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Wavelet-based Spatiotemporal Multiscaling in Diffusion Problems with Chemically Reactive Boundary

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ABSTRACT

Chemically reacting flows over catalytic and noncatalytic surfaces are one of the elementary operations in chemical processing plants. The underlying physical phenomena span time and length scales over several orders of magnitude, which a robust and flexible modeling framework must efficiently account for. With this purpose as the eventual goal, we propose a wavelet-based multiscale numerical framework and demonstrate it on the coupling of two prototype methods for the problem of species generated on a chemically reactive boundary and diffusing through the bulk. The two methods consider different time and length scales. The first method in this coupling, termed “fine,” models the chemical reactions on the reactive boundary stochastically by the kinetic Monte Carlo method and the diffusion in the medium deterministically using relatively small time increments and small spatial discretization mesh size. The second method, termed “coarse,” models both the reaction and the diffusion deterministically and uses drastically larger time increments and spatial discretization size than the fine model. The two methods are coupled by forming a spatiotemporal compound wavelet matrix that combines information about the time and spatial scales contained in them.

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1. INTRODUCTION

A demanding challenge in many branches of physical science is to bridge as seamlessly as possible the appropriate range of length and time scales that are relevant to a problem. Reactive flow over a catalytic surface is such a multiscale, multiphysics problem involving the interaction of distinctly different types of processes such as wall (boundary) chemical reactions, reactant species transport, fluid motion, and fluid-boundary (wall) interaction. Each of these processes involves characteristic time and length scales that evolve with local thermodynamic and chemical conditions. We describe a procedure here that links spatiotemporally the first two of the four above processes, i.e., boundary reactions and transport of species. The former process is, in general, microscopic and the latter one mesoscopic. Fluid motion and fluid-boundary interactions are, in general, macroscopic and are not addressed in the present study. Our aim is rather to illustrate the process of the wavelet-based multiscaling in one spatial dimension (in a way that is extendable to higher dimensions).

For problems of diffusion of species from a reactive boundary to the bulk, the time scales in the chemical reactions, modeled herein by the kinetic Monte Carlo method (KMC), are usually much smaller than the time scales involved in the diffusion, which can also extend over a large spatial domain. For the case at hand, namely, diffusion of species in 1D from a reactive boundary, temporal scaling is of prime importance since time scales of two different techniques are to be bridged, while the spatial scales are involved only in the coarse domain, i.e., in the governing equation for diffusion (the reaction and diffusion domains intersect only at the reactive boundary).

Multiscaling has recently received increasing attention in several branches of physical science. A large part of the work is devoted to modern simulation methods involving the coupling of length scales and sometimes time scales. Simulation methods for coupling length scales can be characterized as either sequential or concurrent. In sequential methods, a set of calculations at a fundamental level (small length scale) is used to evaluate parameters for use in a phenomenological model at a longer length scale. For example, atomistic simulations can be used to deduce constitutive behavior of finite elements, which are then used to simulate larger-scale problems [1,2] where, traditionally, modelers have been using molecular properties and other parameters derived from experiments.

Concurrent methods rely on seamlessly coupling different computational methodologies applied to different regions of a material. For example, crack propagation is a problem that was tackled early on by multiscale methods [1,3]. Atomic simulation techniques (molecular dynamics) were used to model the crack tip where large deformations (even bond breakage) occur and continuum approaches [finite element (FE) methods] were used to model the region far away from the crack tip.

A recent relatively general review on multiscale methods citing over 200 works is that of Vvedensky [4]. Discipline-specific review papers are also available in the literature, e.g., in general chemical engineering [5], surface science [6], reactor technology [7], heat transfer and thermal modeling [8,9], and works implementing general approaches such as gap tooth and time stepping [10,11]. A general multiscale methodology based on wavelets has been examined for both spatial scales [12–15] as well as temporal scales [16]. These works fully take advantage of the inherent capabilities of wavelet analysis to represent objects in a multiscale fashion. The wavelet-based approach, termed the compound wavelet matrix (CWM) method, establishes a communication bridge between phenomena at different scales. In this sense, some similarities between the CWM and the so-called heterogeneous multiscale methodology (HMM) [17] can be identified, namely, in the sense that the influence of small scales on large-scale behavior and vice versa can be identified by the methods.

For either CWM or HMM, however, there is not a single universal framework applicable and efficient to a variety of problems. The specific formulation and implementation of either method affects the way information can be transferred from fine to coarse scales and vice versa, or whether information at all scales becomes available, i.e., without transfer of information along scales. For example, the time-scaling approach reported herein for the diffusion problem with a reactive boundary is quite different from the one for the dispersion problem reported in [16], even though both are based on the CWM.

The remainder of this paper first describes the two methodologies to be bridged in space and time,
followed by a description of the construction of the CWM and the information it contains. Examples illustrate the method and its efficiency and accuracy. Finally, conclusions and relevant open questions are presented and discussed.

