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The effect of initial spatial correlations on late time kinetics of bimolecular irreversible reactions

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ABSTRACT

We study anomalous kinetics associated with incomplete mixing for a bimolecular irreversible kinetic reaction where the underlying transport of reactants is governed by a fractional dispersion equation. As has been previously shown, we demonstrate that at late times incomplete mixing effects dominate and the decay of reactants follows a fundamentally different scaling comparing to the idealized well mixed case. We do so in a fully analytical manner using moment equations. In particular the novel aspect of this work is that we focus on the role that the initial correlation structure of the distribution of reactants plays on the late time scalings. We focus on short range and long (power law) range correlations and demonstrate how long range correlations can give rise to different late time scalings than one would expect purely from the underlying transport model. For the short range correlations the late time scalings deviate from the well mixed t^{-1} and scale like $t^{-1/2\alpha}$, where $1 < \alpha \leq 2$ is the fractional dispersion exponent, in agreement with previous studies. For the long range correlation case it scales like $t^{-\beta/2\alpha}$, where $0 < \beta < 1$ is the power law correlation exponent.

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1. Introduction

Physical mixing is a fundamental process that brings species together. As such it is the driver of many chemical reactions and correctly modeling it is a prerequisite to being able to accurately model chemical reactions. While this principle may seem simple, reaction kinetics observed in many systems differ from those observed under ideal well-mixed reactor laboratory settings (e.g. Refs. [1,2]). The root cause for this is often incomplete mixing, where concentration fields are heterogeneous and there is a segregation of chemical species that limits reactions by how quickly reactants can diffuse/mix with one another [3].

The field of incomplete mixing and its impact on reactive transport is a rich one with many studies aiming to quantify the effective dynamics. There has been much scientific interest with real practical application ranging from transport in porous media [1,2,4,5], in living cells [6,7] and in turbulent and chaotic flows [8]. In this work we will focus on perhaps the simplest form of chemical reaction, namely a bimolecular kinetic irreversible one $A + B \rightarrow \emptyset$. We ignore the resulting species and assume it plays no role in the system. This might for example apply to a species that precipitates out of the system. We choose to concentrate on bimolecular reaction, since, as highlighted by Gillespie [9], understanding this simple case is fundamental as more complex reactions can be built as combinations of bimolecular ones. In a well mixed system with initially identical concentrations of A and B it is well known that the concentration will evolve as $C_A(t) = C_B(t) = \frac{C_A(0)}{1+kC_A(0)t}$, which for large times scales as t^{-1} . Countless numerical studies have shown that at late times the concentration actually evolves like $t^{-\frac{d}{4}}$, where d is the number of spatial dimensions of the system [3,10–17,13]. This deviation from the t^{-1} scaling

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can be attributed to incomplete mixing effects. Most studies identifying this behavior have been numerical, but the work of Refs. [18,19] showed and validated these ideas under laboratory experimental conditions also. The phenomenon is often called Ovchinnikov–Zeldovich segregation after the work of Ref. [3].

Another rich field of physics is the field of anomalous transport [20], which is transport which deviates from classical Fickian dispersion. Again, the number of systems where anomalous transport has been observed is large, including the disciplines of porous media [21–23,4], cell dynamics [24,25] and turbulent and chaotic flows [26,27] mentioned above. In fact such anomalous transport has been observed so frequently so as to actually be thought ubiquitous [28]. Anomalous transport can broadly be classified as super-diffusive or sub-diffusive depending on whether the second centered moment scales faster or slower with time than the diffusive case, where it scales linearly with time. Anomalous transport has been shown to have a potentially significant impact on chemical reactions in a variety of studies that couple the two [29–35].

In this particular study we restrict ourselves to $d = 1$ dimensions. We will focus on transport that displays super-diffusive behavior and model it with space fractional dispersion, which is a continuum description of a system with Levy flights, again said to occur frequently in physics [36]. In the continuum limit such transport can be governed by a fractional dispersion equation. A particular example of practical interest where the one-dimensional fractional dispersion has been successfully applied in porous media, is for the study of the transport of contaminants at the highly heterogeneous MADE field site [37]. For transport governed by fractional dispersion it has been shown that incomplete mixing effects similar to those of the Fickian case discussed above also occur. In direct analogy, the late time scaling of the concentration fields has been shown to scale as $t^{-\frac{1}{2\alpha}}$, where α is the fractional dispersion exponent [38–41] and $\alpha = 2$ corresponds to the Fickian case of $t^{-\frac{1}{4}}$.

