Diffusion Limited Kinetics Accounting for Reactive Species in 3D, 2D, and at 2D/3D Interfaces

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Abstract

Proper representation of chemical kinetics is vital to understanding, modeling and optimizing many important chemical processes. In liquid and surface phases, where diffusion is slow, the rate at which the reactants diffuse together limits the overall rate of many elementary reactions. Commonly the textbook Smolchowski theory is utilized to estimate effective rate coefficients in liquid phase. On surfaces, modelers commonly resort to much more complex and expensive Kinetic Monte Carlo (KMC) simulations. Here we extend the Smolchowski model to allow the diffusing species to undergo chemical reactions, and derive analytical formulae for the diffusion limited rate coefficients for 3D, 2D and 2D/3D interface cases. With these equations we are able to demonstrate that when species react faster than they diffuse they can react orders of magnitude faster than predicted by Smolchowski theory, through what we term "the reactive transport effect." We validate the derived steady state equations against particle Monte Carlo (PMC) simulations, KMC simulations and non-steady
state solutions. Furthermore, using PMC and KMC simulations, we propose corrections that agree with all limits and the computed data for the 2D and 2D/3D interface steady state equations, accounting for unique limitations in the associated derived equations. Additionally, we derive equations to handle couplings between diffusion limited rate coefficients in reaction networks. We believe these equations should make it possible to run much more accurate mean-field simulations of liquids, surfaces, and liquid-surface interfaces accounting for diffusion limitations and the reactive transport effect.

Introduction

Accurately determining the rate coefficients for chemical reactions is vital to understanding, modeling, and optimizing important chemical processes. Transition state theory\(^1\) has proven incredibly powerful for predicting the rate coefficients of chemical reactions accurately in a plethora of contexts.\(^2\) Broadly, canonical transition state theory calculates rate coefficients by examining individual reaction paths and assuming that the reactants are in equilibrium with the reaction path bottle neck, often referred to as the transition state and often equated with the highest energy point along the minimum energy path. By assuming statistical mechanical equilibrium, the population of this transition state can be estimated, and with suitable assumptions one can estimate the rate at which reactants will cross over to products.

Despite its tremendous popularity and success, the assumption that the transition state is in equilibrium with the reactants is often not true. In gas phase at high temperatures and low pressures, the high energy products of reactions often do not thermalize with the rest of the gas before reacting again, causing them to react at non-equilibrium energy distributions deviating significantly from canonical transition state theory.\(^3,4\) These non-equilibrium energy distributions create strong couplings among the phenomenological rate coefficients within a network of reactions, and can manifest "well-skipping” reactions between species that are not connected by a single transition state. Many techniques are available to account for these couplings\(^3-5\) and software are available for generating\(^6-8\) the networks of interest.
and calculating the rate coefficients.\textsuperscript{4,9,10}

In the liquid and surface phases thermalization is typically fast, however, mass transfer is slow. While in the gas-phase molecules are far apart, in liquid phase they are in constant contact with other molecules. This means that in order to bring two molecules in contact, all the molecules between them need to be displaced. For adsorbed species on surfaces, diffusing from one surface site to another has a significant barrier even if there are no other species on the surface. Consequently, as a fast reaction between two species

\[ A + B \rightarrow \text{products} \quad (1) \]

proceeds, \( A \) that are close to \( B \) and \( B \) that are close to \( A \) will tend to react with each other leaving us with the well separated \( A \)'s and \( B \)'s that are farther apart than one would expect statistically. This causes the concentration of \( A \) and \( B \) near each other to be lower than equilibrium, lowering the concentration of the transition state (which naturally requires \( A \) and \( B \) to be near each other) and slowing the reaction relative to the transition state theory prediction. This effect is quite significant when the reaction rate is fast compared to diffusion.\textsuperscript{11}

This effect is commonly accounted for using a model developed by Smoluchowski.\textsuperscript{12} In this model a single molecule of \( B \) is set at the origin of a 3D coordinate system and the radial concentration profile of \( A \) around \( B \) is modeled. The concentration of \( A \) is assumed to evolve according to Fick's second law. Far away from \( B \) it is assumed that the concentration of \( A \) equals the bulk \( A \) concentration. At some close distance \( R \) from the origin it is assumed that \( B \) reacts with the present \( A \) concentration at the transition state theory rate coefficient and that this reactive flux is equal to the diffusive flux. This forms a common textbook transport problem.\textsuperscript{13,14} Assuming the concentrations rapidly approach steady state one comes to the well known result

\[ k_{\text{eff}} = \frac{4\pi RDk_{\text{TST}}}{4\pi RD + k_{\text{TST}}} \quad (2) \]
where $k_{TST}$ is the transition state theory rate coefficient, $D$ is the diffusion coefficient and $k_{eff}$ is the effective phenomenological rate coefficient.

Much work has been done extending the Smoluchowski model to handle intermolecular interactions, higher order reactions, and surfaces.\textsuperscript{13,15–17} Freeman and Doll,\textsuperscript{17} in particular, extended the Smoluchowski model to surfaces. They arrived to the surprising conclusion that it is not possible to solve the original Smoluchowski model equations for 2D surfaces. However, they showed that the model can be solved when augmented with inter-phase transport processes between the gas and surface.

However, in many common systems there are many important reactions all occurring in parallel. Recently much work has been done on systematically constructing and simulating liquid phase chemical kinetic mechanisms.\textsuperscript{9,18–23} These approaches primarily use Equation 2 augmented with the work of Flegg\textsuperscript{16} for higher order reactions to represent diffusion limited kinetics.

Much work has also been done on constructing and simulating microkinetic models on surfaces.\textsuperscript{20,22,24–27} However, in addition to typical mean field models use in gas and liquid phases, since catalytic surfaces typically have well defined sites, it is possible to enumerate all the possible states of a reasonably sized slice of the system and simulate it using Kinetic Monte Carlo (KMC) techniques. KMC simulations are significantly more expensive and harder to run than phenomenological models, however, they can account for lateral interactions between adjacent adsorbates and explicitly resolve the diffusion processes. It is known that in KMC simulations even without lateral interactions the concentration of adjacent adsorbates that can rapidly react with each other is significantly lower than the concentration assumed within phenomenological models.\textsuperscript{26} In spite of this discrepancy, the approach of Freeman and Doll\textsuperscript{17} is not commonly used in phenomenological models.

While interactions between gas-phase reactions within kinetic mechanisms due to slow thermalization are very well studied and vital to account for at many important conditions. Little work has been done on the analogous problem of how reactions within kinetic mecha-
nisms interact with slow mass transfer processes.

However, it is easy to give examples where the above approaches fail. First, suppose \( B \) is highly concentrated with either very high coverage on the surface or is the solvent in a liquid. In this case, \( A \) and \( B \) cannot be reasonably separated in a way that would create a diffusion gradient, and thus, must react at close to \( k_{\text{TST}} \), no matter how slow diffusion is. However, based on Equation 2 the rate coefficient can never be faster than \( 4\pi R D \). This issue occurs because the Smolchowski model assumes that \( A \) can only react with the \( B \) at the origin.

Second, suppose diffusion is very slow and that \( A \) is a highly reactive species. In liquid this could be the result of having a high viscosity solvent. On a surface this may be the result of the metal and facet having high diffusion barriers. \( A \) might be an \( OH \) radical in liquid phase that can rapidly react with most molecules in the system. In liquid phase the Smolchowski model predicts that the rate coefficient cannot be larger than \( 4\pi R D \). However, since \( D \) is very small the effective rate coefficient must be much smaller than \( k_{\text{TST}} \). However, \( A \) reacts instantly with whatever is around it, it does not diffuse at all and there can be no diffusive gradients around it, so it must react at \( k_{\text{TST}} \). This contradiction occurs because the Smolchowski model does not account for production of \( A \) within \( R \) of \( B \) without involvement of a diffusion process.

Overall, it is very important to handle reactions involving reactive species. While there are exceptions, typically reactions between two unreactive species are very slow, unimportant in simulations, and unaffected by the diffusion limit. However, reactions involving at least one reactive species are typically much faster, highly relevant in simulations and affected by diffusion limitations.

To solve shortcomings in the Smoluchowski model we present a new model for computing the effective rate coefficient \( k_{\text{eff}} \) that allows \( A \) to undergo external reactions. We discuss how, what we refer to as the reactive-transport effect causes effective reaction rate coefficients to increase as \( A \) becomes more reactive. Analyzing this model analytically in both 2D and 3D
cases we validate the analytic results against stochastic simulation methods. We present new expressions for diffusion limited rate coefficients that account for reactions involving $A$ in the system. In common cases we show accounting for the reactivity of $A$ can result in rate coefficients that are orders of magnitude different from both $k_{TST}$ and the traditional Smolckowski limit. Lastly, we explain and contrast the coupling these interactions create between rate coefficients within kinetic mechanisms with those in non-thermal gas phase systems.

Theory

We will first derive appropriate diffusive fluxes that are definable in terms of estimable parameters. Then we will present and define our new model and solve it analytically in 3D and 2D.

Diffusive Fluxes in 2D and 3D

In 3D Fick’s law gives that

$$J_A = -D_A \frac{dc_A}{dr}$$

where $D_A$ is the diffusion coefficient and $c_A$ is the concentration of species $A$, $r$ is a radial coordinate, and $J_A$ is the flux per unit area. Diffusion coefficients in liquid and gas phases are readily available. In particular, liquid phase diffusion coefficients are commonly estimated from the Stokes-Einstein equation

$$D_A = \frac{k_B T}{6\pi \eta R_A}$$

where $\eta$ is the dynamic viscosity of the solvent, $R_A$ is the radius of $A$, $T$ is the thermodynamic temperature, and $k_B$ is the Boltzmann constant.

On a surface, in 2D, the description of diffusion is significantly different. Diffusion occurs...
as a series of individual steps that move a species from one site to another. The rate coefficients for these diffusion steps can be calculated using transition state theory, however, the flux depends not just on the amount of $A$, but also on the number of empty sites available for $A$ to move to, which depends on the concentrations of all species on the surface.