2. MODELING THE CHEMICAL REACTIONS AND THE DIFFUSION OF SPECIES

The prototype problem of boundary reaction-diffusion is solved herein by operator splitting [18]. That is, the reaction operator at the spatial boundary of the problem, described below, is applied first for a (small) time increment, and then the diffusion operator, also described below, is applied for the same time increment. The only difference from traditional operator splitting is that the reaction and diffusion operators overlap at the boundary node, while only the diffusion operator is active away from the boundary. The process is repeated in this segregated fashion till the desired stopping time for the simulation, which yields the final results. The chemical reactions on the surface are handled by either simple integration of the reaction kinetic equations or by the KMC, depending on the coarse or fine model, respectively. The discretized version of the diffusion equation is solved by finite differences. The choice or simplicity of the examples along with selection of the fine and coarse models is not tied with the coupling model illustrated in this paper, and the purpose is to illustrate the effectiveness and feasibility of the multiscale methodology on prototypical problems.

The theoretical framework within which the chemical processes at a boundary are treated is that of reaction kinetics. First-order reactions are considered in this work, i.e., ones where the reaction rate is proportional to the concentration of the reactant to the first power. For reversible reactions such as

\[ A \xrightarrow{k_{AB}} B \]

\[ B \xrightarrow{k_{BA}} A \]

the first-order rate constants \( k_{AB}, k_{BA} \), each of inverse time units, define the reaction kinetics governed by

\[
\frac{d[A]}{dt} = -k_{AB} [A] + k_{BA} [B] \\
\frac{d[B]}{dt} = -k_{BA} [B] + k_{AB} [A]
\]

Straightforward integration yields the following analytical equations for the two species concentrations as a function of time:

\[
[A] = [A_0] e^{-(k_{AB} + k_{BA})t} + \frac{k_{BA} ([A_0] + [B_0])}{k_{AB} + k_{BA}} \left( 1 - e^{-(k_{AB} + k_{BA})t} \right) \\
[B] = [A_0] + [B_0] - [A]
\]

where \([A_0], [B_0] \) denote the initial concentration of \([A], [B] \), respectively, i.e., at \( t = 0 \). From Eq. (3), the time intervals \( t_{AB}, t_{BA} \) for the reaction process to change the concentration of species \([A]\) from \([A_1]\) to \([A_2]\) and of \([B]\) from \([B_1]\) to \([B_2]\), respectively, can be evaluated. Since no stochasticity is imparted in the simulation for determining the reaction time, simulations based on (1)–(3) are referred to as deterministic in the following and represent the coarse model.

The stochastic formulation of (1) yielding a KMC process is based on the probability distribution function for reaction events [19] expressed by an exponential distribution, which yields the reaction times for a unit change in the concentration of \([A], [B] \) as

\[
t_{AB} = -\frac{1}{k_{AB} [A]} \ln(1 - R_1) \\
t_{BA} = -\frac{1}{k_{BA} [B]} \ln(1 - R_2)
\]

where \( R_1 \) and \( R_2 \) are independent uniformly distributed random numbers between zero and unity. At any time in the simulation, the reaction that requires the least time is the one that will occur. Thus, at every KMC iteration step, two random numbers are generated, i.e., \( R_1, R_2 \), and \( t_{AB}, t_{BA} \) are evaluated based on Eq. (4). The minimum of \( t_{AB}, t_{BA} \) is the time increment associated with the selected reaction event. The KMC model simulates the reaction kinetics in the coarse model. At every time step, the above procedure is executed to give the new species concentrations on the boundary node and are coupled to the diffusion process by operator splitting as described before. The details of the diffusion model implementation are described below.

Mass transport of the reactive species \( A \) and \( B \) are described within the theoretical framework of diffusion. The governing equations for the diffusion of species in the \( x \) direction (1D diffusion) read as
where \( D_A, D_B \) denote the diffusion coefficients, considered constant, for the spatially varying (function of \( x \)) concentration of \([A], [B]\), respectively. Various numerical methods can be employed for solving Eq. (5). Here, we use a finite difference explicit Euler scheme, first-order in time and second-order in space, with fixed time steps and fixed spatial discretization. As mentioned before, the choice of the method is only to construct a simple prototype solution algorithm to test the coupling strategies, and not to efficiently solve each of the components. For stability of the numerical integration process, the inequality

\[
\frac{2D(\Delta t)}{(\Delta x)^2} < 1
\]

should be satisfied, where \( \Delta t, \Delta x \) denote the time increment and spatial discretization size, respectively, and \( D \) is the diffusion coefficient for either the first or the second equation in (5). In this work, the diffusion of species in the \( x \) domain is considered deterministic. The stochastic version of the diffusion process yields a Brownian motion process [20], not examined herein.