While anomalous transport may indeed not be all that anomalous as highlighted by Refs. [28,36] the underlying origin of anomalous transport is often unknown and thus it is not always clear, which model of anomalous transport is truly applicable [42]. Merely observing anomalous transport is not sufficient to identify its root cause. For example anomalous scalings of particle displacement variances can arise due to strong disorder correlations or broad disorder point distributions [43]. Such ambiguities could certainly also occur in the case of anomalous kinetics. Moreover, in real-world applications, it is often difficult to distinguish anomalous diffusion from Fickian diffusion of multiple components (e.g., Refs. [44,45]), or one component with spatial constraints (e.g. Refs. [46,47]).

In this work we aim to demonstrate precisely that correlation structure in the initial distribution of reactants can lead to late time scalings in concentrations that deviate from the *classical* predictions of $t^{-\frac{1}{2\alpha}}$.

2. Model

2.1. Governing equations

We begin by considering a system where two components A and B react kinetically and irreversibly with one another, $A + B \xrightarrow{k} \emptyset$. The components A and B are distributed in an infinite one dimensional space and move by symmetric fractional dispersion [48], such that the governing equation for transport of each is given by

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^\alpha C_i}{\partial |x|^\alpha} - r, \quad i = A, B, \quad -\infty < x < \infty \quad (1)$$

where $C_i = C_i(x, t)$ is the concentration of component i , D is the dispersion coefficient, $1 \leq \alpha \leq 2$ is the fractional derivative exponent and $r = r(x, t)$ is the reaction rate, given by the law of mass action

$$r = kC_A C_B \quad (2)$$

where k is the rate constant for the specified reaction. For a system that is well mixed in space at all times no spatial gradients will exist and Eq. (1) can be simplified to

$$\frac{\partial C_i}{\partial t} = -kC_A C_B, \quad i = A, B, \quad -\infty < x < \infty. \quad (3)$$

If we consider the case where the initial concentrations are equal $C_A(t = 0) = C_B(t = 0) = C_{A0}$, Eq. (3) has a well known analytical solution

$$C_i = \frac{C_{A0}}{1 + C_{A0}kt} \quad (4)$$

which asymptotically at late times scales as t^{-1} . As mentioned in the Introduction it is well known that deviations from this solution can occur due to stochastic fluctuations of concentration, leading to segregation of species A and B and thus incomplete mixing in space. To this end we aim to quantify the deviations from the well mixed thermodynamic solution (4), and begin by assuming that A and B are initially distributed randomly in the one-dimensional domain. To represent this we break the concentrations into a mean and deviation such that $C_i(x, t) = \bar{C}_i(t) + C_i'(x, t)$. In this context the overbar refers to the ensemble average and the prime to fluctuations about this. By definition the average of the fluctuation term is zero. We furthermore assume an ergodic system.

For consistency and comparison with the well-mixed case we consider that the initial mean concentrations of both A and B are the same, i.e.

$$\overline{C_A}(x, 0) = \overline{C_B}(x, 0) \equiv \overline{C_{A0}}. \quad (5)$$

Due to the stoichiometry of the reaction, the mean concentrations of the two species are identical at *all* times. Substituting the decomposition of concentration into mean and deviation into (1) and taking the ensemble average of the governing equations for the mean concentrations we obtain

$$\frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_A}\overline{C_B} - k\overline{C'_A C'_B}. \quad (6)$$

Note the similarity of this equation with Eq. (3) but with an additional term representing the stochastic fluctuations. When fluctuations are small relative to the mean concentration we expect the mean field to dominate and the system to evolve as it does for the well mixed solution in (4). It is when $\overline{C'_A C'_B}$ is no longer negligible that incomplete mixing effects kick in. Similarly we can combine (1) and (6) to write an equation for the fluctuation concentrations such that

$$\frac{\partial C'_i}{\partial t} = D \frac{\partial^\alpha C'_i}{\partial |x|^\alpha} - k\overline{C_A}C'_B - kC'_A\overline{C_B} - kC'_A C'_B + k\overline{C'_A C'_B}. \quad (7)$$

