Interfacial Reactions: Mixed Order Kinetics and Segregation Effects

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ABSTRACT

We study A-B reaction kinetics at a fixed interface separating A and B bulks. Initially, the number of reactions $\mathcal{R}_t \sim t^2 n_A^\infty n_B^\infty$ is 2nd order in the far-field densities $n_A^\infty, n_B^\infty$. First order kinetics, governed by diffusion from the dilute bulk, onset at long times: $\mathcal{R}_t \approx x_t n_A^\infty$ where $x_t \sim t^{1/z}$ is the rms molecular displacement. Below a critical dimension, $d < d_c = z - 1$, mean field theory is invalid: a new regime appears, $\mathcal{R}_t \sim x_t^{d+1} n_A^\infty n_B^\infty$, and long time A-B segregation (similar to bulk $A + B \to \emptyset$) leads to anomalous decay of interfacial densities. Numerical simulations for $z = 2$ support the theory.
A considerable analytical and numerical research effort has addressed the kinetics of bimolecular reactions in a bulk phase [1][2][3][4]. These are complex many body systems; correlation functions of different order are coupled in an infinite hierarchy of dynamical equations [5]. Analytical treatments have employed decoupling approximations which allow truncation of the hierarchy [1], and more recently renormalization group techniques [6]. From these studies it is known that the classical mean field (MF) theory is valid only above a critical spatial dimension $d_c$. According to MF kinetics, the net reaction rate is simply proportional to a product of spatially and thermally averaged densities. For the single-species case ($A + A \rightarrow \emptyset$) $d_c = 2$, while $d_c = 4$ in the two-species case ($A + B \rightarrow \emptyset$). In lower dimensions behavior is very different. For example in the two-species case, Ovchinnikov and Zeldovich, and Toussaint and Wilczek [2] established a remarkable segregation at long times into A-rich and B-rich domains; MF kinetics break down and the asymptotic decay of density fields no longer follows the $1/t$ MF prediction. All of these findings concern non-interacting small molecules, for which the rms diffusive displacement after time $t$ follows Fick’s law, $x_t \sim t^{1/2}$, independently of spatial dimension $d$. For systems with arbitrary (dimension-independent) dynamical exponent $z$, $x_t \sim t^{1/z}$, the generalizations are $d_c = z$ and $d_c = 2z$ for $A + A \rightarrow \emptyset$ and $A + B \rightarrow \emptyset$, respectively [4].

In contrast to the bulk, little is understood theoretically about interfacial reaction kinetics. Unlike the bulk $A + B \rightarrow \emptyset$ situation, the species A and B may now only react at a permanent interface separating the bulk A and B phases (see fig. 1). Applications involving reactions of this type include a large class where small molecules ($z = 2$) react at liquid-liquid, liquid-solid or solid-solid interfaces [7]. In another important class, functional groups attached to long polymer chains ($z = 4, 8$) react at an interface separating immiscible polymer melts. The A-B copolymers formed by reactions stabilize and reinforce the interface [8]. In these systems, which are the subject of this letter, the two bulk phases are forever separated by a permanent interface of fixed width. A very different but conceptually related class of systems, which has been addressed by many works [9], is that of non-stationary reactive chemical fronts where the A and B bulk phases mix and the interface broadens as reactions proceed. Other more distantly related models include catalytic reactions on surfaces such as the “monomer-monomer” model [10], $A + B \rightarrow \emptyset$ with spontaneous generation of particles [11], and reaction fronts near semipermeable walls [12].

In this letter we present a theoretical study of interfacial reaction kinetics [13][14]. Our principal findings are as follows. (1) MF kinetics break down below a critical dimension $d_c = z - 1$. (2) For spatial dimensions $d < d_c$, a short time diffusion controlled (DC) regime occurs with the number of reactions per unit area growing as $\mathcal{R}_t \approx x_t^{d+1} n_A^\infty n_B^\infty$, where $n_A^\infty, n_B^\infty$ are the far field densities. (3) For $d < d_c$, at long times reactants segregate into A-rich and B-rich domains at the interface. Correspondingly, interfacial densities decay with non-mean-field power laws. (4) Reaction kinetics are of mixed order. In all cases short time 2nd order kinetics cross over at long times to kinetics which are 1st order in the density on the more
dilute A side: $R_t \approx x_t n_A^\infty$.