The two theoretical frameworks, reaction kinetics and mass transport, serve as the foundations of a model of a chemically reactive boundary with diffusive species to and from the boundary. The spatially 1D model considered here consists of the semi-infinite positive half space (diffusion domain) with chemical reactions taking place at the origin (reac\(t\)ion domain). The boundary condition at the reactive site is that both \( A, B \) are specified by the values evaluated from the reaction kinetics during the operation-splitting process. At the far end of the discretized diffusion problem (far from the reactive site), the species are absorbed. Note that for both the fine and coarse grid results described below, the species did not reach the far boundary during the total time for which the problem was solved. In addition, note that the diffusion process is transporting the species away from the boundary and, in a general case where transport of species occurs both ways, a flux boundary condition should be imposed to ensure mass conservation.

3. BRIEF DESCRIPTION OF WAVELET ANALYSIS AND THE COMPOUND WAVELET MATRIX

Wavelet analysis is central to this work, and a variety of wavelet transforms exist [21]. In every case, the wavelets are derived from basic templates by taking scaled versions and placing them in many different positions; choosing an appropriate wavelet family for a specific problem is, in many respects, similar to choosing an appropriate element for a finite element numerical solution process. The complete family of an elementary function contains large-scale and fine-scale wavelets. The major advantage is that this enables one to see broad features on a wide scale while studying fine features one small piece at a time, so that the interaction between small- and large-scale features can be studied.

Here, we provide an abbreviated summary on wavelet transforms while the reader is referred elsewhere [21] for more in-depth study. In one dimension (extendable to higher ones), a wavelet \( \psi(x) \) transforms a fluctuating function \( f(x) \) as

\[
W_f(a, b) = \int_{-\infty}^{\infty} f(x) \psi_{a,b}(x) \, dx
\]

The two-parameter family of functions, \( \psi_{a,b}(x) = (1/\sqrt{a}) \psi ([x-b]/a) \) is obtained from a single one, \( \psi_0 \), called the mother wavelet, through dilatations by the scaling factor \( a \) and translations by the factor \( b \). The factor \( 1/\sqrt{a} \) is included for normalization. The parameter \( a \) can take any positive real value, and the fluctuations of \( f(x) \) at position \( b \) are measured at the scale \( a \). When discretized, wavelet analysis can be performed with fast algorithms. In this work, a biorthogonal spline [22] was used as the mother wavelet, of order \( (10,4) \), which preserves symmetry without sacrificing orthogonality; the orders “10,4” are related linearly to the order of the splines used and to the vanishing moments in the dual biorthogonal wavelet basis [21,22].

Given the wavelet coefficients \( W_f(a, b) \) associated with a function \( f(x) \), it is possible to reconstruct \( f \) at a range of scales for \( x \) between \( s_1 \) and \( s_2 (s_1 \leq s_2) \) through the inversion formula

\[
f_{s_1,s_2}(x) = \frac{1}{c_\psi} \int_{s_1}^{s_2} \int_{-\infty}^{\infty} W_f(a, b) \psi_{a,b}(x) \, db \, da
\]
where \( c_{i0} \) is a constant evaluated from the properties of the wavelet function used in (8). A two-dimensional wavelet transform includes transforms in the \( x \) direction, the \( y \) direction, and in the diagonal \( x-y \) direction. The latter is done by constructing wavelet bases from the tensor products of the one-dimensional wavelets in the \( x \) and \( y \) directions. For example, given an image of \( 512 \times 512 \) pixels, the discrete wavelet transform consists of three \( 256 \times 256 \) matrices (one in each direction), three \( 128 \times 128 \) matrices, and so on; each decomposition level is at half the resolution from the previous one. The final level of decomposition represents the image at the coarsest resolution.

Given a function, e.g., the concentration of species in space and time, which is highly hierarchical, its features over a range of length and time scales can be studied with wavelet analysis. Wavelets enable one to overcome the immense difficulty of performing numerical simulations on problems containing features at scales spanning more than a few orders of magnitude. It is feasible, however, to perform appropriate simulations at various scales and thus obtain the function as it appears at these scales. The information gained at each of the scales is then used to synthesize, thereby forming the CWM, the complete function. The region in space and in time where two methods used at different scales overlap provides the framework for their coupling. Synthesizing of information in the overlap region may be pursued through either the fine scales, the coarse scales, or from a combination of the two, depending on the accuracy of each method as well as on the type of information that is matched in the overlap region (e.g., enforcing conservation laws or the second law of thermodynamics). This issue is addressed and discussed in more detail below.

4. COMPOUNDING INFORMATION FROM TWO MODELS

In order to solve the problem of diffusion of species from the reactive boundary, we consider two models addressing a diverse range of time and spatial scales. The first one, termed fine, utilizes the KMC methodology for the reactions and the finite difference numerical solution for the diffusion of species. The governing time increment is, under normal circumstances, that of the KMC. The average time increment for this method, denoted as \( \langle \Delta t_1 \rangle \), is used in conjunction with (6) for the spatial discretization \( \Delta x_1 \). Thus, this method uses relatively small time increments \( \Delta t_1 \), small spatial discretization size \( \Delta x_1 \), and the system is solved for a total time \( T_1 \) and total spatial domain \( X_1 \) that are both relatively small, as dictated by computer power, for example. Of course, for the “simple” 1D case examined herein and first-order reactions, computer power is not an issue. The purpose here is to formulate and illustrate the multiscale process, the ultimate goal being the simulation of flow over catalytic surfaces in multiple spatial dimensions with accurate coupling between the physics at atomistic and fluid flow scales.