Suppose we have a 2D surface with $c_s$ sites of diameter $a$ per unit area. Also suppose the unimolecular rate coefficient for diffusion of $A$ from one site to any adjacent site is $k_{A\text{diff}}$. Given a circular dividing surface, such as that shown in Figure 1, at radius $r \gg a$ we can conclude that for each empty site along but inside the circular dividing surface if there is an $A$ present on the opposite site of the dividing surface (a further out) those $A$ molecules will cross the dividing surface at a rate of $k_{A\text{diff}}/4$. The number of sites along the dividing surface is given by $\frac{2\pi r}{a}$, giving us an outward flux of

$$N_{A^+} = \frac{2\pi r k_{A\text{diff}}}{4a} \theta_A(r) \theta(r + a)$$  \hspace{1cm} (5)$$

where $\theta_A$ is the fraction of sites that contain $A$ and $\theta$ is the fraction of empty sites, and the
dimension of $N_{A+}$ is number of $A$ per time. The inward flux can then be written

$$N_{A-} = \frac{2\pi r k_{\text{Adiff}}}{4a} \theta_A(r+a) \theta(r)$$  \hspace{1cm} (6)$$

We can then define the net flux

$$N_A = N_{A+} - N_{A-} = \frac{2\pi r k_{\text{Adiff}}}{4a} \theta_A(r) \theta(r+a) - \frac{2\pi r k_{\text{Adiff}}}{4a} \theta_A(r+a) \theta(r)$$  \hspace{1cm} (7)$$

Since we assumed that $a \ll r$, we can approximate continuous differentiable functions of $r$ at $r + a$ as:

$$y(r+a) \approx y(r) + a \frac{dy}{dr}$$  \hspace{1cm} (8)$$

and can rewrite $N_A$ as

$$N_A = \frac{2\pi r k_{\text{Adiff}}}{4a} \theta_A(r) \left( \theta(r) + a \frac{d\theta}{dr} \right) - \frac{2\pi r k_{\text{Adiff}}}{4a} \theta_A(r+a) \left( \theta(r) + a \frac{d\theta_A}{dr} \right) \theta(r)$$  \hspace{1cm} (9)$$

Further simplification gives

$$N_A = \frac{2\pi r k_{\text{Adiff}}}{4} \left( \theta_A \frac{d\theta}{dr} - \theta \frac{d\theta_A}{dr} \right)$$  \hspace{1cm} (10)$$

and dividing by the perimeter of the circular dividing surface gives us a flux per length of

$$J_A = \frac{k_{\text{Adiff}}}{4} \left( \theta_A \frac{d\theta}{dr} - \theta \frac{d\theta_A}{dr} \right)$$  \hspace{1cm} (11)$$

**Conservation Equation**

Let us consider the $A + B$ reaction in Equation 1 and choose a single molecule of $B$ as our origin, and consider the concentration of $A$ nearby. The molar conservation equation for $A$ is

$$\frac{\partial c_A}{\partial t} + \mathbf{v} \cdot \nabla c_A = -\nabla \cdot (c_A \mathbf{v} + J_A) + R_{cA}$$  \hspace{1cm} (12)$$
where $c_A$ is the concentration of $A$, $t$ is time, $v$ is the velocity of the flow and $R$ is the volumetric net production rate of $A$ from reactions. We first assume that on the length and/or time scales of interest $v = 0$, that $A$ and $B$ do not flow significantly relative to each other. We also assume that $c_A(r)$ has radial symmetry giving us

$$\frac{\partial c_A(r)}{\partial t} = -\nabla \cdot J_A(r) + R_{vA}(r)$$

(13)

We assume that

$$R_{vA}(r) = P_A - k_{LA} c_A(r)$$

(14)

where $P_A$ is the volumetric production rate of $A$ and $k_{LA}$ is the pseudo-first order loss rate coefficient for $A$. Note that both of these terms potentially account for many chemical reactions. The approximation in the above equation should be accurate so long as $P_A$ and $k_{LA}$ do not change significantly over the timescale of the $A + B \rightarrow \text{products}$ reaction, and $P_A$ and $k_{LA}$ are not significantly dependent on $c_A$. Rewriting, Equation 13, the conservation equation for the diffusion–reaction processes of $A$ near $B$ this way gives us

$$\frac{\partial c_A(r)}{\partial t} = -\nabla \cdot J_A(r) - k_{LA} c_A(r) + P_A$$

(15)

Naturally, far away from $B$ we expect the concentration of $A$ to equal the overall bulk concentration so we have

$$c_A(r = \infty) = c_{A\text{bulk}}(t)$$

(16)

where $c_{A\text{bulk}}$ is the concentration of $A$ far away from $B$. Thus the conservation equation at $r = \infty$ is

$$\frac{dc_{A\text{bulk}}}{dt} = -k_{LA} c_{A\text{bulk}} + P_A$$

(17)
This equation can be solved, and assuming \( c_{\text{bulk}}(t = 0) = c_{\text{bulk}0} \) the solution becomes:

\[
c_{\text{bulk}}(t) = \frac{P_A}{k_{LA}} + \left( c_{\text{bulk}0} - \frac{P_A}{k_{LA}} \right) e^{-k_{LA}t}
\]  

(18)

Recognizing that \( \frac{P_A}{k_{LA}} \) is the bulk steady state concentration of \( A \), we can write this boundary condition as

\[
c_A(r = \infty, t) = c_{\text{bulk}\infty} + (c_{\text{bulk}0} - c_{\text{bulk}\infty}) e^{-k_{LA}t}
\]  

(19)

where \( c_{\text{bulk}\infty} \) is the steady state concentration.

Now let us turn our attention to the remaining boundary condition near \( B \). We assume that at some \( R \) distance from the origin, \( A \) and \( B \) can react as dictated by the transition theory rate coefficient, and that the corresponding region is well mixed. This region is a volume that corresponds to a solvation shell in a liquid, or an area that encloses a set of nearby sites on a surface. Note that \( R \) is dependent not just on the identity of the reactants, but also on the structure of the transition state. Moreover, as some volume or area is taken up by \( B \), we assume that only some fraction \( \alpha \) of the full volume or area is available to use. Assuming this small region is at steady state and that the concentration of \( A \) inside it is \( c_A(R) \), we obtain a second boundary condition from the balance on \( A \)

\[
k_{\text{TST}} c_A(r = R) = -V_I J_A(r = R) + \alpha V (P_A - k_{LA} c_A(r = R))
\]  

(20)

where \( k_{\text{TST}} \) is the transition state theory rate coefficient, \( V_I \) is the area or perimeter of the interface and \( V \) is the volume or area enclosed within \( R \).

Finally, we assume that the concentration of \( A \) is the same everywhere at start

\[
c_A(r, t = 0) = c_{\text{bulk}0}
\]  

(21)

Our objective is to determine an effective rate coefficient, \( k_{\text{eff}} \), for the \( A + B \) reaction that gives the correct rate when multiplied by the bulk concentrations. Revisiting the molar
balance on $A$ at the $r = R$ boundary gives

$$k_{\text{eff}}(t) c_A(r = \infty, t) = -V_I J_A(r = R) + \alpha V(P_A - k_{LA} c_A(r = R, t)) = k_{\text{TST}} c_A(r = R, t) \quad (22)$$

This gives us an important relation:

$$\frac{k_{\text{eff}}(t)}{k_{\text{TST}}} = \frac{c_A(r = R, t)}{c_A(r = \infty, t)} \quad (23)$$

Note that $k_{\text{eff}}$, in the general case depends on time through $c_A(r = R, t)$ and $c_A(r = \infty, t)$.

A time dependent $k_{\text{eff}}(t)$, however, is not useful macroscopically. For cases where $k_{\text{eff}}(t)$ is time dependent, one needs to calculate the associated expected value, which we denote $k_{\text{avg}}$. Note in the following we assume that $c_{A_{\text{bulk}}}$ is constant in time. This same analysis does apply when $c_{A_{\text{bulk}}}$ is not constant, however, if $c_{A_{\text{bulk}}}$ is time dependent, $k_{\text{avg}}$ will be time dependent as well.

$k_{\text{eff}}(t)c_{A_{\text{bulk}}} dt$ is the probability that $B$ reacts with $A$ in a differential time slice given it has not yet reacted. The probability that $B$ has not reacted at time $t$ can be determined using the molecular balance on $B$

$$\frac{dn_B}{dt} = -k_{\text{eff}}(t)c_{A_{\text{bulk}}} n_B \quad (24)$$

where $n_B(t)$ is the expected number of $B$ or equivalently the probability that $B$ has not reacted at time $t$ and $n_B(t = 0) = 1$. Solving this differential equation gives

$$n_B(t) = e^{-\int_0^t k_{\text{eff}}(t)c_{A_{\text{bulk}}} dt} \quad (25)$$

Our probability distribution function of interest is then given by $k_{\text{eff}}(t)c_{A_{\text{bulk}}} e^{-\int_0^t k_{\text{eff}}(t)c_{A_{\text{bulk}}} dt}$,
and we can calculate the expected waiting time and thus determine $k_{\text{avg}}$:

$$\int_0^\infty t k_{\text{eff}}(t) c_{A_{\text{bulk}}} e^{-\int_0^t k_{\text{eff}}(t') c_{A_{\text{bulk}}} dt'} dt = \langle t \rangle = \frac{1}{k_{\text{avg}} c_{A_{\text{bulk}}}}$$

(26)

This provides us with a way to compute an effective rate coefficient even when $k_{\text{eff}}$ is a function of $t$.

**The Reactive Transport Effect**

![Diagram of the reactive transport effect](image)

Figure 2: Diagram of the reactive transport effect. Green circles denote solvent molecules, purple circles denote $A$ molecules, red denotes $A$ molecules being produced and light blue denotes $A$ molecules being consumed.

Before we solve the model, it is worth discussing what we will show analytically in the math physically. A diagram is available in Figure 2. Suppose the bulk concentration of $A$ is at steady state, and suppose we have its concentration profile associated with no external reaction. This concentration profile of $A$ starts at $c_{A_{\text{bulk}}}$ at $r = \infty$, and monotonically decays to a smaller value at $r = R$. Now let us introduce external reactions along the profile,
both production and loss of $A$, as illustrated in Figure 2. Close to the bulk, at large $r$, this has little effect because the concentration of $A$ is at steady state, so there is no net production or loss of $A$. However, while the production of $A$ is generally independent of $A$, the loss of $A$ is not. As we approach $B$, the reactive loss flux of $A$ (which is proportional to $c_A(r)$) decreases, while the reactive production flux (independent of $c_A(r)$) remains the same, resulting in a net production of $A$ that increases as $r$ decreases. Since close to $B$ the net production of $A$ is always positive, $c_A(R)$ and $k_{eff}$ are higher when steady state reaction effects are introduced.