2.2. Moment equations

The details of the stochastic fluctuations do not interest us, but rather we want to know how they affect and alter the evolution of the mean concentrations $\overline{C_i}$. This will depend on the evolution of the $\overline{C'_A C'_B}$ term in (6). In order to ultimately predict the evolution of this term let us introduce the correlation function $\overline{C'_A(x, t)C'_A(y, t)}$ and aim to quantify its evolution. We begin by assuming that components A and B will have statistically identical initial correlation structures such that

$$\overline{C'_A(x, 0)C'_A(y, 0)} = \overline{C'_B(x, 0)C'_B(y, 0)} = R(x, y). \quad (8)$$

Furthermore, due to the stationary nature of the system, we have that $R(x, y) = R(|x - y|)$. We know physically that deviations from the well mixed prediction occur when islands or isolated patches of A and B emerge, which suggests that the initial field should be anti-correlated in A and B . To this end we assume that the anticorrelation between A and B has the same form as the correlation of A or B such that

$$\overline{C'_A(x, 0)C'_B(y, 0)} = -R(x, y). \quad (9)$$

We will now develop the equation for the covariance $f(x, y, t) = \overline{C'_A(x, t)C'_B(y, t)}$. Multiplying (7) for $i = A$ by $C'_B(y, t)$ and discarding terms of higher than second order in fluctuations we obtain

$$C'_B(y, t) \frac{\partial C'_A(x, t)}{\partial t} = D \frac{\partial^\alpha C'_A(x, t)C'_B(y, t)}{\partial |x|^\alpha} - \overline{kC_A(x, t)C'_B(x, t)C'_B(y, t)} - k\overline{C_B(x, t)C'_A(x, t)C'_B(y, t)}. \quad (10)$$

Similarly multiplying (7) for $i = B$ by $C'_A(y, t)$ and discarding terms of higher than second order in fluctuations we obtain

$$C'_A(y, t) \frac{\partial C'_B(x, t)}{\partial t} = D \frac{\partial^\alpha C'_B(x, t)C'_A(y, t)}{\partial |x|^\alpha} - \overline{kC_B(x, t)C'_A(x, t)C'_A(y, t)} - k\overline{C_A(x, t)C'_B(x, t)C'_A(y, t)}. \quad (11)$$

Next, we take the ensemble average of (10) and (11) and sum the equations. We recognize that by stationarity $\overline{C'_B(y)C'_A(x)} = \overline{C'_A(y)C'_B(x)}$, and that $\overline{C'_A(x)C'_A(y)} = \overline{C'_B(x)C'_B(y)}$ due to the indifference between the statistics of species A and B . Thus we obtain the following equation for the covariance

$$\frac{\partial \overline{C'_A(x, t)C'_B(y, t)}}{\partial t} = 2D \frac{\partial^\alpha \overline{C'_A(x, t)C'_B(y, t)}}{\partial |x|^\alpha} - 2k\overline{C_A(x, t)C'_A(x, t)C'_A(y, t)} - 2k\overline{C_A(x, t)C'_A(x, t)C'_B(y, t)}. \quad (12)$$

By analogy, an equation for $\overline{C'_A(x)C'_A(y)}$ is given by

$$\frac{\partial \overline{C'_A(x, t)C'_A(y, t)}}{\partial t} = 2D \frac{\partial^\alpha \overline{C'_A(x, t)C'_A(y, t)}}{\partial |x|^\alpha} - 2k\overline{C_A(x, t)C'_B(x, t)C'_A(y, t)} - 2k\overline{C_B(x, t)C'_A(x, t)C'_A(y, t)}. \quad (13)$$

Subtracting Eq. (13) from (12) gives:

$$\frac{\partial \overline{C'_A(x, t)C'_B(y, t)} - \overline{C'_A(x, t)C'_A(y, t)}}{\partial t} = 2D \frac{\partial^\alpha \left(\overline{C'_A(x, t)C'_B(y, t)} - \overline{C'_A(x, t)C'_A(y, t)} \right)}{\partial |x|^\alpha}. \quad (14)$$

Recalling the initial condition $\overline{C'_A(x, 0)C'_A(y, 0)} = -\overline{C'_A(x, 0)C'_B(y, 0)} = R(x, y)$, from moment Eqs. (12) and (13) it follows that

$$\overline{C'_A(x, t)C'_B(y, t)} = -\overline{C'_A(x, t)C'_A(y, t)}. \quad (15)$$