The second model, termed coarse, includes the deterministic representation of the reactions and the diffusion using finite differences in the \( x \) domain. Here, the time increment used, \( \Delta t_2 \) is much larger than \( \Delta t_1 \). In fact, we consider \( \Delta t_2 \) to be a relatively large fraction of \( T_1 \) (end time of fine solution) and, accordingly, the spatial discretization \( \Delta x_2 \) is a relatively large fraction of \( X_2 \). For obvious reasons, the accuracy of this coarse solution process is far inferior to the accuracy of the fine one. However, at long times, i.e., as the system marches toward equilibrium, the accuracy of the coarse solution process increases significantly, as subsequently illustrated. This, together with a CWM composed from overlapping components taken from the two solution processes, allows for an efficient multiscale methodology. The remainder of this paper is primarily devoted to illustrating this basic idea.

Before presenting results, we briefly describe the process of forming the CWM. The solution of the 1D problem yields the concentration of either species \( A \) or \( B \) as a function of the spatial coordinate \( x \) and time \( t \), i.e., it yields \( C(x, t) \) where \( C \) denotes the concentration of species \( A \) or \( B \). The wavelet transform of \( C(x, t) \) in the 2D, i.e., \( x - t \), space yields a decomposition of \( C(x, t) \) in space scales as well as in time scales. The wavelet transform of \( C(x, t) \) includes a transform in the \( x \) direction, one in the \( t \) direction, and one in the \( x - t \) direction. Figure 1(a) schematically illustrates the complete wavelet transform of \( C(x, t) \) as it would be obtained by extending the fine solution process to long time scales and large spatial scales. Such extensions, however, are not possible when computer power is limited; therefore, the substitutions from the fine solution process, Fig. 1(a),
FIGURE 1. (a) Schematic of wavelet transform of $C(x, t)$ obtained from the fine solution process, i.e., for short time scales and small spatial scales; (b) Schematic of wavelet transform of $C(x, t)$ obtained from the coarse solution process, i.e., for long time scales and large spatial scales; (c) CWM formed by transferring information from scales corresponding to parts (a) and (b). Only a few substitutions are shown for illustration. In all matrices, the horizontal axis denotes space $x$, and the vertical axis denotes time $t$. At each scale, the wavelet transform consists of three submatrices, i.e., one denoting the transform in the $x$ direction, one in the $t$ direction, and one in the diagonal $x - t$ direction. Coarse scales are toward the bottom and left, and fine scales toward the top and right.

and from the coarse one, Fig. 1(b), are made to form the CWM, Fig. 1(c).

For the problem herein, information is obtained on a grid as shown in Fig. 2. Note that the two simulation techniques should have an overlap region in both time and space, which is crucial for a robust formation of the CWM [12,16]. For the problem herein, the overlap region is defined in time as the interval from $\Delta t_2$ to $T_1$ and in space as the interval from $\Delta x_2$ to $X_1$. It is possible to match $C(x, t)$ and its spatial and temporal derivatives in the overlap region; this is addressed briefly in the last section. In the present work, however, the concentration $C(x, t)$ in the overlap region is obtained from the more accurate (fine-scale) solution method in forming the CWM. Thus, the main purpose of the overlap in this case is to improve the accuracy of the coarse method to appropriate levels by inclusion of the fine-scale information. When considering $C(x, t)$ at either a fixed value of $x$, $x_0$, or a fixed value of $t$, $t_0$, i.e., $C(x_0, t)$ or $C(x, t_0)$, respectively, the problem becomes one-dimensional, and a compound wavelet vector is formed rather than a CWM. Time scaling is of primary importance for the problems addressed herein. Thus, we focus on $C(x_0, t)$, using specific values for $x_0$, which also offers the simplicity of working in one dimension; however, for generality, we retain the abbreviation CWM instead of referring to a compound wavelet "vector."

For all the illustrations presented in the following, the reactive boundary is at $x = 0$ and the spatial domain extends from $x = 0$ to $x = L$, where $L$ denotes a large value of the spatial coordinate $x$. Unless otherwise specified, the fine solution method uses KMC at the reactive boundary, while the coarse method uses the deterministic solution of the first-order reaction. Both methods use a finite difference explicit Euler scheme for the solution of the diffusion equation, which is first order in time and second order in space, with fixed time steps and fixed spatial discretization. The solution process has also been implemented using finite elements in space and explicit integration in time using an infinite element at $x = L$, thus simulating a species-absorbing condition there. Comparison of the process for formation of the CWM using finite elements and finite differences is quite involved and will be presented elsewhere.

