay et al., 1986; Roberts et al., 1986] and Cape Cod [Garabedian et al., 1988; LeBlanc et al., 1991] field sites. Although double peaking can occur as a result of physical heterogeneity [Freyberg, 1986], it has been suggested that double peaks may also be caused by kinetic sorption [Quinodoz and Valocchi, 1993]. Therefore the SAMM model was used to investigate the conditions under which double peaks can occur as a result of kinetic sorption.

A large range of parameters was used, but the initial condition always involved all the mass being in the aqueous phase. Double-peak behavior was found to occur for any value of the retardation factor, contrary to the suggestion [Quinodoz and Valocchi, 1963] that double peaking can occur only for very large retardation factors. The current study suggests that double peaking is a function of the Damköhler number of the first kind defined as

$$Da_f = k \lambda_s R / v,$$

where $\lambda_s$ is the initial length of the plume. The Damköhler number is a ratio of the advection timescale to the reaction timescale. Therefore a low Damköhler number indicates that the advection rate is fast relative to the reaction rate. Double peaking occurred for all retardation factors for $Da_f \leq 1$ and was very pronounced for $Da_f < 1/3$. In essence, double peaking occurred when the aqueous plume had time to pass ahead of the sorbed plume before the sorbed fraction desorbed. This can be accomplished by a high mean velocity $v/R$, a slow reaction rate $k$, or a short length of the plume $\lambda_s$.

In cases where double peaking occurred, the time at which the double peak is most pronounced was found to be a function of the reaction rate and the retardation factor. A dimensionless time was defined as

$$t^* = k(R - 1)t$$

since double peaking can only occur for $R > 1$, regardless of the value of the Damköhler number. Where double peaking in the aqueous phase occurs, it starts approximately at time $t^* \approx 2$, is most pronounced for $3 \leq t^* \leq 5$, and dies out by $t^* \approx 10$. Maximum double peaking was defined as the time at which the concentrations of the two peaks were equal (see Figure 5a). However, if the local dispersion $D$ is sufficiently large or if the time after which double peaking would occur is sufficiently long (such as in cases where the retardation factor is extremely close to unity), the dispersion-induced smearing of the concentration profile can eliminate the double-peak effect, as was also suggested by Bellin et al. [1991].

Results for $Da_f = 0.1, 0.33, \text{ and } 1.0$ are presented in Figure 5. The Péclet number, defined as
was kept constant at a value of 100. The retardation factor was kept constant at \( R = 2 \), demonstrating that double peaking can occur for low retardation factors. For comparison, an aqueous concentration distribution for \( R = 20 \) and \( Da_f = 4.0 \) is presented in Figure 6c. No double peaking occurs in this case, despite the fact that the retardation factor is very large (\( R \gg 10 \)).

Double-peak formation can also occur in the range \( 1 \leq Da_f \leq 3 \). However, in this range, the occurrence of the double peaks is retardation factor dependent. Double-peak formation for the higher Damköhler number case is related to the behavior of the first aqueous moment for solute starting in the aqueous phase. For all retardation factors greater than 2, the center of mass of solute starting in the aqueous phase (i.e., the rate of change of the first spatial moment) temporarily drops below its asymptotic value. This behavior has been reported for "very high" retardation factors [Quinodoz and Valocchi, 1993], but a threshold had not yet been identified. For retardation factors greater than 12, in fact, the rate of change of this first moment drops below zero. This behavior is illustrated in Figure 7 for \( R = 20 \). This drop in the mean velocity can be explained by the small fraction of solute remaining in the aqueous phase downgradient of the source, as a majority of solute entering uncontaminated zones is sorbed. The sorbed solute remains immobile until the aqueous plume has passed and is then released. If the retardation factor is high enough, the concentration of desorbing solute is larger than the concentration of downgradient aqueous solute, and the velocity of the centroid is thereby slowed to below its asymptotic value and for \( R > 12 \) is slowed to below zero.

Consequently, double-peak formation in this higher Damköhler number range is insignificant for \( R < 2 \) and is most pronounced for \( R > 12 \). Furthermore, the appearance of the peaks is different from the \( Da_f \leq 1 \) case. For the \( 1 \leq Da_f \leq 3 \) case the two peaks have approximately the same width, whereas for the case of an arbitrary retardation factor and \( Da_f \leq 1 \), the upgradient peak is wide relative to the downgradient peak. Examples of double peaking in the higher Damköhler number range are presented in Figures 6a and 6b for \( R = 20 \) and \( Da_f = 1.0 \) and 2.0, respectively.

Double peaking in the higher Damköhler number range is probably the behavior that was reported by Quinodoz and Valocchi [1993], although the authors discussed no limitations on the reaction rates that lead to the double-peak formation, whereas current results suggest a rate limitation based on the dependence on the Damköhler number. Another indication of the dependence on reaction rates is that as the reaction rates increase, the local equilibrium model becomes asymptotically valid, which never exhibits double peaking. Therefore it is clear that double-peak formation is rate-dependent.