From (14), $f(x, y, t) = \overline{C'_A(x, t)C'_B(y, t)}$, has governing equation

$$\frac{\partial f(x, y, t)}{\partial t} = 2D \frac{\partial^\alpha f(x, y, t)}{\partial |x|^\alpha} \quad (16)$$

subject to initial condition $f(x, y, t = 0) = -R(x, y)$. The solution to (16) with natural boundary conditions on an infinite domain can be found with the Green's function, i.e.

$$f(x, y, t) = \int_{-\infty}^{\infty} -R(\xi, y)G(x, \xi, t)d\xi, \quad (17)$$

where

$$G(x, \xi, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-2D_+|k|^\alpha t} e^{ik(x-\xi)} dk. \quad (18)$$

and $D_+ = -D \cos(\frac{\alpha\pi}{2})$ is a positive constant. To solve for the mean concentration in (6) we need to quantify $\overline{C'_A C'_B}$. This can be obtained as the limit of the cross-covariance, $\lim_{y \rightarrow x} f(x, y, t)$, i.e.

$$\lim_{y \rightarrow x} f(x, y, t) = \int_{-\infty}^{\infty} -R(\xi, x)G(x, \xi, t)d\xi. \quad (19)$$

where we have assumed $R(x, y)$ is continuous near $x = y$.

2.3. Mean concentration equation

We can now substitute (19) into (6) and write the governing equation for the mean concentration as

$$\frac{\partial \overline{C}_i}{\partial t} = -k\overline{C}_i^2 + k \int_{-\infty}^{\infty} R(\xi, x)G(x, \xi, t)d\xi. \quad (20)$$

It should now be evident that the second term on the right hand side of (20), which quantifies the effect of the fluctuations, depends on two key features, namely the Green's function associated with transport as well as the initial correlation structure $R(\xi, x)$. To date it seems that most of the research work has focused on the effect of transport, which manifests itself through the Green's function only. However, both can control the long term behavior of the mean concentration, which is the principle topic of this paper. To demonstrate this we will develop our calculations to focus on two types of correlation structure: short range correlation, and long range correlation.

It is well known that at late times the dominant balance in Eq. (20) shifts from being the left hand side and the first term on the right hand side at early times to a balance between the two terms on the right hand side at late times. In other words, at late times the solution to (20) can be determined by balancing the two terms on the right hand side and the scaling of the anomalous kinetics can be inferred from

$$\overline{C}_i(t \rightarrow \infty) = \left(\int_{-\infty}^{\infty} R(\xi, x)G(x, \xi, t)d\xi \right)^{\frac{1}{2}}. \quad (21)$$

3. Correlation structure and influence on anomalous kinetics

3.1. Short range correlation

Here, we include a study of short range correlations for completeness only. Thus we will focus on perhaps the simplest form short range correlation structure, namely a delta correlated initial condition for f such that

$$f(x, y, t = 0) = -R(x, y) = -\sigma^2 \delta\left(\frac{x-y}{l}\right), \quad (22)$$

where σ^2 is the variance and l the correlation length. This can be thought of as an approximation of an exponential or Gaussian correlation and it is straightforward to show that after some initial transient the solution for the delta correlation

displays the same behavior. For this case we can solve Eq. (21) as

$$\bar{C}_i(t \rightarrow \infty) = \left(\frac{\sigma^2 l \Gamma(\frac{1}{\alpha})}{2^{\frac{1}{\alpha}} D_{\dagger}^{\frac{1}{\alpha}} \pi \alpha} \right)^{\frac{1}{2}} t^{-\frac{1}{2\alpha}} \tag{23}$$

which in the Fickian case of $\alpha = 2$ becomes

$$\bar{C}_i(t \rightarrow \infty) = \left(\frac{\sigma^2 l}{\sqrt{8\pi D_{\dagger}}} \right)^{\frac{1}{2}} t^{-\frac{1}{4}}. \tag{24}$$

This means that $\bar{C}_i \sim t^{-\frac{1}{2\alpha}}$, or $\bar{C}_i \sim t^{-\frac{1}{4}}$ for the Fickian case of $\alpha = 2$, which is the classical anomalous scaling that has been predicted many times thus displaying consistency between our theoretical developments and previous work.