These results are derived without resorting to ad-hoc decoupling approximations. Instead, we postulate physically motivated bounds on the correlation functions. It is possible that these bounds might be proved rigorously, but we do not attempt this here. Having made these assumptions, the subsequent analysis is exact.

Our principal aim is the reaction rate per unit area, $\dot{R}_t \equiv dR_t/dt$, proportional to the number of A-B pairs in contact at the interface:

$$\dot{R}_t = \lambda \rho_{AB}^s(t), \quad \lambda \equiv Qha^3.$$  \hfill (1)

Here $Q$ is the local reactivity, $h$ is the interface width, and $a$ the reactive group size. $\rho_{AB}^s$ is the 2-body correlation function evaluated at the interface. In addition, we seek the mean density profiles on the A and B sides, $n_A(r), n_B(r)$, whose characteristic features are: the far field values, $n_A^\infty, n_B^\infty$; the values at the interface ($r = 0$), namely $n_A^s$ and $n_B^s$; and the size of the depletion region (if any) near the interface. Using Doi’s second quantization formalism for classical many-body reacting systems, we have derived the following exact expression:

$$n_A^s(t) = n_A^\infty - \lambda \int_0^t dt' S_{1-t'}^{(1)} \rho_{AB}^s(t'). \hfill (2)$$

Here $S_{1-t'}^{(1)} \approx 1/x_t$ is the one dimensional return probability: the probability an A or B group, initially at the interface, returns to it after time $t$ in the absence of reactions. The integral term simply subtracts off A reactants which failed to arrive at the interface at time $t$ due to earlier reactions.

The technical difficulty is already apparent. The reaction rate and interfacial densities involve the 2-body correlation function $\rho_{AB}$. But one can show (see below) that the dynamics of $\rho_{AB}$ involve 3-body correlation functions; these in turn are coupled to 4-body correlations, and so on. This is the infinite hierarchy. How can one close eqs. (1) and (2)? A simple way to achieve this is to assume MF kinetics, i.e. to neglect density correlations at the interface:

$$\rho_{AB}^s(t) \approx n_A^s(t) n_B^s(t) \hfill (3)$$  \hfill (MF approximation)

The reaction rate is then simply proportional to the product of interfacial densities.

Let us proceed by simply assuming MF kinetics are valid. We return later to the question of when this assumption breaks down. Consider first the symmetric case, $n_A^\infty = n_B^\infty$. Now since the integral term in eq. (2) is zero initially and grows continuously, at short times it must be much less than $n_A^\infty$, and hence $n_A^s = n_B^s \approx n_A^\infty$. Using the MF approximation, eq. (3), one sees that the integral term then increases as $\lambda n_A^\infty n_B^\infty t/x_t \sim t^{1-z}$ and thus becomes of order $n_A^\infty$ at a timescale

$$t^*_m = t_a (\lambda t_a n_B^\infty/a)^{z/(1-z)}, \hfill (4)$$

where $t_a$ is the diffusion time corresponding to $a$. Thus for times greater than $t^*_m$, $n_A^s$ tends to zero and the integral term now balances with $n_A^\infty$ in eq. (2). Seeking a power law solution
for $n_A^s$, one immediately obtains its long time decay:

$$n_A^s \approx \begin{cases} n_A^\infty \ (t \ll t_m^*) \\ (x_t n_A^\infty/t\lambda)^{1/2} \sim t^{(1-z)/(2z)} \\
(t \gg t_m^*) \end{cases} \quad \text{(MF)}.$$

The number of reactions, from eqs. (3) and (3), is thus

$$R_t \approx \begin{cases} \lambda t n_A^\infty n_B^\infty \ (t \ll t_m^*) \\ x_t n_A^\infty \sim t^{1/z} \ (t \gg t_m^*) \end{cases} \quad \text{(MF)}.$$

These reaction kinetics are rather novel: they are not of fixed order. The short time 2nd order behavior crosses over to long-time 1st order kinetics.

