Interfacial Reactions: Mixed Order Kinetics and Segregation Effects

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We study A-B reaction kinetics at a fixed interface separating A and B bulks. Initially, the number of reactions $\mathcal{R}_t \sim t n_A^\infty n_B^\infty$ is second order in the far-field densities n_A^∞, n_B^∞. 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 $A + B \rightarrow 0$) leads to anomalous decay of interfacial densities. Numerical simulations for $z = 2$ support the theory.

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A considerable analytical and numerical research effort has addressed the kinetics of bimolecular reactions in a bulk phase [1–4]. 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 ($A + A \rightarrow 0$) $d_c = 2$, while $d_c = 4$ in the two-species case ($A + B \rightarrow 0$). In lower dimensions, the 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 noninteracting 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 $A + A \rightarrow 0$ and $A + B \rightarrow 0$, respectively [4].

In contrast to the bulk, little is understood theoretically about *interfacial* reaction kinetics. Unlike the bulk $A + B \rightarrow 0$ 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 *nonstationary* 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, $A + B \rightarrow 0$ with spontaneous generation of particles, and reaction fronts near semipermeable walls Ref. [10].

In this Letter we present a theoretical study of interfacial reaction kinetics [8,11]. Our principal findings are as follows: (i) MF kinetics break down below a critical dimension $d_c = z - 1$. (ii) 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^∞, n_B^∞ are the far-field densities. (iii) 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. (iv) Reaction kinetics are of mixed order. In all cases, short time second order kinetics cross over at

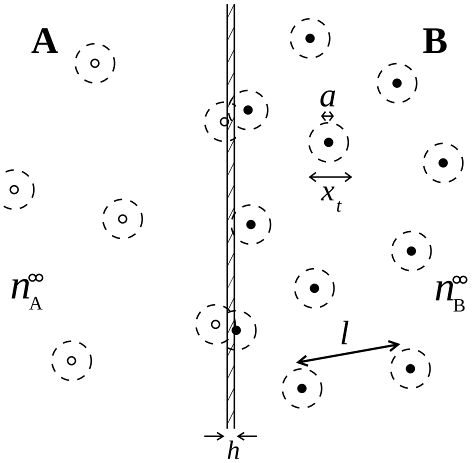

FIG. 1. A and B molecules (size a) reacting at an interface of fixed width h separating immiscible bulks. Reactions are confined to those molecules whose exploration volumes of size x_t overlap at the interface.

long times to kinetics which are first order in the density on the *more dilute A* side: $\mathcal{R}_t \approx x_t n_A^\infty$.

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, $\dot{\mathcal{R}}_t \equiv d\mathcal{R}_t/dt$, proportional to the number of A-B pairs in contact at the interface:

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

Here, Q is the local reactivity, h is the interface width, and a is the reactive group size. ρ_{AB}^s is the two-body correlation function evaluated at the interface. In addition, we seek the mean density profiles on the A and B sides, $n_A(\mathbf{r})$, $n_B(\mathbf{r})$, whose characteristic features are the following: the far-field values, n_A^∞, n_B^∞; the values at the interface ($\mathbf{r} = 0$), namely, n_A^s and n_B^s; and the size of the depletion region (if any) near the interface. Using Doi's [5] second quantization formalism for classical many-body reacting systems, we have derived the following exact expression:

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

Here $S_t^{(1)} \approx 1/x_t$ 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 two-body correlation function ρ_{AB}. But one can show (see below) that the dynamics of ρ_{AB} involve three-body correlation functions; these in turn are coupled to four-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. The reaction rate is then simply proportional to the product of interfacial densities:

$$\rho_{AB}^s(t) \approx n_A^s(t) n_B^s(t) \qquad \text{(MF approximation)}. \tag{3}$$

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^∞, 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 $\lambda n_A^\infty n_B^\infty t/x_t \sim t^{1-1/z}$ and thus becomes of order n_A^∞ at a time scale $t_m^* = t_a(\lambda t_a n_B^\infty/a)^{z/(1-z)}$, 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^∞ in Eq. (2). Seeking a power law solution for n_A^s, one immediately obtains its long time decay:

$$\begin{aligned} n_A^s &\approx n_A^\infty \quad (t \ll t_m^*), \\ n_A^s &\approx (x_t n_A^\infty/t\lambda)^{1/2} \sim t^{(1-z)/(2z)} \quad (t \gg t_m^*) \qquad \text{(MF)}. \end{aligned} \tag{4}$$