The spatial extent $L$ is not the same for the fine and coarse grid solution processes. In fact, the compounding technique is designed to be effective for $L$ in the coarse grid method, $L_c$ being much larger...
than the $L$ in the fine grid one, $L_f$. The large value of $L_c$ justifies the absorbing of species there. However, should species reach $L_f$ during the time period in which the fine grid process is solved, an improved boundary condition at $L_f$ calls for obtaining the concentration of species there from the coarse grid solution process. This and other related issues are discussed in the last section of this paper. A much simpler approach, followed herein, calls for ensuring that $L_f$ is large enough that species do not reach it during the solution time for the fine grid. Given the short time periods in the fine grid process, this does not increase the computational time of the compounded solution process and generates fine field species to be used in the CWM.

**Illustration I**

As a first illustration, we consider, in arbitrary units of space and time, $k_{AB} = k_{BA} = 1.0$/unit time, $D_A = D_B = 0.05$ (unit space)$^2$/unit time. For the KMC, the process is solved for 2048 iterations, and for the diffusion in the fine solution process, $\Delta x_1 = 0.125$, $X_1 = 2000 * \Delta x_1$. As mentioned before, note that the time increments for the KMC are not constant; thus, $T_1 = 2048 * (\Delta t_1)$. By carrying out the KMC over 2048 time steps, we find that $\langle \Delta t_1 \rangle \approx 0.04516$. For the coarse solution method, $\Delta x_2 = 0.625$, $\Delta t_2 = 1.045$, $X_2 = 4000 * \Delta x_2$, $T_2 = 2138 * \Delta t_2 = (2048 + 90) * \Delta t_2$. The overlap between the two methods in time is over 90 intervals in the coarse method, i.e., $\Delta t_2 = T_1/90$. The overlap in space is $X_1/\Delta x_2 = 400$ intervals in the coarse method. The initial concentrations (at time $t = 0$) of species at the boundary $x = 0$ are $A(0, 0) = 100.0, B(0, 0) = 0.0$. Also, no species are present in the diffusion domain at $t = 0$; thus, $A(x, 0) = B(x, 0) = 0, 0 < x \leq L$. The choice of appropriate values for the spatial and temporal scales in the two methods should be determined by the length and time scales corresponding to the physics, simulation strategy, and desired error bounds. In this simple prototypical example, a more ad hoc choice is made to test the capabilities of the compounding scheme. For the results presented herein, the fine method is first discretized adequately in space and time so that the error is small enough or negligible. The search for adequate discretization of the coarse method starts by first assigning $\Delta t_2 \sim T_1, \Delta x_2 \sim X_1$ and then increasing the discretization overlap in both space and time. A relevant error estimation process is presented with respect to illustration II below for which an analytical solution is available.

Figure 3(a) shows the concentration of $A$ at $x = 0$, i.e., $A(0, t)$, as obtained by the fine and coarse solution methods. As expected, the coarse method is not accurate for short times, while it becomes more accurate as the system marches toward equilibrium.
FIGURE 3. (a) $A(0, t)$ resulting from the fine and coarse models. (b) $A(0, t)$ after performing the inverse wavelet transform of the CWM, for $m = 2$. (c) Same as part (b), for $m = 4$. (d) Same as part (b), for $m = 5$. (e) Same as part (a), where the only parameter change is in the coarse method, where the spatial discretization is twice as large as the one that was used for producing (a). (f) Detail of part (c) in the vicinity of $t = T_1$, for $m = 5$, showing artificially large fluctuations for a short period of time. (g) Same as part (b), for $m = 0$. (h) $A(0, t)$ after interpolating the coarse method solution and performing the inverse wavelet transform of the CWM, for $m = 2$. (i) Same as part (h), for $m = 4$. (j) Same as part (h), for $m = 5$. 
In fact, from Fig. 3(a) and also from Fig. 3(e) described below, it is clear that the surface concentration for the coarse grid solution falls more slowly than in the fine one. This is due to an underestimation of the flux (gradient) at \( x = 0 \) (which is better estimated on the fine grid—hence the faster fall in concentration.)

The coarse process extends over long period of time, up to a total time of \( T_2 = 2138 \times \Delta t_2 = 2234 \) time units; a shorter time period is shown in Fig. 3(a) for clarity. It is important to note that the time overlap between the two methods is decisive with respect to the accuracy of the coarse method. Since here \( \Delta t_2 = T_1/90 \) was used, there is relatively large overlap (no overlapping would imply \( \Delta t_2 \geq T_1 \)). It is noted that the overlap in relation to the spatial and temporal discretization for the coarse method is crucial, as illustrated in Fig. 3(e) where spatial resolution has been halved. If a lower spatial resolution [Fig. 3(e)] is used, an increased temporal overlap is needed to compensate for the reduced spatial information.