The above results have a very clear physical interpretation. At short times, interfacial densities are unchanged from their initial values. But by time $t$ an A reactant initially within diffusive range of the interface (i.e. closer than $(t/t_0)(h/x_t)$ times. Each collision produces reaction with probability $\approx n_B^\infty a^d Q t_a$. By time $t_m^*$, therefore, the net reaction probability becomes of order unity. Thus for $t > t_m^*$ a depletion hole of size $x_t$ grows at the interface, the reaction rate is diffusion controlled and first order kinetics onset. The expression $R_t \approx x_t n_A^\infty$ is just the total number of A molecules per unit area within $x_t$ of the interface. Equating its time derivative to the expression for $\dot{R}_t$ implied by eqs. (3) and (3), one immediately obtains the long-time decay of the interfacial density, $n_A^s \sim t^{(1-z)/(2z)}$.

The analysis for the asymmetric case, $n_B^\infty > n_A^\infty$, is similar except that we find $n_B^s$ asymptotes a finite value, $n_B^s(t \to \infty) \approx n_B^\infty - n_A^\infty$, while $n_A^s$ tends to zero. The reaction kinetics of eq. (3) are unchanged. Physically, this means a density hole of size $x_t$ grows on the more dilute A side. It is delivery of the A species to the interface which determines $R_t$.

When are these MF results valid? To answer this question properly, one must examine the dynamics of $\rho_{AB}^s$. Using Doi’s formalism [3] we have derived an exact self-consistent relation for $\rho_{AB}^s$ which involves the 3-body correlation $\rho_{BAB}(r|0,0;t)$, namely the conditional density of B groups at $r$, given an A-B pair at the origin. This relation reads

$$\rho_{AB}^s(t') = n_A^\infty n_B^\infty - \lambda \int_0^t dt' S_t^{(d+1)} \rho_{AB}^s(t') - I_{BAB}(t) - I_{ABA}(t);$$

$$I_{BAB}(t) \equiv \lambda \int_0^t dt' \int d\mathbf{r} \mathcal{G}_{t-t'}(\mathbf{r}) \rho_{BAB}(\mathbf{r}|0,0;t') \rho_{AB}^s(t'), \quad (7)$$

where $I_{ABA}$ equals $I_{BAB}$ with A and B interchanged. Here $S_t^{(d+1)} \approx 1/x_t^{d+1}$ is the probability an A-B pair is in contact at the interface at $t$, given its members were in contact at the interface initially, in the absence of reactions. $\mathcal{G}_t(\mathbf{r})$ is the probability a pair is in contact at the interface at $t$, given initial pair separation $\mathbf{r}$ with one member being at the interface.

Now eq. (7) is not in a closed form for $\rho_{AB}^s$, since it contains unknown 3-body terms. We are able to close eq. (7) after postulating physically motivated bounds on the 3-body
correlation functions. These are much weaker assumptions than those involved in the typical procedure which entails approximating $\rho_{BAB}$ as a product of lower order correlation functions. We postulate that there exist constants $U$ and $L$ of order unity such that: (1) $\rho_{BAB}(r|0,0;t) \leq U n_B^\infty$ and (2) $\rho_{BAB}(r|0,0;t) \geq L n_B^\infty$ for $x > x_t$, where $x$ is the distance from the interface. Assumption (1) states our physical expectation that conditional densities never become much greater than the far-field densities. Assumption (2) states that conditional densities at points beyond diffusional range of the interface are uncorrelated with it.

These assumptions immediately imply a maximum and a minimum value for $\rho_{BAB}$ for each $r$. The maximum value is $Un_B^\infty$ for all $r$, while the minimum value is zero for $x < x_t$ and $Ln_B^\infty$ for $x > x_t$. We can thus obtain bounds on $I_{BAB}$ by substituting these two extreme cases into its definition, eq. (7). The important point is that these two bounds are of the same order; we have thus specified $I_{BAB}$ to within a time-dependent prefactor of order unity. Doing the same for $I_{ABA}$, we find after substitution in eq. (7)

$$\rho_{AB}^s(t) = n_A^\infty n_B^\infty - \lambda \int_0^t dt' S_{l-t'}^{(d+1)} \rho_{AB}^s(t') - \lambda n(t) \int_0^t dt' S_{l-t'}^{(1)} \rho_{AB}^s(t') ,$$

where $n(t) \equiv A(t) [n_A^\infty + n_B^\infty]$, and $A$ is a bounded positive function of order unity. The exact form of $n(t)$ is unknown; however, we have found that the vanishing of the interfacial density on the A side at long times implies $n(\infty) = n_B^\infty$ exactly. Since the term involving $n(t)$ is relevant at long times only, in effect $n$ may be replaced by $n_B^\infty$.