In essence, introducing external reactions to the model adds a new transport process to the system. Without external reactions an $A$ molecule must diffuse from the bulk to $B$ to react. When reactions are accounted for, $A$ can be produced closer to $B$, allowing it to either immediately be available to react with $B$, or shortening the distance needed to diffuse to $B$. The balancing and importance of reactive and diffusive transport is determined based on how quickly $A$ is produced relative to how quickly $A$ diffuses. For low-reactivity species the difference is relatively minor unless diffusion is very slow. However, for high-reactivity species that are being produced and consumed rapidly in the bulk, the reactive-transport can dominate causing $A$ to reach $B$ much faster than by a pure diffusion processes. We term this phenomenon the reactive transport effect. In the rest of this section we will solve the model in 3D, 2D and at a 2D/3D interface and develop equations that demonstrate this effect analytically.

**Diffusion Limitations with External Reaction in 3D**

**Problem Definition**

In 3D the reaction-diffusion model of Equation 15 becomes

$$\frac{\partial c_A}{\partial t} = D \left( \frac{2}{r} \frac{\partial c_A}{\partial r} + \frac{\partial^2 c_A}{\partial r^2} \right) - k_{LA} c_A + P_A$$

\[ (27) \]
while the boundary condition related to \( r = R \) (Equation 20) becomes

\[
k_{\text{TST}} c_A(r = R, t) = 4\pi R^2 D \frac{dc_A}{dr}(r = R, t) + \alpha \frac{4}{3} \pi R^3 (P_A - k_{LA} c_A(r = R))
\]

(28)

using \( V_I = 4\pi R^2 \) and \( V = \frac{4}{3} \pi R^3 \).

**Nondimensionalization**

To simplify our expression of the solution we define a set of dimensionless quantities. We measure the concentration against the steady state concentration

\[
\Theta = \frac{c_A}{c_{A_{\text{bulk}}}}
\]

(29)

we measure the initial concentration relative to the steady state concentration

\[
Ca = \frac{c_{A_0}}{c_{A_{\text{bulk}}}}
\]

(30)

we measure the radial coordinate relative to \( R \)

\[
\rho = \frac{r}{R}
\]

(31)

we measure time relative to the diffusion time scale

\[
\tau = \frac{D t}{R^2}
\]

(32)

we measure the reaction rate of \( A \) relative to the diffusion rate yielding a Damköhler number

\[
Da = R \sqrt{\frac{k_{LA}}{D}}
\]

(33)
and we measure the transition state theory rate coefficient and the effective rate coefficient relative to the Smoluchowski theory rate coefficient

\[ T_s = \frac{k_{TST}}{4\pi RD} \]  

\[ E_f(\tau) = \frac{k_{\text{eff}}(\tau)}{4\pi RD} \]  

We also define an additional nondimensional representation of bulk concentrations

\[ PQ = \frac{4}{3} \pi R^3 c_{Q\text{bulk}} \]  

for \( Q = a, b \), where \( a \) corresponds to species \( A \) and \( b \) corresponds to species \( B \).

With these definitions and keeping in mind \( \frac{p_a}{k_{LA}} = c_{A\text{bulk,}x} \), we are able to rewrite the conservation equation, Equation 27, as

\[ \frac{\partial \Theta}{\partial \tau} = \left( \frac{2}{\rho} \frac{\partial \Theta}{\partial \rho} + \frac{\partial^2 \Theta}{\partial \rho^2} \right) + Da^2(1 - \Theta) \]  

Equation 28, the boundary condition at \( r = R \), as

\[ 0 = \frac{d\Theta}{d\rho}(r = R) + \frac{\alpha}{3} Da^2(1 - \Theta(r = R)) - T_s \Theta(r = R) \]  

Equation 19, the boundary condition at \( r = \infty \), as

\[ \Theta(\rho = \infty, \tau) = 1 + (Ca - 1)e^{-Da^2 \tau} \]  

and Equation 21, the initial condition, as

\[ \Theta(\rho, \tau = 0) = Ca \]  

defining a non-dimensional partial differential equation (PDE) in \( \tau \) and \( \rho \). We are also able
to nondimensionalize Equation 23 to give

\[ Ef(\tau) = Ts \frac{\Theta(\rho = 1, \tau)}{\Theta(\rho = \infty, \tau)} \] (41)

and Equation 26 to give

\[ 9Pa^2 \int_0^\infty \tau Ef(\tau)e^{-3Pa^2 \int_0^\tau Ef(\tau)d\tau} d\tau = \frac{1}{Ef_{\text{avg}}} \] (42)

where \( Ef_{\text{avg}} \) is the value of \( Ef \) that corresponds to the expected waiting time for the reaction.

**Solution**

We do not believe the PDE defined by Equations 37-40 is in general solvable in terms of standard functions. However, it is possible to solve the PDE in terms of standard functions at \( \rho = 1 \), which is all that is needed to compute \( Ef(\tau) \) from Equation 41. We solved the PDE at \( \rho = 1 \) using the Laplace transform method and computed \( Ef(\tau) \). The derivation is available in the Supporting Information here we simply present the resulting equation for \( Ef \). If we define \( A = Ts + \frac{\alpha}{3} Da^2 + 1 \) then \( Ef(\tau) \) is given by

\[
Ef(\tau) = \frac{A - \frac{\alpha}{3} Da^2 - 1}{1 + (Ca - 1)e^{-Da^2 \tau}} \frac{1}{A(A^2 - Da^2)} \left( 
A^3 Ca - A^2 Ca - A^2 \frac{\alpha}{3} Da^2 - A Ca Da^2 + A Da^2 + Ca Da^2 - Da^2 \right) e^{\tau(A^2 - Da^2)} \text{erfc}(A \sqrt{\tau}) \\
+ \left( A^2 Da - A \frac{\alpha}{3} Da^3 - A Da \right) \text{erf}(Da \sqrt{\tau}) \\
+ \left( A^2 Ca - A^2 - Ca Da^2 + Da^2 \right) e^{-Da^2 \tau} \\
+ \left( A^2 \frac{\alpha}{3} Da^2 + A^2 - A Da^2 \right) \right) \] (43)

If we take \( \tau \to \infty \) and substitute in for \( A \), this gives the steady state solution

\[
Ef(\tau = \infty) = \frac{Ts(1 + Da + \frac{\alpha}{3} Da^2)}{(1 + Da + \frac{\alpha}{3} Da^2) + Ts} \] (44)
and in the limit of Da = 0 (i.e., no external reaction) we recover the original Smoluchowski model in the scaled version of Equation 2

$$Ef(\tau = \infty, Da = 0) = \frac{Ts}{1 + Ts} \quad (45)$$

If we instead take Ts → ∞ (i.e., A and B react instantly within the reactive radius), we get

$$Ef(\tau = \infty, Ts = \infty) = 1 + Da + \frac{\alpha}{3} Da^2 \quad (46)$$

It should also be noted that substituting Equation 46 back into Equation 44 we get

$$Ef(\tau = \infty) = \frac{Ts Ef(\tau = \infty, Ts = \infty)}{Ts + Ef(\tau = \infty, Ts = \infty)} \quad (47)$$

a relationship between the diffusive limit rate coefficient, the transition state theory rate coefficient, and the effective rate coefficient. We will refer to this as the diffusion limit relation. Since Da is strictly positive, this tells us that as the reaction becomes faster relative to diffusion, the effective rate coefficient, as expected, increases. In the diffusive limit (Ts → ∞), this relationship is quadratic.

If we take Ts → ∞ in Equation 43, the full solution, we have A → ∞, and we can generate a more tractable equation for understanding the non-steady state case

$$Ef(\tau, Ts = \infty) = \frac{Da \text{ erf}(Da \sqrt{\tau}) + (Ca - 1)e^{-Da^2 \tau} + 1 + \frac{\alpha}{3} Da^2}{1 + (Ca - 1)e^{-Da^2 \tau}} \quad (48)$$

This equation contains two separate decay time scales. The faster time scale goes as erf($\sqrt{\tau}$) and is associated with the relaxation of the concentration gradients. The slower decay goes as $e^{-\tau}$ and is associated with the relaxation of the bulk A concentration. Note that if Ca = 1, implying A is at steady state in the bulk, the exponential terms disappear.

Using this timescale separation between the gradient relaxation and the bulk relaxation,
we can separate the two to give us equations that are valid when $A$ is not at steady state. To do this, we return to Equation 43 and take $\tau \to \infty$ for the error function terms, but not for the exponential terms, giving us

$$\text{Ef} = \frac{\text{T}_s}{1 + (\text{Ca}-1)e^{-\alpha \text{Da}^2 \tau}} \left( \frac{\frac{2}{3} \text{Da}^2 + \text{Da} + 1}{1 + \text{Da} + \frac{\alpha}{3} \text{Da}^2 + \text{T}_s} + \frac{\text{Ca} - 1}{1 + \frac{\alpha}{3} \text{Da}^2 + \text{T}_s} e^{-\alpha \text{Da}^2 \tau} \right) \quad (49)$$

If we assume that the concentration gradients relax much faster than the bulk concentration, we can take $\tau = 0$ to give

$$\text{Ef} = \frac{\text{T}_s}{\text{Ca}} \left( \frac{\frac{2}{3} \text{Da}^2 + \text{Da} + 1}{1 + \text{Da} + \frac{\alpha}{3} \text{Da}^2 + \text{T}_s} + \frac{\text{Ca} - 1}{1 + \frac{\alpha}{3} \text{Da}^2 + \text{T}_s} \right) \quad (50)$$

Taking $\text{T}_s \to \infty$ gives

$$\text{Ef} = \frac{\alpha \text{Da}^2}{3 \text{Ca}} + \frac{\text{Da}}{\text{Ca}} + 1 \quad (51)$$

and taking $\text{Ca} \to \infty$ (analogous to taking $P_A \to 0$) here gives

$$\text{Ef} = \frac{\text{T}_s}{1 + \frac{\alpha}{3} \text{Da}^2 + \text{T}_s} \quad (52)$$

It is important to note that the way we have derived Equations 50-52 is not entirely self-consistent, because we have simultaneously taken $\tau \to \infty$ for some terms and $\tau \to 0$ for others. While the error function decay is much faster than the exponential decay the exponential will still measurably decay on the timescale the error function decays creating. However, that does not mean this is not a useful approximation. Computing the average rate coefficient from Equation 42 is quite expensive, so one would ideally like to use an expression that is not dependent on $\tau$. Equations 44 and 46 have this advantage, but require the assumption that $A$ is at steady state. Equations 50 and 51 do not require the assumption that $A$ is at steady state and conveniently reduce to Equations 44 and 46 when $A$ is at steady state ($\text{Ca} = 1$).