\[ A(0, t), \quad 0 < t \leq T_1 \] is discretized in \( 2^{11} = 2048 \) intervals under the fine solution process; thus, its wavelet transform \( W_{A(0, t)}^1(a, t), a \) denoting scale, contains 11 scales, 11 being the finest scale and 1 the coarsest. Similarly, \( A(0, t), \quad \Delta t_2 < t \leq T_2 \) is discretized in \( 2^{14} + 90 \) intervals under the coarse solution process. The first 90 intervals were used to increase the accuracy of the coarse solution process; thus, its wavelet transform \( W_{A(0, t)}^2(a, t) \), performed over the 2048 points, contains 11 scales as well. Note that the scales in \( W_{A(0, t)}^2(a, t) \) are different from those in \( W_{A(0, t)}^1(a, t) \). These two transforms are compounded in accordance to their scales, and the inverse wavelet transform is performed. Furthermore, the wavelet coefficients in \( W_{A(0, t)}^1(a, t) \) representing the finest scales, and thus the highly oscillating fluctuations, are substituted in their corresponding positions in \( W_{A(0, t)}^2(a, t) \) before the inverse wavelet transform is performed. Let \( m \) denote the number of fine scales for which this substitution is performed. Figure 3(b) shows the results from the inverse wavelet transform for \( m = 2 \). Note that for the part inside the ellipse in Fig. 3(b), the plot discretization in time is \( \Delta t_2 \), while to the left of that, i.e., for \( t < T_1 \), the discretization is \( \Delta t_1 \). As a result, it appears that the pattern of the fluctuations changes abruptly (at the left end of the ellipse), while this is not the case. Figures 3(c) and 3(d) are similar to Fig. 3(b), yet for \( m = 4, 5 \), respectively. Finally, it is noted that the inverse wavelet transform extends in time to \( T_2 = 2138 \times \Delta t_2 = 2234 \) units of time, yet only a fraction of that is shown for clarity.

As \( m \) increases, the information at long times is distorted, partly because the inverse wavelet transform has to match the values at the intersection of the two solution techniques. Figure 3(f) shows the details. Figure 3(g) shows the inverse wavelet transform for \( m = 0 \), i.e., no fluctuations are transferred as in Figs 3(b)–3(d). These results indicate that \( m = 2 \) or \( 3 \) is an appropriate optimum choice for the present problem.

In the results presented in Figs. 3(b)–(d), it is saliently assumed that the fluctuations in \( A(0, t) \) scale invariantly as the discretization scale changes from \( \langle \Delta t_1 \rangle \) to \( \langle \Delta t_2 \rangle \). This assumption can be alleviated by interpolating the coarse solution to the discretization of the fine solution and plotting results as those in Figs. 3(b)–3(d). Such plots are shown in Figs. 3(b)–3(j), where a cubic polynomial interpolation was performed on the data from the coarse solution, and then the substitution of coefficients for various values of \( m \) was performed prior to evaluating the inverse wavelet transform of the CWM. This process assumes that \( \langle \Delta t_1 \rangle \) remains the same in the solution regime of the fine and of the coarse method, even though \( \langle \Delta t_1 \rangle \) increases as time marches. Thus, in a sense, Figs. 3(b) and 3(g) provide bounds in the statistics of the fluctuations of \( A(0, t) \) in the coarse time regime.

For the illustration presented in this subsection, there is no analytical solution available to compare it to the CWM one. However, as expected, the fine solution process is much more accurate than the coarse one, especially for short time periods. By running the fine solution process for the entire time period \( T_2 \), it is easy to verify the efficiency of the CWM technique. Note that the extension of the fine method to longer times, i.e., from Fig. 3(a), can be easily visualized. If, however, the CPU time is considered to follow a relation of the form \( \text{CPU} \sim n_x^\alpha \cdot n_t \), where \( n_x \) denotes the number of spatial discretization points, \( n_t \) the number of time steps, and \( \alpha \) is a constant greater than unity, it is easy to evaluate that the CWM offers a gain of at least 2 orders of magnitude in CPU even for this problem, where quite large overlap was considered. For problems in higher spatial dimensions, the gain is expected to
be higher, i.e., on the order of at least 3 or even 4 orders of magnitude, even for $\alpha$ not much larger than unity.

In the following, a relevant problem for which an analytical solution is available is presented. Before this, it is noted that the diffusion part of the problem damps the fluctuations coming from the KMC. Figure 4 illustrates this by showing the concentration of $A$ at $x = 20$ spatial units as a function of time as obtained from the fine solution process. The formation of the CWM for $x = 20$, not shown for compactness, yields satisfactory results as for $x = 0$; a relevant illustration is presented in the following subsection.

Figure 5 shows a phase-time density plot of the wavelet coefficients for the fine and coarse processes. Note that the fine solution shows information at all scales, while the coarse one only at coarse scales. The fact that $m = 2$ or $3$ provides the best solution for the entire compounded process verifies the fact that the fluctuations in the fine process are of white noise type, i.e., uncorrelated in time. This is because for white noise, the energy of the wavelet transform is concentrated at fine scales, mostly on the finest 2 or 3 scales. As time correlations increase, the energy of the wavelet transform “spreads” toward the coarser scales.