It should be noted that we have performed this investigation assuming a linear driving-force model for sorption, and it is unclear if a different kinetics model for sorption would yield identical results. Specifically, double peaking in the higher Damköhler number range may be an artifact of assuming linear driving-force kinetics, since it appears to be a result of the velocity of the center of mass of the aqueous phase, for solute starting in the aqueous phase, temporarily dropping below its asymptotic value for \( R > 2 \). Such behavior has neither been confirmed nor refuted for other nonequilibrium sorption models.
6. Conclusions and Future Directions

We have presented zeroth, first, and second spatial moments for kinetically sorbing solutes following a linear reversible mass transfer model for both initial and both final phases. Owing to the linearity of the problem, moments resulting from all possible initial distributions between the phases can be obtained by superposition. Moments resulting from nonpoint and non-instantaneous sources can also be determined by summation and convolution, respectively. Therefore a general analytical description of solute transport is available for any source in terms of effective velocities and dispersion coefficients.

The general expression relating the Fourier coefficients to the spatial moments of the solute (equation (13)) applies also to the third and higher moments. Hence extending our analysis to these moments would be straightforward. However, expressions become increasingly long and complicated for higher moments, and since these moments were not necessary for the presented applications, their development is beyond the scope of the current study.

The analytical moment expressions derived in this paper allow for the implementation of a highly efficient and accurate random-walk method. The approach automatically simplifies to the local-equilibrium case for very large reaction rates, whereas other methods, such as the continuous time step method and the small time step (operator split) method, become inefficient and/or inaccurate at high reaction rates, where the local-equilibrium assumption becomes more applicable. Therefore the implementation of these methods requires one to determine, a priori, whether the local-equilibrium assumption is valid. No such limitations are encountered with the new method, as the entire range of reaction rates is covered efficiently and accurately.

Using the new technique, we found that, contrary to past hypotheses, double concentration peak behavior resulting from kinetic sorption can occur even for low retardation factors, but it is controlled by the Damköhler number of the first kind, with double peaks occurring for $Da_1 \leq 1$ for all retardation factors. For higher retardation factors, double peaking can also occur for higher Damköhler numbers but is limited to...
the range $Da_1 \leq 3$. Double peaking in this higher Damköhler number range, however, may be an artifact of assuming linear driving-force kinetics, as other nonequilibrium sorption models may not exhibit a transient aqueous center of mass velocity drop below its asymptotic value for solute starting in the aqueous phase.

Although the analysis presented in this paper was limited to spatially and temporally constant coefficients, extensions to heterogeneous fields are possible. The analytical results found in this paper could be extended to spatially varying velocity fields with negligible local dispersion and constant sorption properties. These analytical expressions could be derived by using the stochastic-convective approach [Simmons, 1982; Sellar and Cvetkovic, 1992]. For cases where the sorption parameters are not constant or where the local dispersion is not negligible, analytical expressions cannot yet be readily obtained. However, the random-walk method developed in this work can be applied directly to gradually varying heterogeneous media without significant increases in the computational cost, although the potential limitations of such an application require further study.

Appendix A: Derivation of First Moment Equations

The equations for the first moments in Fourier space are (from (13))

$$\mu_1 = \frac{\eta}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{dC}{ds} \bigg|_{s=0}\, v_1 = \frac{\rho}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{dS}{ds} \bigg|_{s=0}. \quad (A1)$$

Taking the first derivative of (11) and (12) with respect to $s$, substituting (16) and (A1), and setting $s = 0$ yields

$$\mu_1 = \frac{1}{(R-1)} \left( \frac{1}{k} \frac{\partial v_1}{\partial t} + v_1 \right) \quad (A2)$$

$$v_1(t = 0) = 0 \quad \mu_1(t = 0) = 0, \quad (A3)$$

Letting the initial conditions for the first moments be

$$v_1(t = 0) = 0 \quad \mu_1(t = 0) = 0,$$

the solutions to (A2) and (A3) are developed after substituting the transient solutions for the zeroth moment $\mu_0$ and the first moment $\mu_1$.

Appendix B: Derivation of Second Moment Equations

The equations for the second moments in Fourier space are (from (13))

$$\mu_2 = \frac{\eta}{4\pi^2} \int_{-\infty}^{\infty} \frac{d\tilde{C}}{d\tilde{s}} \bigg|_{\tilde{s}=0} \quad v_2 = \frac{\rho}{4\pi^2} \int_{-\infty}^{\infty} \frac{d\tilde{S}}{d\tilde{s}} \bigg|_{\tilde{s}=0}. \quad (B1)$$

Taking the second derivative of (11) and (12) with respect to $s$, substituting (16), (A1), and (B1), and setting $s = 0$ yields

$$\mu_2 = \frac{1}{(R-1)} \left( \frac{1}{k} \frac{\partial v_2}{\partial t} + v_2 \right) \quad (B2)$$

$$v_1(t = 0) = 0 \quad \mu_2(t = 0) = 0, \quad (B3)$$

Letting the initial conditions for the first moments be

$$v_2(t = 0) = 0 \quad \mu_2(t = 0) = 0,$$

the solutions to (B2) and (B3) are developed after substituting the transient solutions for the zeroth moment $\mu_0$ and the first moment $\mu_1$.

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