The number of reactions, from Eqs. (1) and (3), is thus

$$\begin{aligned} \mathcal{R}_t &\approx \lambda t n_A^\infty n_B^\infty \quad (t \ll t_m^*), \\ \mathcal{R}_t &\approx x_t n_A^\infty \sim t^{1/z} \quad (t \gg t_m^*) \qquad \text{(MF)}. \end{aligned} \tag{5}$$

These reaction kinetics are rather novel: they are not of fixed order. The short time second order behavior crosses over to long time first 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 x_t), will have collided with it of order $(t/t_a)(h/x_t)$ 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 $\mathcal{R}_t \approx x_t n_A^\infty$ 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 $\dot{\mathcal{R}}_t$ implied by Eqs. (1) 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 $n_B^s(t \to \infty) = n_B^\infty - n_A^\infty$, $n_A^s(t \to \infty) = 0$. A density hole of size x_t grows on the more *dilute* A side.

When are these MF results valid? To answer this question properly, one must examine the dynamics of ρ_{AB}^s. Using Doi's formalism [5], we have derived an exact self-consistent relation for ρ_{AB}^s which involves the three-body correlation $\rho_{BAB}(\mathbf{r}\,|\,0,0;t)$, namely, the conditional density of B groups at $\mathbf{r}$, given an A-B pair at the origin. This relation reads

$$\begin{aligned} \rho_{AB}^s(t') = {}& n_A^\infty n_B^\infty - \lambda \int_0^t dt'\, S_{t-t'}^{(d+1)} \rho_{AB}^s(t') \\ & - I_{BAB}(t) - I_{ABA}(t), \end{aligned} \tag{6}$$

where $I_{BAB}(t) \equiv \lambda \int_0^t dt' \int d\mathbf{r}\, \mathcal{G}_{t-t'}(\mathbf{r}) \rho_{BAB}(\mathbf{r}\,|\,0,0;t') \times \rho_{AB}^s(t')$, and similarly for I_{ABA}. Here, $S_t^{(d+1)} \approx 1/x_t^{d+1}$ is the probability that 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.

Equation (6), which contains unknown three-body correlations, can be closed for ρ_{AB}^s by postulating physically motivated bounds on the three-body terms. This is a much milder measure than approximating ρ_{BAB} as a product of lower order correlation functions [1]. We postulate the existence of constants U and L such that (i) $\rho_{BAB}(\mathbf{r}\,|\,0,0;t) \leq U n_B^\infty$ and (ii) $\rho_{BAB}(\mathbf{r}\,|\,0,0;t) \geq L n_B^\infty$ for $x > x_t$, where x is the distance from the interface. Assumption (i) states that conditional densities never become much greater than far-field densities. Assumption (ii) states that conditional densities at points beyond diffusional range of the interface are uncorrelated with it. These assumptions imply that $U n_B^\infty$ is an upper bound for ρ_{BAB} for each $\mathbf{r}$, while a lower bound is zero for $x < x_t$ and $L n_B^\infty$ for $x > x_t$. We thus obtain bounds on I_{BAB} (and similarly for I_{ABA}) by substituting these two extreme cases into its definition. We find, after substitution into Eq. (6),

$$\rho_{AB}^s(t) = n_A^\infty n_B^\infty - \lambda \int_0^t dt'\, S_{t-t'}^{(d+1)} \rho_{AB}^s(t') - \lambda n(t) \int_0^t dt'\, S_{t-t'}^{(1)} \rho_{AB}^s(t')\,, \tag{7}$$

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^∞.

It is now straightforward to solve Eq. (7) for ρ_{AB}^s and thus obtain the reaction rate via Eq. (1). One can show that deletion of the term containing $S^{(d+1)}$ reproduces the MF kinetics of Eq. (5). 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 $t_2^* < t < t_l$ this same term, the term containing $S^{(d+1)}$ in Eq. (7), is dominant. The MF approximation then breaks down and reaction kinetics are of second order and DC. This is a new regime whose physical origin is as follows. Consider A and B molecules 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, $\mathcal{N}_{\text{coll}}$, 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 $\mathcal{N}_{\text{coll}} \approx (t/t_a)\,(ha^d/x_t^{d+1})$, and the total reaction probability $Qt_a\mathcal{N}_{\text{coll}} \sim t^{(d_c-d)/z}$ is thus an increasing function of time for $d < d_c$. It reaches unity at a time $t_2^* = t_a(Qt_a h/a)^{z/(d-d_c)}$. 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 two-body correlation function, invalidating the MF assumption. Instead, $\mathcal{R}_t$ is proportional to the number of such pairs per unit area, $x_t^{d+1} n_A^\infty n_B^\infty$. The kinetic sequence is now