Illustration II

As a second illustration, we consider a relevant problem for which there is an analytical solution. For a boundary condition of the form $A(0, t) = \alpha e^{\gamma t}$ and initial condition $A(x, 0) = 0$, there exists an analytical solution of the diffusion problem, where $\alpha$ and $\gamma$ are constants ($\gamma$ can be either positive or negative) [23]. Such a deterministic boundary condition implies, from the reactive boundary problem perspective, that the species source on the boundary is large enough that the diffusing species does not change the surface concentration appreciably. Even though this may not exactly represent the reactive/diffusing conditions under illustration I, the existence of an analytical solution makes its examination attractive. It turns out that both the solution for $A(0, t) = \text{constant (}\gamma = 0\text{)}$ and for $\gamma \neq 0$ illustrate the CWM process equally well. Thus, for this illustration, we consider the following values for the fine and coarse solution processes. Table 1 shows
TABLE 1. Values used for the fine and coarse solution processes

<table>
<thead>
<tr>
<th>Description</th>
<th>Fine method</th>
<th>Coarse method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time increment (s)</td>
<td>$\Delta t_1 = 0.001$</td>
<td>$\Delta t_2 = 0.4$</td>
</tr>
<tr>
<td>Total time (s)</td>
<td>$T_1 = 0.4$</td>
<td>$T_2 = 20.0$</td>
</tr>
<tr>
<td>Spatial Discr. (µm)</td>
<td>$\Delta x_1 = 14.2$</td>
<td>$\Delta x_2 = 213.0$</td>
</tr>
<tr>
<td>Total length (µm)</td>
<td>$X_1 = 1420.0$</td>
<td>$X_2 = 2130.0$</td>
</tr>
<tr>
<td>Diffusion Coeff. (µm²/s)</td>
<td>$5 \times 10^4$</td>
<td>$5 \times 10^4$</td>
</tr>
<tr>
<td>$\alpha$(mol), $\gamma = 0$</td>
<td>$10^4$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>$2D\Delta t/\Delta x^2$</td>
<td>0.49</td>
<td>0.94</td>
</tr>
</tbody>
</table>

the values used for the fine and coarse solution processes.

As can be seen, for this problem, there is no overlap between the two methods in time, yet there is a small overlap in space. In fact, the coarse method with the values used is not accurate for short times, yet not numerically unstable. Furthermore, the fine method was solved for a relatively short time $T_1$ in order to investigate the behavior of the method toward its limits of effectiveness. The effectiveness of the method as the overlapping between the two methods changes is addressed in more detail at the end of this subsection.

Both methods were implemented using the same finite difference algorithm as in illustration I above. However, it was solved numerically using built-in routines in the program MATHEMATICA, which yields the solution as an interpolation function. As a result, the solution can be obtained at any time $(0 \leq t \leq T_1$ for the fine method and $0 \leq t \leq T_2$ for the coarse method), and it can be discretized to any number of points (without increasing the accuracy, of course, since discretization is based on a fixed interpolating function).

Figure 6 shows the solution obtained from the fine and coarse methods in their respective $x$ and $t$ domains. The two methods differ significantly for short times and differ much less as the system approaches equilibrium. Figure 7(a) shows the solution at a specific $x$ value, i.e., $x = 213.0$ µm, as obtained from the two methods for a total time of 0.4 s (the coarse method solution is expressed through the interpolating function solution in this time interval) as well as the analytical solution expressed as

$$A(x, t) = A(0, t) \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right)$$

(9)
FIGURE 7. (a) $A(213.0, t)$ resulting from the fine solution process (bottom curve), the coarse solution process (top curve), and from the exact solution (practically identical to the one from the fine solution). (b) Exact solution (bottom curve) and coarse solution (top curve) at $x = 213.0 \mu m$ for time between 0.4 and 4 s. (c) Plot of $A$ at $x = 213.0 \mu m$ as obtained from the inverse wavelet transform of the CWM (top line) and exact solution obtained from Eq. (9) (smooth line). (d) Detail of part (c) at the time the two methods intersect in time, i.e., at 0.4 s

where erfc denotes the complementary error function. Figure 7(b) shows that the accuracy of the coarse solution increases as time marches toward equilibrium.

The CWM is formed, for the solution $A(213.0, t)$, using 2048 discretization points in time for each solution process. However, since both the fine and coarse methods are deterministic with relatively smooth solutions in both space and time, the small-scale wavelet coefficients from both fine and coarse methods contain very little information about the solution. Thus, substitution of wavelet coefficients from the fine to the coarse method can be omitted without any significant loss of information from the compounded methods.

After forming the CWM, its inverse wavelet transform provides $A(213.0, t)$ at the union of time scales handled by each method. Figure 7(c) shows the result of this transformation and how it compares to the exact solution. Again, at the intersection of the two methods, sort of the handshake region between the fine and coarse solution methods, each method has to adjust in order to perfectly match each other, as shown in Fig. 7(d).