In order to take advantage of Equation 42, we are interested in computing integrals of
Ef. If Ca = 1, Equation 43 is integrable in terms of standard functions and we have

$$Ef(\tau, Ca = 1) = \frac{(A - \frac{\alpha}{3} Da^2 - 1)}{A(A^2 - Da^2)} \left( A^3 - A^2 - A^2 \frac{\alpha}{3} Da^2 \right) e^{\tau (A^2 - Da^2)} \text{erf}(A \sqrt{\tau})$$

$$+ (A^2 Da - A^2 \frac{\alpha}{3} Da^3 - A Da) \text{erf}(Da \sqrt{\tau})$$

$$+ (A^2 \frac{\alpha}{3} Da^2 + A^2 - A Da^2) \right) (53)$$

and we are able to compute

$$\int_0^\tau Ef(\tau, Ca = 1) d\tau = \frac{(A - \frac{\alpha}{3} Da^2 - 1)}{A(A^2 - Da^2)} \left( A^3 - A^2 - A^2 \frac{\alpha}{3} Da^2 \right) \frac{A \text{erf}(Da \sqrt{\tau}) + Da e^{\tau (A^2 - Da^2)} \text{erfc}(A \sqrt{\tau}) - Da}{Da(A^2 - Da^2)}$$

$$+ (A^2 Da - A^2 \frac{\alpha}{3} Da^3 - A Da) \frac{(2 Da^2 \tau - 1) \text{erf}(Da \sqrt{\tau}) + e^{-Da^2 \tau} \sqrt{4Da^2 \tau}}{2 Da^2}$$

$$+ (A^2 \frac{\alpha}{3} Da^2 + A^2 - A Da^2) \tau \right) (54)$$

As Ts → ∞, this becomes

$$\int_0^\tau Ef(\tau, Ts = \infty, Ca = 1) d\tau = Da(\tau - \frac{1}{2 Da^2}) \text{erf}(Da \sqrt{\tau}) + \sqrt{\frac{\tau}{\pi}} e^{-Da^2 \tau} + (1 + \frac{\alpha}{3} Da^2 \tau). \quad (55)$$

These expressions can be used to reduce computing Ef_{avg} to a single integral in Equation 42.

**Diffusion Limitations with External Reaction in 2D**

**Problem Definition**

In 2D the conservation equation becomes

$$\frac{\partial c_A}{\partial t} = - \frac{1}{r} \frac{\partial}{\partial r} (r J_A) + R \quad (56)$$
Substituting in Equation 11 and the same reactive contributions as in 3D, we get

\[
\frac{\partial c_A}{\partial t} = \frac{k_{\text{diff}}}{4r} \left( \left( \theta \frac{d\theta_A}{d\theta} - \theta_A \frac{d\theta}{d\theta} \right) + r \left( \theta \frac{d^2\theta_A}{d\theta r^2} - \theta_A \frac{d^2\theta}{d\theta r^2} \right) \right) - k_{ALc_s} \theta_A + P_A \tag{57}
\]

There are two common limiting cases. If \( A \) has a low concentration on the surface relative to other species, \( \theta \) will be approximately independent of \( \theta_A \), and thus within our coordinate system it is also independent of \( r \). This gives us

\[
\frac{\partial c_A}{\partial t} = \frac{k_{\text{diff}}}{4r} \left( \frac{d\theta_A}{d\theta} \right) - k_{ALc_s} \theta_A + P_A \tag{58}
\]

On the other hand, if \( A \) is highly concentrated relative to other species, we can conclude \( \theta \approx 1 - \theta_A \) giving us

\[
\frac{\partial c_A}{\partial t} = \frac{k_{\text{diff}}}{4r} \left( \left( 1 - \theta_A \right) \frac{d\theta_A}{d\theta} + \theta_A \frac{d\theta_A}{d\theta} \right) + r \left( \left( 1 - \theta_A \right) \frac{d^2\theta_A}{d\theta r^2} + \theta_A \frac{d^2\theta_A}{d\theta r^2} \right) - k_{ALc_s} \theta_A + P_A \tag{59}
\]

And after trivial simplifications

\[
\frac{\partial c_A}{\partial t} = \frac{k_{\text{diff}}}{4r} \left( \frac{d\theta_A}{d\theta} + r \frac{d^2\theta_A}{d\theta r^2} \right) - k_{ALc_s} \theta_A + P_A \tag{60}
\]

this equation is nearly identical to the other limiting case. We can combine them by defining a diffusion coefficient \( D \)

\[
D = \begin{cases} 
\frac{k_{\text{diff}}}{4c_s} \theta & \text{if } \theta_A \ll 1 \\
\frac{k_{\text{diff}}}{4c_s} & \text{if } \theta_A \gg \theta_i \text{ for all } i \neq A 
\end{cases} \tag{61}
\]

This definition makes the surface flux identical to the Fick’s law flux.

With this definition, both limiting cases simplify to a single conservation equation

\[
\frac{\partial c_A}{\partial t} = \frac{D}{r} \left( \frac{dc_A}{d\theta} + r \frac{d^2c_A}{d\theta r^2} \right) - k_{ALc_A} + P_A \tag{62}
\]
and the boundary conditions are the same as in 3D (Equations 39 and 40) except for at
\( r = R \) where we have

\[
k_{\text{TST}} c_A(r = R) = 2\pi R D \frac{dc_A}{dr} + \alpha \pi R^2 (P_A - k_{LA} c_A(r = R))
\]

(63)

**Nondimensionalization**

Most of the nondimensionalizations are identical to the 3D case, (Equations 29-33) except
that here we define

\[
T_s = \frac{k_{\text{TST}}}{2\pi D}
\]

(64)

\[
E_f = \frac{k_{\text{eff}}}{2\pi D}
\]

(65)

\[
PQ = \pi R^2 c_{R_{\text{bulk}}}
\]

(66)

for \( Q = a, b \), where \( a \) corresponds to \( A \) and \( b \) corresponds to \( B \). Nondimensionalizing
Equation 62 yields

\[
\frac{\partial \Theta}{\partial \tau} = \frac{1}{\rho} \frac{d \Theta}{d \rho} + \frac{d^2 \Theta}{d \rho^2} + D a^2 (1 - \Theta)
\]

(67)

and nondimensionalizing Equation 63 yields

\[
T_s \Theta(\rho = 1) = \frac{d \Theta}{d \rho} (\rho = 1) + \frac{\alpha}{2} D a^2 (1 - \Theta(\rho = 1))
\]

(68)

**Solution**

Unfortunately, unlike in the 3D case, the 2D case likely cannot be solved in terms of standard
functions using the Laplace transform method. Instead, we will present the steady state
solution only. The derivation of the steady state solution is available in the Supporting
Information.
The steady state solution to the 2D problem is given by

\[
Ef = \frac{Ts(Da K_1(Da) + \frac{\alpha}{2} Da^2 K_0(Da))}{Da K_1(Da) + (Ts + \frac{\alpha}{2} Da^2)K_0(Da)} \tag{69}
\]

where \( K_0 \) and \( K_1 \) are Bessel functions of the associated order. As \( Ts \to \infty \), we obtain

\[
Ef = \frac{Da K_1(Da)}{K_0(Da)} + \frac{\alpha}{2} Da^2 \tag{70}
\]

These results are similar to the equations derived by Freeman and Doll,\textsuperscript{17} however, they assumed that there was no external reaction inside the reactive radius. Consequently, Equations 69 and 70 agree with their solution when the reactive volume is considered to be zero or equivalently \( \alpha = 0 \). Note Equation 47, the diffusion limit relation, still holds for the steady state solution here. However, unintuitively here \( \lim_{Da \to 0} Ef(\tau = \infty, Ts = \infty) = 0 \). Through Equation 47 this implies that \( Ef(Da = 0) = 0 \). This suggests that if \( A \) does not undergo external reactions on the surface, the rate at which it can react with \( B \) is zero, which is clearly unphysical, but is entirely in agreement with the derivation of Freeman and Doll.\textsuperscript{17} This behavior is likely related closely to the fact that, as noted in Freeman and Doll, the boundary condition at \( r = \infty \) is not solvable in 2D without an external reaction term.\textsuperscript{17} We will handle this unique challenge with numerical methods later in the paper.

**Diffusion Limitations with External Reactions at a 3D-2D Interface**

**Problem Definition**

We have discussed diffusion limitations within 3D and 2D phases, however, diffusion limitations can also occur at the interface between 3D and 2D phases. The model we define is somewhat different in this case: instead of setting the origin of the coordinate system at an
individual molecule, we set it at the interface and assume symmetry across axes parallel to
the interface. This allows us to define the problem in terms of a single coordinate \( x \) that is
the distance from the surface. We will use \( x \) here to avoid confusion regarding the geometry,
however, we will also say that more broadly \( x = r \).

The conservation equation in this case becomes

\[
\frac{\partial c_A(x)}{\partial t} = D \frac{d^2 c_A}{dx^2} - k_{LA} c_A(x) + P_A
\]  

(71)

Most of the boundary conditions are identical to the previous cases (keeping in mind \( x = r \)).
However, the boundary condition at \( x = R \) becomes

\[
k_{TST} c_A(x = R) c_{B\text{bulk}} = D \frac{d c_A}{dx}(x = R) + \alpha R (P_A - k_{LA} c_A(x = R))
\]

(72)

Note that \( c_{B\text{bulk}} \) is present here because unlike in the 3D and 2D cases, our origin is not a
single \( B \) molecule, but is instead a surface containing many \( B \) molecules.

Nondimensionalization

The nondimensionalization is mostly identical to the 3D case except that

\[
T_s = \frac{k_{TST} c_{B\text{bulk}} R}{D}
\]

(73)

and

\[
E_f = \frac{k_{eff} c_{B\text{bulk}} R}{D}
\]

(74)

\[
P_a = R \frac{c_{A\text{bulk}}}{c_{B\text{bulk}}}
\]

(75)

Taking \( \rho = r/R = x/R \), nondimensionalizing Equation 71 gives us

\[
\frac{\partial \Theta}{\partial \tau} = \frac{\partial \Theta^2}{\partial \rho^2} + Da^2 (1 - \Theta)
\]

(76)
nondimensionalizing Equation 72 gives us

\[ Ts \frac{\partial \Theta}{\partial \rho}(\rho = 1) = \frac{d \Theta}{d \rho}(\rho = 1) + \alpha Da^2 (1 - \Theta(\rho = 1)) \quad (77) \]

and nondimensionalizing Equation 26 in this case gives us

\[ P a^2 \int_0^\infty \tau \text{Ef}(\tau) e^{(-Pa \int_0^\tau \text{Ef}(\tau) d\tau)} d\tau = \frac{1}{\text{Ef}_{ave}} \quad (78) \]

**Solution**

Fortunately, we are able to solve Equation 76 and the boundary conditions Equations 77, 39, and 40 using the Laplace transform method as in the 3D case. The details are available in the Supporting Information.