It is now straightforward to solve eq. (8) for $\rho_{AB}^s$, and thus obtain the reaction rate via eq. (10). One can show that deletion of the term containing $S^{(d+1)}$ reproduces the MF kinetics of eq. (8). This term is indeed irrelevant above a critical dimension, $d > d_c = z - 1$. It is also irrelevant for $d < d_c$ if the reactivity $Q$ is smaller than a certain value, $Q < Q^*$ (see below).

For lower dimensions and high reactivities, however, we find that during a certain interval $t_a^* < t < t_1$ this same term, the term containing $S^{(d+1)}$ in eq. (8), is dominant. Then the MF approximation breaks down and reaction kinetics are of second order and DC. This is a new regime whose physical origin is as follows. Consider an A and a B molecule which happen to be so close to each other that their exploration volumes overlap by time $t$ (see fig. 1). How many A-B collisions, $N_{coll}$, have there been by time $t$? The A molecule visited the interface of order $(t/t_a)(h/x_t)$ times, and during each visit encountered the B molecule with probability $(a/x_t)^d$. Hence $N_{coll} \approx (t/t_a)(ha^d/x_t^{d+1})$, and the total reaction probability $Qt_aN_{coll} \sim t^{(d_c-d)/z}$ is thus an increasing function of time for $d < d_c$. It reaches unity at a time $t_2^*$

$$t_2^* = t_a(Qta^h/a)^{z/(d-d_c)} ,$$

Below the critical dimension, therefore, for $t > t_2^*$ any A-B pair with separation $x_t$ or less will definitely have reacted by time $t$. Thus a depletion hole develops in the 2-body correlation function, invalidating the MF assumption. Instead, $R_i$ is proportional to the number of such
pairs per unit area, \( x_t^{d+1} \propto N_A^\infty n_B^\infty \). The kinetic sequence is now

\[
\mathcal{R}_t \approx \begin{cases} 
\lambda t n_A^\infty n_B^\infty & (t \ll t^*_2) \\
 n_A^\infty n_B^\infty \sim t^{(d+1)/z} & (t^*_2 \ll t \ll t_1) \\
x_t n_A^\infty \sim t^{1/z} & (t \gg t_1)
\end{cases} \quad (d < d_c, \ Q > Q^*) \quad (10)
\]

which may be explicitly verified by direct substitution into eq. \((8)\). For times \( t > t_1 \), where \( t_1 \equiv t_0 (n_B^\infty a^d)^{-z/d} \) is the time to diffuse the mean separation between B molecules, at least one B lies within the exploration volume of any A within \( x_t \) of the interface. Hence any such A must have reacted, and we cross over to 1st order DC kinetics as in eq. \((3)\). These arguments have implicitly assumed that \( t^*_2 < t_1 \), i.e. \( Q > Q^* \equiv ah^{-1}t_0^{-1}(n_B^\infty a^d)^{(d_c-d)/d} \). For weakly reactive groups, \( Q < Q^* \), the new 2nd order DC regime is absent; A reactants collide with many B’s before reaction is likely. The relevant timescale is then \( t^*_m \) and the kinetics of eq. \((3)\) are recovered.

MF theory does not give the correct reaction rate in low dimensions. In fact the density decay of eq. \((2)\) is also incorrect. For the symmetric situation, \( n_A^\infty = n_B^\infty \), peculiar correlations develop at the interface at long times which invalidate this MF decay. Consider a region of volume \( \Omega \), half of which is on the A and half on the B side. The fluctuations \( \Delta N_\Omega \) in the initial difference between the number of A and B reactants in \( \Omega \) is of order \( (n_A^\infty \Omega)^{1/2} \). Since reactions conserve this difference, these difference fluctuations can decay through diffusion only. Now if \( \Omega \geq x_t^d \), such fluctuations had insufficient time to decay by \( t \). Hence the density in a region of size \( x_t^d \) at the interface is at least \( \Delta N_{x_t^d}/x_t^d \sim t^{-d/(2z)} \). For \( d < d_c \), this is a slower decay than the MF prediction of eq. \((3)\). Thus fluctuations determine the \( n_A^\infty \)

asymptotics in low dimensions:

\[
n_A^\infty (t) \approx (n_A^\infty x_t^{-d})^{1/2} \sim t^{-d/(2z)}, \quad (d < d_c) \quad (11)
\]

Correspondingly, reactants segregate into A-rich and B-rich regions of size \( x_t \) at the interface. Such anticorrelations are of course unaccounted for by the MF approximation, eq. \((3)\). These segregation effects are very similar to those found at long times for bulk 2-species reactions, \( A + B \rightarrow \emptyset \) \[2\].