The effectiveness of the method increases with the overlap between the two methods. Figure 8 shows results similar to those of Fig. 7, yet the time overlap is increased by assigning $\Delta t_2 = 0.1$, and all other parameters remain the same (thus, the overlap on space remain the same). Obviously, the efficiency of the method increased. Yet, further increase in overlap not only increases the efficiency minimally, but fluctuations and thus error in the handshake regime between the two methods remains, as illustrated in Fig. 9, which shows results similar to those in Fig. 8; yet the time overlap is increased further by assigning $\Delta t_2 = 0.01$, and all other parameters remain the same. In short, there is room for improvement of the technique, and some suggestions appear in the following section. At this point,
FIGURE 8. Results, as those in Fig. 7, for increased time overlap between the two methods as described in the text. (a) $A(213.0, t)$ resulting from the fine solution process (bottom curve), the coarse solution process (top curve), and from the exact solution (practically identical to the one from the fine solution). (b) Exact solution (bottom curve) and coarse solution (top curve) at $x = 213.0$ µm for time between 0.4 and 4 s. (c) Plot of $A$ at $x = 213.0$ µm as obtained from the inverse wavelet transform of the CWM (top line) and exact solution obtained from Eq. (9) (smooth line). (d) Detail of part (c) at the time the two methods intersect in time, i.e., at 0.4 s

it is mentioned that a minor improvement calls for performing the wavelet transform on an interval instead of assuming the fixed boundary conditions used herein (fixed value at the boundary equal to the value of the analyzed function there) or periodic boundary conditions.

Error and convergence analysis of the CWM technique is not similar to that often used in single-scale finite difference or finite element techniques. The reason for this is that the solution depends on the spatial discretization of each of the two methods, the temporal discretization of each of the two methods, and the relevant overlap. All these affect error and convergence. Even though sophisticated procedures can be employed, here, for illustration, the spatial discretization is fixed and the behavior of the solution with respect to the temporal discretization is examined. Thus, for the values of the constants as in illustration II, let us consider $\Delta x_1 = 64.2$ µm, $\Delta x_2 = 205.9$ µm, and four pairs of $\Delta t_1$, $\Delta t_2$, i.e., $\{0.001, 0.01\}$, $\{0.005, 0.05\}$, $\{0.01, 0.1\}$, $\{0.04, 0.4\}$. For each of the four pairs, the same process as in illustration II is followed and from the inverse transform of the CWM the relevant solution $A(213.0, t)$ is obtained. Let $A(213.0, t)$ be denoted as $J \rightarrow$ solution form the numerical CWM method $J \rightarrow$ exact solution

The norm

$$N_i = \left\| \frac{J - \hat{J}}{J} \right\|_i$$

where $i$ denotes the order of the norm, is a measure of error and can also be used for examining the rate of convergence. Figure 10 shows relevant results for $i = 1$ and $i = 2$. Note that even though the error drops fast as the temporal discretization de-
FIGURE 9. Results, as those in Fig. 8, for further increased time overlap between the two methods as described in the text. (a) $A(213.0, t)$ resulting from the fine solution process (bottom curve), the coarse solution process (top curve), and from the exact solution (practically identical to the one from the fine solution). (b) Exact solution (bottom curve) and coarse solution (top curve) at $x = 213.0$ µm for time between 0.4 and 4 s. (c) Plot of $A$ at $x = 213.0$ µm as obtained from the inverse wavelet transform of the CWM (top line) and exact solution obtained from Eq. (9) (smooth line). (d) Detail of part (c) at the time the two methods intersect in time, i.e., at 0.4 s.

FIGURE 10. Log-log plot of $1/\Delta t_1$ versus normalized error in the form of a norm. (a) $1/\Delta t_1$ versus $N_1$. (b) $1/\Delta t_1$ versus $N_2$. 
creases, further decrease does not improve the (already small) error. This is because for this example, the spatial discretization is fixed, thus the analytical solution can only be reached to a certain level.

**DISCUSSION AND CONCLUSIONS**

The purpose of this paper is to introduce and examine the idea of utilizing the CWM as means for addressing temporal as well as spatial scaling in boundary reaction-diffusion problems. The results are encouraging and show the great utility of wavelet analysis as a multiscale tool capable of synthesizing information along scales and transferring information as needed.

The overlap between the fine method (involving stochastic input and output) and the coarse one (deterministic, much more computationally efficient) could be handled adaptively, increasing the overall efficiency and accuracy of the combined simulation. Since the coarse method is computationally efficient, it can be run concurrently with the fine one until a satisfactory overlap region is established. A satisfactory overlap region should preferably match the relevant concentrations and their spatial and temporal derivatives from the two methods, as well as ensure complete overall conservation of appropriate quantities such as mass and energy. This is presently being investigated and will be presented elsewhere. Furthermore, constrained superposition of the wavelet transforms from each scale offers a potentially efficient way to address the overlap regime issue, and the appropriate rules for doing this are also being investigated. Finally, since the coarse method is computationally efficient, the two methods might be alternated in time as shown schematically in Fig. 11. In effect, the statistics of the small-scale fluctuations may change with time, and by alternating between the two models, such changes can be captured in the form of occasional updates to the CWM. The latter approach may be more efficient for highly nonlinear problems if appropriate criteria can be defined for indicating when updates are needed.

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