Defining \( B = Ts + \alpha Da^2 \) this gives us

\[
\text{Ef}(\tau) = \frac{B - \alpha Da^2}{(B^2 - Da^2)(1 + (Ca - 1)e^{-Da^2\tau})} \left( (-B\alpha Da^2 + Da^2 + Ca(B^2 - Da^2))e^{(B^2 - Da^2)\tau} \text{erfc}(B\sqrt{\tau}) \\
+ (-\alpha Da^3 + B Da) \text{erf}(Da \sqrt{\tau}) + (B\alpha Da^2 - Da^2) \right) \quad (79)
\]

We can inspect the limits of this equation, just as done in 3D. As \( Ts \to \infty \), we have \( B \to \infty \) and

\[
\text{Ef}(\tau, Ts = \infty) = \frac{Da \text{ erf}(Da \sqrt{\tau}) + \alpha Da^2}{(1 + (Ca - 1)e^{-Da^2\tau})} \quad (80)
\]

Taking \( \tau \to \infty \) gives us the steady state solution

\[
\text{Ef}(\tau = \infty) = \frac{Ts(\alpha Da^2 + Da)}{\alpha Da^2 + Da + Ts} \quad (81)
\]

and with \( Ts \to \infty \) and \( \tau \to \infty \) we have
\[ Ef(\tau = \infty, Ts = \infty) = \alpha Da^2 + Da \]  

(82)

If we relax only the error function terms, we get

\[ Ef = \frac{Ts(\alpha Da^2 + Da)}{(\alpha Da^2 + Da + Ts)(1 + (Ca - 1)e^{-Da^2 \tau})} \]

(83)

and setting \( \tau = 0 \) gives us the relaxed non-steady state equation

\[ Ef(\tau = \infty/2) = \frac{Ts(\alpha Da^2 + Da)}{Ca(\alpha Da^2 + Da + Ts)} \]

(84)

These equations are similar to those in 3D. Once again Equation 47, the diffusion limit relation, holds. However, like in 2D, we have unphysically \( Ef(Da = 0) = 0 \). Much like in the 2D case, the 3D-2D interface equations are not solvable with \( Da = 0 \).

As in the 3D case for \( Ca = 1 \) we are able to provide analytic expressions for useful integrals of \( Ef \). Letting \( Ca = 1 \) gives us

\[
Ef(\tau, Ca = 1) = \frac{B - \alpha Da^2}{(B^2 - Da^2)} \left( (-B\alpha Da^2 + B^2) e^{(B^2 - Da^2)\tau} \text{erfc}(B\sqrt{\tau}) \right.
\]

\[
+ \left. (-\alpha Da^3 + B Da) \text{erf}(Da\sqrt{\tau}) + (B\alpha Da^2 - Da^2) \right) \]

(85)

and we are able to compute the integral

\[
\int_0^\infty Ef(\tau, Ca = 1) d\tau = \frac{B - \alpha Da^2}{(B^2 - Da^2)} \left( (-B\alpha Da^2 + B^2) \frac{B \text{erf}(Da\sqrt{\tau}) + Da e^{(B^2 - Da^2)\tau} \text{erfc}(B\sqrt{\tau}) - Da}{Da(B^2 - Da^2)} \right.
\]

\[
+ (-\alpha Da^3 + B Da) \left( (\tau - \frac{1}{2 Da^2}) \text{erf}(Da\sqrt{\tau}) + \sqrt{\frac{\tau}{\pi Da^2}} e^{-Da^2 \tau} \right)
\]

\[
\left. + (B\alpha Da^2 - Da^2) \right) \]

(86)
as $T_s \to \infty$ we have the simpler expression

$$\int_0^\infty \text{Ef}(\tau, T_s = \infty, Ca = 1)d\tau = D_a \left( (\tau - \frac{1}{2D_a^2}) \text{erf}(D_a \sqrt{\tau}) + \sqrt{\frac{\tau}{\pi D_a^2}} e^{-D_a^2 \tau} \right) + \alpha D_a^2 \tau$$ \hspace{1cm} (87)

These integrals can be used to evaluate the average rate coefficient in non-steady state cases.

**Computational Methods**

We leveraged a variety of computational methods for validation. What we will refer to as particle Monte Carlo enables us to calculate Ef at the diffusion limit for all three cases. Kinetic Monte Carlo simulations using KinCat allow us to simulate most possible cases in 2D. However, it did not allow us to validate diffusion coefficients, so we developed a “simple” kinetic Monte Carlo implementation that allows us to validate the diffusion coefficient definition in 2D.

**Particle Monte Carlo**

We implemented a simple stochastic simulation program that simulates the motion of $A$ molecules in Julia.\(^{29}\) This simulator models diffusion of $A$ around a single $B$. One $B$ is set at the origin of a n-sphere (n=1,2,3) of radius $L$. $A$ molecules are generated randomly within the sphere by sampling uniformly from the associated hypercube with sides of $2L$ centered around the origin, and rejecting samples that are not inside the sphere. Particles are simulated purely in terms of their radial distance from the origin. Each time step we first check if any particle is within $R$ of the origin. If so, the simulation is terminated and the time is returned. Otherwise it first takes a reaction step. For the reaction step we compute a reaction probability

$$p_{\text{react}} = \frac{D D_a^2}{R^2} \Delta t$$ \hspace{1cm} (88)
where $\Delta t$ is the time step and $p_{\text{react}}$ is the reaction probability. With probability $p_{\text{react}}$ each given particle is removed, and immediately regenerated at another location using the procedure described above. Lastly, the algorithm takes a diffusion step where it perturbs the radial coordinate of each particle based on

$$\Delta r \sim N\left(0, \frac{\sqrt{2D\Delta t}}{n}\right)$$

where $N$ is the normal distribution and $n$ is the dimension of the simulated system (1, 2 or 3). The time step is chosen by taking the largest time step allowed such that

$$p_{\text{react}} \leq 0.1$$

and

$$\Delta t \leq 0.3 \frac{(nR)^2}{2D}$$

When particles attempt to diffuse to $r > L$, they are wrapped to $2L - r$ instead, enforcing a reflective boundary condition.

To differentiate this from kinetic Monte Carlo we will refer to this as particle Monte Carlo (PMC). This approach allows us to simulate diffusion limited reactions for different system dimensions under the assumptions that $T_s = \infty$, $C_a = 1$ and $\alpha = 1$. By running many of these simulations we can evaluate directly

$$k_{\text{eff}} = \frac{1}{c_A\langle t \rangle}$$

or taking advantage of cancellation of errors

$$E_f(D_a) = \frac{\langle t(D_a = 0) \rangle}{\langle t(D_a = D_a) \rangle}$$

where $\langle t \rangle$ is the average time it takes for an $A$ to react with $B$. 

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Kinetic Monte Carlo

Kinetic Monte Carlo (KMC) simulations utilize random numbers to stochastically simulate events that move a system between discrete states such as molecules hopping between binding sites on a lattice. Here we use an algorithm that has been variously termed the Gillespie algorithm, the Stochastic Simulation Algorithm (SSA), the N-fold Way, the BKL algorithm, or the Residence Time Algorithm (RTA).\textsuperscript{30,31} For each KMC step, all possible events $i$ are determined from the current system state. Each event $i$ is determined to occur with a particular rate $s_i$. The total rate of all events possible can then be computed as $S = \sum_i s_i$. Two independent random numbers, $u_0$ and $u_1$, are drawn from a uniform distribution in the range $(0,1]$. The timestep of the event is then calculated as $\Delta t = -\ln(u_0)/S$. Then the particular event $i$ is chosen and applied with probability $p_i = r_i/R$ by choosing $i$ such that $\sum_{j=0}^{i-1} p_i \leq u_1 < \sum_{j=0}^{i} p_i$. Steps then continue to be taken until some stopping criterion is met.

Simple Kinetic Monte Carlo

To handle 2D simulations with $Da = 0$, we implemented a simple KMC code in Julia.\textsuperscript{29} This code simulates three species on the surface $A$, $B$, and $C$, where only $A$ and $C$ are allowed to diffuse. The simulation is initialized based on the grid size, $\theta_A$, $\theta$, and diffusion rate coefficients associated with $A$ and $C$. The code partitions the total number of sites first achieving $\theta_A$, including only one $B$ on the surface, and adding $C$ to best achieve the set $\theta$. These species are distributed randomly on the surface. Sites are considered adjacent on the square grid for purposes of diffusion and reaction of $A$ and $B$ if they are directly above, below, to the left, or to the right of each other. The code uses periodic boundary conditions and diffusion is only allowed to empty sites. The system is simulated using the Gillespie algorithm until an $A$ is adjacent to a $B$, at which point the time is returned. After running a sufficient number of simulations, one can calculate $k_{eff}$ using Equation 92.
**KinCat Kinetic Monte Carlo**

For simulations with $Da > 0$, we were able to use KinCat, our open-source software to perform KMC simulations in 2D systems.$^{32}$

We simulated $A$ and $B$ on a square 2D lattice with adsorption and desorption and diffusion. The simulation is initialized with a grid size, $\theta_A$, $\theta_B$, and rate coefficients associated with all permissible processes of the system. As in the simple KMC simulations described above, sites are considered adjacent for the purposes of diffusion and reaction if they are directly above, below, right, or left of one another. Further, adsorption and diffusion processes are only allowed to empty sites. $A$ are initially scattered randomly on the lattice and a single $B$ is placed at random in a remaining open site. Low, steady-state concentrations of species are maintained on the lattice throughout the simulation by careful selection of the ratios between adsorption and desorption rates.

We examined two different reactive systems. The first is referred to as the *singly* reactive system in which only $A$ may adsorb to, desorb from, and diffuse across the surface, while $B$ is stationary on the lattice. The *doubly* reactive system additionally allows for the adsorption and desorption of $B$. A full reaction system with all possible processes of both $A$ and $B$ was initially defined, and then any undesired processes, such as diffusion of $B$ were ‘turned off’ by assigning processes rate coefficients of zero to those events.