To summarize, we find that an interface lowers the critical dimension, \( d_c = z - 1 \), relative to simple one-species bulk reactions where \( d_c = z \) \[4\]. (We note this also is different to the problem of non-stationary reactive chemical fronts where for \( z = 2 \), \( d_c = 2 \) has been found \[3\].) For spatial dimensions above \( d_c \), densities on either side of the interface are decorrelated and mean field kinetics apply. Below \( d_c \) strong anticorrelations develop at the interface. Correspondingly, a short time 2nd order DC regime arises for very reactive species, and in the symmetric case at long times reactants are segregated along the interface and interfacial densities decay with an anomalous power law in time. A peculiarity is that kinetics are of mixed order in the far-field densities \( n_A^\infty, n_B^\infty \). Intuition suggests 2nd order kinetics, since reaction requires an A-B pair to meet at the interface. But at long times reaction rates
are controlled by diffusion of molecules on the more dilute A side to the interface, i.e. they depend on $n_A^\infty$ only. The more dense side plays a different role: characteristic timescales involve $n_B^\infty$ rather than $n_A^\infty$.

The simplest application is small molecules where $z = 2$ (Fickian diffusion) and $d_c = 1$. MF kinetics apply for $d = 3$ and $d = 2$, while $d = 1$ is marginal. We have not considered marginal cases here for reasons of space, but we find logarithmic corrections to the 2nd order DC regime (the 2nd of the regimes listed in eq. (10)). The result for $d = 1$, $z = 2$ is $R_t \sim t / \ln t$. We have tested our theory for small molecules by numerical simulations in $d = 1$ and $d = 2$. These exhibit 2nd order kinetics for short times (see fig. 2(a)), with MF kinetics in $d = 2$ and logarithmically corrected DC kinetics in the marginal case $d = 1$. At long times there is a cross-over to 1st order DC behavior with $R_t \sim n_A^\infty t^{1/2}$ governed by the more dilute side; see fig. 2(b). These numerical results are all consistent with our theoretical predictions. On the experimental side, we hope this work will motivate future studies of, for example, interfacial polymer systems involving laser-induced macroradicals [15]. These can help to resolve fundamental issues in interfacial science.

This work was supported by the National Science Foundation, grant no. DMR-9403566. We thank Uday Sawhney for helpful discussions.
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Figures

FIG. 1. A and B molecules (size $a$) reacting at an interface of fixed width $h$ separating immiscible bulks. Reactions occur within the interfacial region only. The local chemical reactivity (rate of reaction when in contact) is $Q$. For short times, reactions are confined to those molecules whose exploration volumes of size $x_t$ overlap at the interface. The number of such pairs per unit area is $x_t^{d+1} n_A^\infty n_B^\infty$.

FIG. 2. A and B random walkers on a square lattice annihilating on contact at an interface separating A and B bulks with various densities $n_A^\infty, n_B^\infty$. Time in units of site hopping time. Standard deviation of mean for each point is less than 3% in all cases. Empty (filled) symbols: $d = 1$ ($d = 2$). (a) $n_A^\infty n_B^\infty t/4 R_t$ v. $t$ for short times ($t_m^*, t_l > 10^6$): 2nd order kinetics. The $d = 2$ data asymptote a constant (MF kinetics), while $d = 1$ data approach a straight line, consistent with theoretical law $R_t \sim t/\ln t$. (b) $R_t/n_A^\infty$ v. $t$, long times ($t_m^* < 100$). Collapse of data onto straight line of slope $1/2$ indicates 1st order DC kinetics governed by dilute A bulk, $R_t \sim n_A^\infty t^{1/2}$. 
Fig. 1
Fig. 2