$$\mathcal{R}_t \approx \begin{cases} \lambda t n_A^\infty n_B^\infty & (t \ll t_2^*) \\ x_t^{d+1} n_A^\infty n_B^\infty \sim t^{(d+1)/z} & (t_2^* \ll t \ll t_l) \\ x_t n_A^\infty \sim t^{1/z} & (t \gg t_l) \end{cases} \tag{8}$$
$$(d < d_c, Q > Q^*)\,,$$

which may be explicitly verified by direct substitution into Eq. (7). For times $t > t_l$, where $t_l \equiv t_a(n_B^\infty a^d)^{-z/d}$ 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 first order DC kinetics as in Eq. (5). These arguments have implicitly assumed that $t_2^* < t_l$, i.e., $Q > Q^* \equiv ah^{-1}t_a^{-1}(n_B^\infty a^d)^{(d_c-d)/d}$. For weakly reactive groups, $Q < Q^*$, the new second order DC regime is absent; A reactants collide with many B's before reaction is likely. The relevant time scale is then t_m^* and the kinetics of Eq. (5) are recovered.

MF theory does not give the correct reaction rate in low dimensions. In fact, the density decay of Eq. (4) 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 Ω, half of which is on the A and half of which is on the B side. The fluctuations ΔN_Ω in the initial difference between the number of A and B reactants in Ω 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. (4). Thus fluctuations determine the n_A^s asymptotics in low dimensions:

$$n_A^s(t) \approx (n_A^\infty x_t^{-d})^{1/2} \sim t^{-d/2z}, \qquad (d < d_c)\,. \tag{9}$$

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 two-species reactions, $A + B \to 0$ [2].

In summary, 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 from the problem of nonstationary reactive chemical fronts where, for $z = 2$, $d_c = 2$ has been found [9].) 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 second 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^∞, n_B^∞. Intuition suggests second order kinetics, since reaction requires an

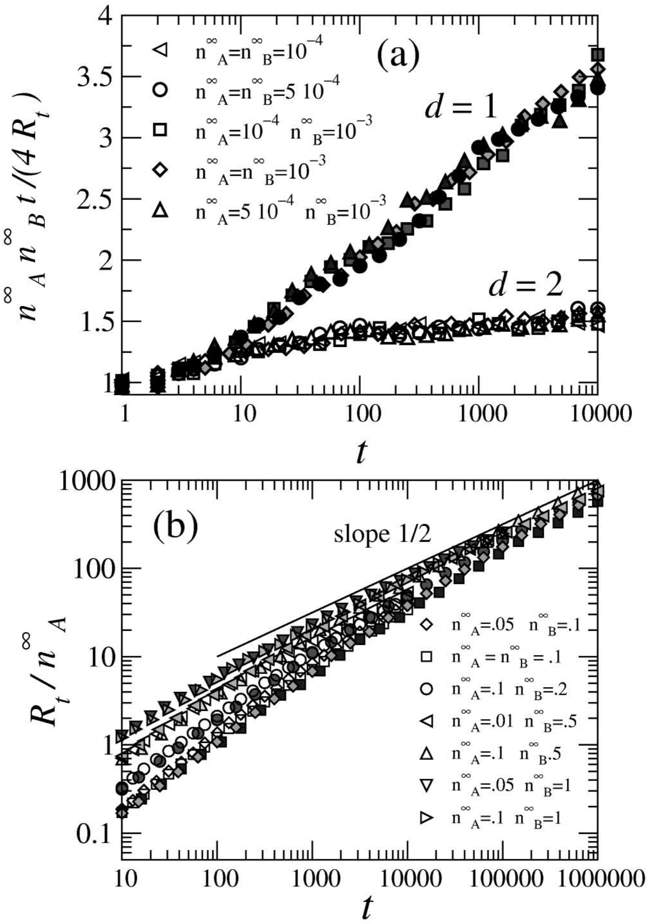

FIG. 2. A and B random walkers on a square lattice annihilating on contact at an interface separating A and B bulks with various densities n_A^∞, n_B^∞. Time is in units of site hopping time. Standard deviation of mean for each point is less than 3% in all cases. Open (filled) symbols: $d = 2$ ($d =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

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^∞ only. The more dense side plays a different role: Characteristic time scales involve n_B^∞ rather than n_A^∞.

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 second order DC regime [the second of the regimes listed in Eq. (8)]. The result for $d = 1$, $z = 2$ is $\mathcal{R}_t \sim t/\ln t$. We have tested our theory for small molecules by numerical simulations in $d = 1$ and $d = 2$. These exhibit second 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 crossover to first order DC behavior with $\mathcal{R}_t \sim n_A^\infty t^{1/2}$ 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 [12]. These can help to resolve fundamental issues in interfacial science.

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