While the simple KMC simulations described above were terminated after the first $A+B$ event and repeated a set number of times. In KinCat when the $A+B$ event occurs we record the event and remove $A$ leaving $B$ on the surface. This allows us to collect multiple mean waiting times from a single simulation by taking advantage of the underlying probability distribution of the KMC algorithm. That is, it is well known that a Poisson distribution in time underlies the evolution of processes in KMC. As a consequence, the *interevent times* are independently and identically distributed exponential random values, and the expected interevent time is exactly the mean waiting time $\langle t_1 \rangle$ that we wish to find.

Thus, we obtained the desired mean waiting time by running a time-limited simulation.
which terminated only after a set maximum time was reached. The stopping time was empirically chosen to ensure that at least 2000 reaction events occurred. We then found the elapsed time between each \( A + B \) reaction event and computed the mean interevent time from the average.

From these simulations, we evaluated directly the effective rate given in Equation 92. Taking advantage of cancellations as before, we found, for the singly reactive case,

\[
\text{Ef}(D_a) = \frac{\theta_A(D_a = 0) \langle t(D_a = 0) \rangle}{\theta_A(D_a = D_a) \langle t(D_a = D_a) \rangle}.
\] (94)

In the doubly reactive case the coverage of \( B \) is not constant and we use

\[
\text{Ef}(D_a) = \frac{\theta_A(D_a = 0) \theta_B(D_a = 0) \langle t(D_a = 0) \rangle}{\theta_A(D_a = D_a) \theta_B(D_a = D_a) \langle t(D_a = D_a) \rangle}.
\] (95)

which accounts for differences in coverage of \( B \) between simulations.

**Results**

**Non-Reactive Limit Rate Coefficients**

Considering the 3D, 2D and 2D/3D interface cases physically in the limit as \( D_a \to 0 \) without any external reactions we expect the rate coefficient and \( \text{Ef} \) to approach a finite positive value. However, as noted earlier, the solutions for both 2D and the 2D/3D interface imply that as \( D_a \to 0 \), \( \text{Ef} \to 0 \) as well. This occurs due to the fact that unlike in the 3D case, the partial differential equation is not solvable in the 2D and 2D/3D interface cases if \( D_a = 0 \), causing the solution to break down in that limit. However, PMC and simple KMC can be used to simulate this limit.

Fortunately the functional forms of the non-reactive limit rate coefficients are relatively simple, in the 3D case we know \( \text{Ef}(D_a = 0, T_s = \infty, C_a = 1) = 1 \), or equivalently \( k_{eff} = 4\pi RD \). So we might anticipate that \( \text{Ef} = 1 \) or is at least a constant for
Figure 3: Plot of computed rate coefficients for $T_s = \infty$ and $Da = 0$ using PMC and the simple KMC implementation for the 2D case. The PMC simulation was run with $R = 1\text{ nm}$, $L = 60R$, $D = 10^{-10}\text{ m}^2/\text{s}$ and 1000 molecules. The results were obtained by averaging 1000 samples. We plot the 2D normalization, $2\pi D$, showing it matches the simulations.
Figure 4: Plot of computed rate coefficients for $T_s = \infty$ and $D_a = 0$ using PMC for the 2D/3D interface case. The MC simulation was run with $R = 1$ nm, $L = 1000R$, $D = 10^{-10}$ m$^2$/s and 1000 molecules and averaged over 1000 samples. For KMC a $30 \times 30$ grid was used and the diffusion coefficient was varied by changing the diffusive rate coefficient while keeping $\theta = 0.05$ constant. We plot the 2D/3D interface normalization, $\frac{D}{R}$, showing it matches the simulations.
the 2D and 2D/3D interface cases. We have plotted the diffusion limit rate coefficients \( k_{\text{diffnonreactive}} = k_{\text{eff}}(Da = 0, Ts = \infty, Ca = 1) \) from PMC and KMC simulations against the Ef normalizations from Equations 65 and 74 in Figures 3 and 4. These figures strongly suggest that like in the 3D case \( Ef(Da = 0, Ts = \infty, Ca = 1) = 1 \) for all cases. This result in 2D gives us

\[
k_{\text{diffnonreactive}} = 2\pi D \tag{96}
\]

and for the 2D/3D interface

\[
k_{\text{diffnonreactive}} = \frac{D}{Rc_{\text{Bbulk}}} \tag{97}
\]

While, unlike in 3D, the rate coefficient in 2D is not dependent on the choice of \( R \), the expression looks largely similar. The result in Equation 97 for the 2D/3D interface, however, has a bit more nuance. As we have modeled the 2D/3D interface as \( A \) diffusing to the surface and reacting with \( B \) as \( Ts \to \infty \), the concentration of \( B \) on the surface is irrelevant to the rate of reaction at the interface, and concentration falls out of the equation. Therefore, in the diffusive limit for the 2D/3D interface case the flux is simply \( \frac{D}{R}c_{\text{Abulk}} \).

**Coverage Dependence of the Diffusion Coefficient**

Equation 61 establishes a diffusion coefficient on a 2D surface that is coverage dependent. As shown in Figure 5, we are able to validate this result using the simple KMC implementation.

**The Reactive Transport Effect**

It is of most practical interest to test our predicted effective rate coefficients for reactions (essentially \( Ef \)) as a function of \( Da \).

Figure 6 shows the the 3D steady state solution (Equation 44) against the full solution (Equation 42) and a PMC simulation. The PMC simulation is particularly difficult to converge in this higher dimensional case. However, noting that the MC simulation should never be below the non-reactive limit, we can tell there is a significant amount of uncertainty
Figure 5: Coverage dependence of the 2D diffusion coefficient. $\theta$ is the empty site fraction. Simulations were done for a $20 \times 20$ grid varying the empty site fraction with the coverage of $A$ fixed at 0.05. Identical diffusion rate coefficients were used for both $A$ and $C$, the latter being the non-reactive species that controls the overall coverage.

Figure 6: $E_f$ as a function of $Da$ for the 3D case as $Ts \to \infty$. The MC simulation used $R = 1$ nm, $L = 40R$, $D = 10^{-10}\, \text{m}^2/\text{s}$ and 1000 molecules and averaged 1000 samples.
in the simulation for smaller Da. With this in mind, the MC simulation agrees quite well with the full solution, which agrees very well with the steady state solution. This suggests that the 3D steady state solution (Equation 44) is an accurate representation of the relationship between Da and Ef.

![Figure 7: Ef as a function of Da for the 2D case as Ts → ∞. The MC simulations used R = 1 nm, L = 60R, D = 10^{-10}\frac{m^2}{s} and 1000 molecules and averaged 1000 samples. The KinCat KMC simulations used a square 25 x 25 grid with a chain burn in of 100 time steps and 5 chains per ensemble. For the KinCat KMC analysis R is assumed double the site radius to best match the area of the sites around B where A can react with B in the simulation.](https://doi.org/10.26434/chemrxiv-2023-n5clv)

The 2D and 2D/3D interface cases are more complicated because they break down as Da → 0. The 2D case is shown in Figure 7 and the 2D/3D interface case is shown in Figure 8. For Da < 1 the theoretical solutions rapidly diverge from the PMC and KMC simulation results and drop unphysically below the non-reactive limit. To correct the limiting behavior of the theoretical solution we propose the following modification.

We believe the solutions in these cases should look similar to the 3D case in that they converge to 1 at low Da values. Furthermore, we would like to retain the form of Equation 47, the diffusion limit relation. Therefore, we simply add 1 to Ef(τ = ∞, Ts = ∞) for both...
Figure 8: Ef as a function of Da for the 2D/3D interface case as Ts → ∞. The MC simulation used \( R = 1 \) nm, \( L = 1000R \), \( D = 10^{-10}\text{m}^2\text{s}^{-1} \) and 1000 molecules and averaged 1000 samples.

In the 2D and 2D/3D scenarios, which causes \( \text{Ef}(\tau = \infty, T_s = \infty, Da = 0) = 1 \) for both. We then compute \( \text{Ef}(\tau = \infty) \) from Equation 47. This gives us in the 2D case

\[
\text{Ef}(\tau = \infty) = \frac{Ts(1 + Da \frac{K_i(Da)}{K_0(Da)} + \frac{\alpha}{2} Da^2)}{1 + Da \frac{K_i(Da)}{K_0(Da)} + \frac{\alpha}{2} Da^2 + Ts}
\]  

(98)

and in the 2D/3D interface case

\[
\text{Ef}(\tau = \infty) = \frac{Ts(1 + Da + \alpha Da^2)}{1 + Da + \alpha Da^2 + Ts}
\]  

(99)

These equations, as \( T_s \to \infty \), correspond to the adjusted lines in Figures 7 and 8, which agree very well with the PMC simulations and the non-reactive limits for the 2D and 2D/3D interface cases. The KinCat KMC result in Figure 7 is very consistently between a factor of two and three below the adjusted line irrespective of Da and dipping below the Ef = 1 line in a way the MC simulation does not. This seems to suggest that KMC agrees qualitatively with the adjusted model, but is not achieving the same accuracy as the PMC simulations.
It is likely also of interest to have adjusted non-steady-state equations for these cases. However, validating such equations poses a challenge. As noted before, the semi-relaxed state between timescales is already somewhat nonphysical and it is difficult to maintain Ca ≠ 1 in any realistic simulation as the production/loss fluxes will always cause it to tend to one.

Nevertheless, we speculate that such equations should look like Equation 50, match the adjusted equations when Ca = 1, and in the 2D/3D interface case should approach Equation 84 for large Da. In this view we might decompose the terms in the Ef(\(\tau = \infty, T_s = \infty\)) solutions into three components. The first component, the 1, is the non-reactive component that is the same for all cases. The second is the contribution from reaction that occurs along the diffusion gradients, which is the term that is dependent on Da, but not on \(\alpha\). The third is the contribution from reaction inside \(R\), which is the term that is dependent on \(\alpha\). We can then take Equation 50 and swap out all of the 3D contributions for 2D contributions

\[
Ef = \frac{T_s}{Ca} \left( \frac{\frac{9}{2} Da^2 + Da \frac{K_1(Da)}{K_0(Da)} + 1}{1 + Da \frac{K_1(Da)}{K_0(Da)} + \frac{\alpha}{2} Da^2 + T_s} + \frac{Ca - 1}{1 + \frac{\alpha}{2} Da^2 + T_s} \right)
\]  

(100)

and for 2D/3D interface contributions

\[
Ef = \frac{T_s}{Ca} \left( \frac{\alpha Da^2 + Da + 1}{1 + Da + \alpha Da^2 + T_s} + \frac{Ca - 1}{1 + \alpha Da^2 + T_s} \right)
\]

(101)

Both of these equations reduce to Equations 98 and 99 when Ca = 1. How well Equation 101 reduces to Equation 84 for large Da is not immediately clear. For Da >> 1 the left-most term becomes the right-hand side of Equation 84. However, the right-most term only truly goes to zero for Da >> Ts. At first glance this seems to be a flaw in our speculation particularly for the Ca >> 1 case when the right-most term dominates. However, in this large Ca case Equation 84 goes unphysically to \(Ef = 0\) unlike the adjusted case that goes to \(\frac{T_s}{1 + \alpha Da^2 + T_s}\) and the 3D case which goes to \(\frac{T_s}{1 + \frac{3}{2} Da^2 + T_s}\). So we are inclined to believe the adjusted equation over Equation 84 with regards to the right-most term. Without any simulations to compare to, Equations 100 and 101 are our best guess as to how to calculate \(Ef\) at non-steady state.
conditions for the 2D and 2D/3D interface cases.

The Reactive Transport Effect with Two Reactive Species

An important embedded assumption in the model we have developed, thus far, is that species B, the species used as the reference frame, only reacts with A. When species B reacts with any other species on the time scale of reaction with A, the reference frame of the model vanishes. However, we can attempt to probe this situation by considering limiting cases and with KMC.

Suppose A and B react separately and together much faster than they diffuse (Da_A >> 1, Da_B >> 1 and Ts → ∞). In this limit, in 2D on the surface, reactions between A and B will always and only occur when an A happens to be produced within the reactive radius of B or a B happens to be produced within the reactive radius of A. Without any of the embedded assumptions used before we can write

\[ k_{\text{eff}}^{cA}c_{B\text{bulk}} = P_A c_{B\text{bulk}} \alpha_B \pi R^2_B + P_B c_{A\text{bulk}} \alpha_A \pi R^2_A \]  \hspace{1cm} (102)

where \( P_X \) is the production rate of X, \( R_X \) is the reactive radius of X, \( \alpha_X \) is the fraction of available area to react around X, and \( X = A, B \). Canceling the concentrations and assuming A and B are at steady state we have

\[ k_{\text{eff}} = k_{L1}^{cA} \alpha_B \pi R^2_B + k_{L2}^{cA} \alpha_A \pi R^2_A \]  \hspace{1cm} (103)

where \( k_{LX} \) is the reactive loss coefficient for \( X = A, B \). Nondimensionalization gives us

\[ \text{Ef}(\tau \rightarrow \infty, \text{Ts} \rightarrow \infty, \text{Da}_A >> 1, \text{Da}_B >> 1) = \frac{\alpha_B}{2} \text{Da}_A^2 + \frac{\alpha_A}{2} \text{Da}_B^2 \]  \hspace{1cm} (104)

which looks like a sum of the leading term in Equation 70 for the cases when A and B are separately the reference frame. This suggests a summation form for the reactive components.
of these cases

\[
\text{Ef}_{AB}(\tau \rightarrow \infty, Ts \rightarrow \infty) = \text{Ef}_A(\tau \rightarrow \infty, Ts \rightarrow \infty) + \text{Ef}_B(\tau \rightarrow \infty, Ts \rightarrow \infty) - 1
\]

(105)

where \( \text{Ef}_X \) is \( \text{Ef} \) with species \( X \) modeled diffusively with the other species being the reference frame. The \(-1\) term is added to cancel out the duplicate component in \( \text{Ef}_X \) that is not associated with the reactivity of either \( A \) or \( B \). We might then propose to insert this form into Equation 47 to give us a formula for \( \text{Ef}_{AB} \) in each case. In 3D, based on Equation 46, this gives us

\[
\text{Ef}_{AB}(\tau \rightarrow \infty) = \frac{\text{Ts}(1 + \text{Da}_A + \text{Da}_B + \frac{\alpha_B}{3} \text{Da}_A^2 + \frac{\alpha_A}{3} \text{Da}_B^2)}{\text{Ts} + (1 + \text{Da}_A + \text{Da}_B + \frac{\alpha_B}{3} \text{Da}_A^2 + \frac{\alpha_A}{3} \text{Da}_B^2)}
\]

(106)

in 2D based on Equation 98

\[
\text{Ef}_{AB}(\tau = \infty) = \frac{\text{Ts}(1 + \text{Da}_A \frac{K_i(Da_A)}{K_0(Da_A)} + \text{Da}_B \frac{K_i(Da_B)}{K_0(Da_B)} + \frac{\alpha_B}{2} \text{Da}_A^2 + \frac{\alpha_A}{2} \text{Da}_B^2)}{(1 + \text{Da}_A \frac{K_i(Da_A)}{K_0(Da_A)} + \text{Da}_B \frac{K_i(Da_B)}{K_0(Da_B)} + \frac{\alpha_B}{2} \text{Da}_A^2 + \frac{\alpha_A}{2} \text{Da}_B^2) + \text{Ts}}
\]

(107)

and at the 2D/3D interface based on Equation 99

\[
\text{Ef}_{AB}(\tau = \infty) = \frac{\text{Ts}(1 + \text{Da}_A + \text{Da}_B + \alpha_B \text{Da}_A^2 + \alpha_A \text{Da}_B^2)}{(1 + \text{Da}_A + \text{Da}_B + \alpha_B \text{Da}_A^2 + \alpha_A \text{Da}_B^2) + \text{Ts}}
\]

(108)

this gives us equations that, while not predicted by the model in this paper, may give good approximations in these doubly reactive situations.

The 2D form can be tested in KMC simulations. We should expect this doubly reactive case to be most different from the singly reactive case when both species are equally reactive, where \( \text{Da}_A = \text{Da}_B \) and \( \alpha_A = \alpha_B \). In this special case as we have

\[
\text{Ef}_{AB}(\tau = \infty, Ts = \infty) = 1 + 2 \text{Da} \frac{K_i(Da)}{K_2(Da)} + \alpha \text{Da}^2
\]

(109)
and taking the ratio with the singly reactive case we have

\[
\frac{E_{f, AB}(\tau = \infty, T_s = \infty)}{E_{f, A}(\tau = \infty, T_s = \infty)} = \frac{1 + 2 Da \frac{K_1(Da)}{K_2(Da)} + \alpha Da^2}{1 + Da \frac{K_1(Da)}{K_2(Da)} + \frac{\alpha}{2} Da^2}
\]

(110)
a ratio that it is relatively straightforward to compute accurately from KMC. A comparison between Equation 110 and KMC is available in Figure 9.

Figure 9: Enhancement of Ef when both species are reactive based on Equation 110 and on KinCat KMC simulations. The KinCat KMC simulations used a square 25 x 25 grid with a chain burn in of 100 time steps and 5 chains per ensemble.

First one should observe that this enhancement asymptotes with large Da at a factor of 2 and naturally should not be less than 1. The predictions from Equation 110 only exceed the KMC results by \(\sim 30\%\) at the first data point, and that point is appreciably below 1 suggesting a significant amount of uncertainty in the KMC result. This shows that Equation 110 is accurate in this circumstance, suggesting that Equation 105 can accurately extend our model to these doubly reactive cases.
Discussion

Coupling

Broadly, the equations we have discussed so far give us $\text{Ef}(T_s, \text{Da}, \text{Ca})$ for an individual reaction. However, so far we have assumed that $A$ and $B$ only react through one reaction, and have discussed $\text{Da}$ as if it is simply known and not dependent on many $\text{Ef}$ values. In reality, these diffusion limitations create important couplings both through reaction channels and through reactive species.

Couplings for the diffusion limitations discussed here occur in two different ways. The first occurs between channels that share concentration gradients, i.e., the reactants ($A$ and $B$) are the same, and the two channels are thus parallel reactions leading to different products. These reactions, when considered together can result in a significantly different $c_A(r = R)$ than when considered (improperly) separately. The second occurs between reactions that share reactive reactants. Since these reactive species are reactants, they are consumed in the course of the reaction. This means that each of these reactions contributes to $k_{LA}$, affecting $\text{Da}$ for the reactive species, which affects the rate coefficients of all reactions involving the same reactive reactant. In the next two sections we are going to describe the details of these couplings.

Channel Coupling

Suppose we have two reactions $A + B \rightarrow P_1$ and $A + B \rightarrow P_2$. Both of these reactions cause depletion of $A$ near $B$ and, therefore, share a concentration gradient. In this case we can simply calculate an overall effective rate coefficient associated with an overall TST rate coefficient to capture their coupling

$$k_{\text{TST}} = \sum_i k_{\text{TST},i} \quad (111)$$
where $k_{TST,i}$ is the individual rate coefficient for the $i$th reaction associated with the same concentration gradient. Since all of these competing reactions occur at the same concentration, their branching ratios are preserved. Their branching ratios can be calculated simply by

$$Bn_i = \frac{k_{TST,i}}{k_{TST}} \quad (112)$$

where $Bn_i$ is the branching ratio of the $i$th reaction. The effective rate coefficient for the $i$th reaction can then be calculated from

$$k_{eff,i} = Bn_i k_{eff} \quad (113)$$

where $k_{eff}$ is the overall effective rate coefficient including all of the reactions in the channel and $k_{eff,i}$ is the effective rate coefficient of the particular reaction $i$. It should be noted that this coupling is unrelated to the reactivity of $A$ and $B$, and is very important even when $Da = 0$.

It should also be noted that the 2D/3D interface case is a special case for this type of coupling, because it is coupled through the concentration gradient of the 3D species away from the surface rather than between two species. So in that case this coupling occurs for all reactions between the same 3D species and any species on the surface. For example $A($liq$) + B($surf$) \rightarrow P_1$ will be coupled in this way to $A($liq$) + C($surf$) \rightarrow P_2$.

### Reactive Species Coupling

The other primary source of coupling is due to the fact that $k_{LA}$ and $P_A$ often can have contributions that are dependent on the $k_{eff}$ of other reactions. In this sense $k_{LA}$ and $Ca$ for a species $A$ is coupled to the rate coefficients of every $k_{eff}$ that contributes to $P_A$ or $k_{LA}$. Summing these contributions first gives us

$$k_{Lj} = \sum_i k_{unirxn,i} + \sum_i k_{eff,i}c_{n(i)} \quad (114)$$
where $k_{Lj}$ is the loss coefficient for species $j$, $k_{\text{unirxn},i}$ is the rate coefficient associated with a unimolecular reaction $i$ that consumes $j$, $c_{n(i)}$ is the concentration of a species $n$ that reacts with species $j$ in reaction $i$, $k_{\text{eff},i}$ is $k_{\text{eff}}$ for reaction $i$. Doing the same for Ca gives us

$$Ca_j = \frac{k_{Lj}c_{\text{Abulk}_0}}{\sum_q k_q c_{l(q)} + \sum_q k_{\text{eff},q} c_{n(q)}c_{m(q)}}$$

(115)

where $Ca_j$ is Ca for species $j$ and $c_{l(q)}$ is the concentration of the species reacting unimolecularly to produce species $j$ in reaction $q$, $c_{m(q)}$ is the concentration of one of the species reacting bimolecularly to produce species $j$ and $c_{n(q)}$ is the concentration of the other species reacting bimolecularly to produce species $j$ in reaction $q$.

**Case Study:** $k_{LA} = k_{\text{eff}}c_{B\text{bulk}}$

A common special case occurs when $A + B \rightarrow \text{products}$ is the only reaction in the system. Even in this case $k_{LA}$ is not actually zero because $A$ can react with molecules of $B$ that are not the $B$ at the center of the coordinate system. This case is quite common if $B$ is highly concentrated, e.g. it is the solvent species or it is a high coverage species. In this case at steady state normalizing Equation 114 gives the simple relation

$$Da^2 = nPb\, Ef$$

(116)

where $n$ is the dimension of the system. Let us consider this for the simplest 3D case with $Ts \rightarrow \infty$. Substituting Equation 116 into Equation 46 we have

$$Ef = 1 + \sqrt{3Pb\, Ef + \alpha Pb\, Ef}$$

(117)

We can solve this using the quadratic formula with respect to $\sqrt{Ef}$ to give

$$Ef = \frac{(6 - 4\alpha)Pb + 4 + 2\sqrt{3Pb((3 - 4\alpha)Pb + 4)}}{4(1 - \alpha Pb)^2}$$

(118)
The singularity in Equation 118 is important as it causes $E_f \to \infty$ as $\alpha Pb \to 1$. This implies that this reaction can be arbitrarily fast, if $B$ is concentrated enough and $k_{TST}$ is fast enough. Physically, $\alpha Pb$ is the probability that there is a molecule of $B$ present in a sphere of radius $R$. Since we have $Ts \to \infty$, if $A$ and $B$ are present in such a sphere, we assume they react instantly. So as we approach having a $B$ in every such sphere with $Ts \to \infty$, we expect $E_f \to \infty$. We do not believe this equation is physically meaningful for $\alpha Pb > 1$.

![3D: $\alpha = 1, Pb = 1, Da^2 = 3PbEf$](image)

Figure 10: $E_f$ as a function of $Ts$ in 3D for the $k_{LA} = k_{eff}c_{Bbulk}$ case with $Pb = 1$ and $\alpha = 1$.

However, the above analytic analysis has limited utility because it only considers $Ts \to \infty$. It is far more interesting to look at the relationship this case creates between $E_f$ and $Ts$. In Figures 10 and 11 we look at this relationship for $Pb = 1$ and $\alpha = 1$ and compare to the transition state theory limit $E_f = Ts$ and the limit with no external reaction ($Da = 0$) $E_f = Ts/(1+Ts)$. $Pb = 1$ corresponds very roughly to a solvent in liquid phase or a coverage fraction of about 0.1 on a surface.

We are able to see that if $Pb = 1$, $E_f$ for $Ts > 1$ is significantly slower than the transition state limit and dramatically faster than the non-reactive diffusion limit. This demonstrates
that the reactive transport effect can easily cause the rate coefficient to be orders of magnitude faster than the non-reactive limit and still significantly lower than the transition state theory limit.

How this Fixes the Flaws in the Smolchowski Model

In the introduction we discussed two particular cases where the Smolchowski model fails to describe the kinetics properly. In the first case we considered a reaction involving a highly concentrated $B$ where we would expect the reaction to take place at $k_{TST}$ for sufficiently high $c_{B_{bulk}}$ concentration. This example is explicitly the situations discussed in the last section and shown analytically for $Ts \to \infty$ in Equation 118. Fundamentally within these models this case is about $A$ reacting with $B$ that aren’t the reference frame $B$ that it is not possible to handle within the Smolchowski model. Our model is able to handle this because that reaction with other $B$ can be simply incorporated into $k_{LA}$. This makes $Da^2 \propto k_{LA} \propto c_{B_{bulk}}$. Since in all of our models as $\lim_{Da \to \infty} Ef(Da) = Ts$ naturally for large enough $c_{B_{bulk}}$ Ef will
approach \( T_s \).

In the second case we considered a reaction of a reactive species with another species under conditions where diffusion is very slow. In this case we also expect for the reaction to occur at \( k_{TST} \) for sufficiently large \( k_{LA} \). Fundamentally this case is about the balance between diffusion and reaction. In our model when reaction dominates transport the diffusion gradients breakdown and concentrations approach their bulk values causing the reactions to occur at their transition state theory rate coefficients.

Let us consider the 3D steady state solution in Equation 44. If we divide each side by \( T_s \) and multiply top and bottom of the right hand side by \( 4\pi RD \) we get

\[
\frac{k_{eff}}{k_{TST}} = \frac{4\pi RD + 4\pi R^2 \sqrt{D} k_{LA} + 4\pi R^3 \alpha^3 k_{LA}}{4\pi RD + 4\pi R^2 \sqrt{D} k_{LA} + 4\pi R^3 \alpha^3 k_{LA} + k_{TST}}
\]

(119)

If we then take \( D \to 0 \), this gives us

\[
\frac{k_{eff}}{k_{TST}} = \frac{4\pi R^3 \alpha^3 k_{LA}}{4\pi R^3 \alpha^3 k_{LA} + k_{TST}}
\]

(120)

implying that we have \( \frac{k_{eff}}{k_{TST}} > 0 \) even if \( D \to 0 \), and further implying that if \( k_{LA} \) is large enough, we have \( \frac{k_{eff}}{k_{TST}} = 1 \) as expected intuitively.

**Defining \( R \), \( \alpha \) and \( D \)**

Properly determining the reactive radius \( R \), the available volume/area fraction to react \( \alpha \) and the diffusion coefficient \( D \) is very important for applying the equations developed here.

It is well understood due to the theory of relative diffusion\(^{13,14} \) that the proper diffusion coefficient for \( A \) and \( B \) together to each other is

\[
D = D_A + D_B
\]

(121)
If one knows $R$ and can define a radius for $B R_B$ it is relatively easy to estimate $\alpha$ as

$$\alpha = \frac{V_R - V_{R_B}}{V_R}$$  \hspace{1cm} (122)$$

where $V_R$ is the volume/area enclosed by $R$ and $V_{R_B}$ is the volume/area enclosed by $R_B$.

$R$ is defined here as the largest radius within which the volume is well mixed and species react according to transition state theory. In liquid phase this quantity is more difficult to define unlike on surfaces. Suppose $R_S$ is the radius of a single site on the surface and all sites are roughly the same size. If we suppose the reaction can only occur between adjacent sites, then it is clear that the correct $R$ should enclose both the site $B$ is on and all adjacent sites the reaction can occur between. While the site may have a number of adjacent sites, and for complex lattices each site can be unique, typically only 3 or 4 adjacent sites will have comparable reactivity. This also implies that the reactive area is in reality not circular. However, we can choose $R$ such that the enclosed area is the same as the area covered by the adjacent reactive sites. Analyzing the 3 reactive adjacent site case this way we can cleanly obtain $R = 2R_S$ which implies $\alpha = \frac{3}{4}$. In practice surface reactions that occur between non-neighboring sites may have significantly larger $R$. Applying the same approach to liquid phase gives us $R = R_B + 2R_A$. However, it is likely that the true $R$ in liquid phase is dependent on the solvent size and structure in solution.

**When are these diffusion limitation effects important?**

It is perhaps most useful to look at Equation 50, the semi-steady state equation for $E_f$ in 3D, which is fairly representative of all cases. If we divide each side by $T_s$ in that equation we get

$$\frac{E_f}{T_s} = \frac{k_{\text{eff}}}{k_{\text{TST}}} = \frac{1}{Ca \left( \frac{\frac{2}{3} Da^2 + Da + 1}{1 + Da + \frac{2}{3} Da^2 + T_s} + \frac{Ca - 1}{1 + \frac{2}{3} Da^2 + T_s} \right)}$$  \hspace{1cm} (123)$$

an alternative dimensionless equation that scales $k_{\text{eff}}$ against $k_{\text{TST}}$. This ratio is controlled by three dimensionless numbers: $T_s$, $Da$ and $Ca$. 


In general, if $Da = 0$ in all cases we have $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to 1/(1 + Ts)$. In this situation there is no reactive transport effect, but the diffusion limitation remains if $Ts \sim 1$ or greater. As $Da \to \infty$ in most cases we have $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to \infty$, the interesting exception is the case when $Ca \ll 1$, where $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to 0$, driving rates slower than $k_{\text{TST}}$ even if $Ts$ is slow.

For the remaining cases we consider $Da \sim 1$. For $Ca \ll 1$ (i.e. large $P_A$, small $k_{LA}$) we have $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to \infty$. For $Ca \gg 1$ (small $P_A$, large $k_{LA}$) we have $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to 1/(1 + \frac{2}{3} Da^2 + Ts)$, where both $Da$ and $Ts$ are important. For $Ca = 1$ we reduce to Equation 44. In this case for $Ts \ll 1$ we have $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to 1$ while for $Ts \gg 1$ we have $\frac{k_{\text{eff}}}{k_{\text{TST}}} \to 0$. When $Ts \sim 1$ we expect $\frac{k_{\text{eff}}}{k_{\text{TST}}} < 1$ with the exact deviation depending on the exact values of $Da$ and $Ts$.

**Conclusions**

We have discussed important limitations on the applicability of the textbook Smolchowski model for diffusion limited kinetics and presented a new model framework that allows one of the involved species to be produced and consumed both in the concentration gradients and close to the other species. We have solved this model analytically for 3D, 2D and 2D/3D interfaces and amended unphysical flaws in the 2D and 2D/3D interface analytical solutions based on Monte Carlo and Kinetic Monte Carlo simulations. The resulting equations predict what we term the reactive transport effect, that diffusion limited reactions can occur much faster than the diffusion limit when they involve highly reactive species such as radicals. This theory predicts that very common reactions with steady state radicals, even when the non-radical species is at low concentrations, can occur orders of magnitude faster than the diffusion limit.

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