3.2. Long range correlation

Next, in order to test the other extreme of the spectrum, let us consider an initial correlation structure that displays correlation over long ranges, i.e. a power law or fractal correlation. To this end we chose the following initial correlation structure

$$R(x, y) = C(x - y) = C(s) = \beta l^{\beta} \int_0^{1/l} dm \cos(ms) m^{\beta-1} \tag{25}$$

where $0 < \beta < 1$ is an arbitrary constant. For distances of the order of or smaller than l , the medium appears homogeneous, i.e. the correlation function for $s \ll l$ is approximately constant:

$$C(s) = \beta \int_0^1 dm' \cos(m' s/l) m'^{\beta-1} = \beta \int_0^1 dm' m'^{\beta-1} + \dots = 1 + \dots, \tag{26}$$

where $m' = ml$, and the dots denote subleading contributions of $\mathcal{O}(s/l)$. For $s \gg l$ the correlation function (25) can be approximated by:

$$C(s) = \left(\frac{s}{l}\right)^{-\beta} \beta \int_0^{s/l} dm'' \cos(m'') m''^{\beta-1} = B \left(\frac{s}{l}\right)^{-\beta} + \dots, \tag{27}$$

where $m'' = ms$, the dots denote subleading contributions, and B is a constant given by

$$B = \Gamma(\beta + 1) \cos\left(\frac{\beta\pi}{2}\right) \tag{28}$$

and we can see from (27) that $C(s)$ over long range displays a pure power-law behavior.

Using this long range correlation function, the solution for $f(x, y, t)$ is

$$\begin{aligned} f(x, y \rightarrow x, t) &= -\frac{\beta l^{\beta}}{2\pi} \int_0^{l^{-1}} dm \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dk \cos(mx) m^{\beta-1} e^{-2D_{\dagger}|k|^{\alpha}t} e^{ikx} \\ &= -\frac{\beta l^{\beta}}{2\pi} t^{-\frac{\beta}{\alpha}} \int_0^{l^{-1}t^{\frac{1}{\alpha}}} d\mu \int_{-\infty}^{\infty} dy \mu^{\beta-1} e^{-2D_{\dagger}|y|^{\alpha}} \int_{-\infty}^{\infty} d\chi \cos(\mu\chi) e^{iy\chi} \\ &= -\frac{\beta l^{\beta}}{2} t^{-\frac{\beta}{\alpha}} \int_0^{l^{-1}t^{\frac{1}{\alpha}}} d\mu \int_{-\infty}^{\infty} dy \mu^{\beta-1} e^{-2D_{\dagger}|y|^{\alpha}} [\delta(y + \mu) + \delta(y - \mu)] \\ &= -\beta l^{\beta} t^{-\frac{\beta}{\alpha}} \int_0^{l^{-1}t^{\frac{1}{\alpha}}} d\mu \mu^{\beta-1} e^{-2D_{\dagger}\mu^{\alpha}}. \end{aligned} \tag{29}$$

At large times the integral converges to a constant value of $\frac{1}{\alpha} [(2D)^{-\frac{\beta}{\alpha}} \Gamma(\frac{\beta}{\alpha})]$ and so

$$f(x, y \rightarrow x, t \rightarrow \infty) \sim -t^{-\frac{\beta}{\alpha}}. \tag{30}$$

Thus from the late time dominant balance in (21)

$$\bar{C}_i \sim t^{-\frac{\beta}{2\alpha}} \tag{31}$$

which means that for $0 < \beta < 1$ and $1 < \alpha < 2$ the scaling lies somewhere between t^0 and $t^{-\frac{1}{2}}$, effectively slower than the asymptotic rate expected by the short range correlation functions. More importantly, based on previous work, one might associate a scaling between $t^{-\frac{1}{4}}$ and $t^{-\frac{1}{2}}$ to correspond to an underlying super-dispersive transport or a scaling between t^0 and $t^{-\frac{1}{4}}$ to reflect an underlying sub-diffusive transport. However we here demonstrate that such a conclusion may be misleading without detailed knowledge (which it is typically improbable to have) of the initial concentration distribution correlation structure.

4. Summary and conclusions

We have studied the effect of incomplete mixing on reactions in a super-diffusive system, where two components A and B react kinetically and irreversibly such that $A + B \xrightarrow{k} \emptyset$. The reaction rate was assumed to follow the law of mass action. A and B are transported superdiffusively and the transport is governed by the fractional dispersion equation, which is characterized by exponent $1 < \alpha < 2$. We consider a one-dimensional system with A and B initially distributed randomly therein. The initial spatial correlation of fluctuations in A and B was assumed to be anticorrelated and to have the same form as the autocorrelation of A and B . In particular we considered two correlation structures (i) a short range delta correlation and (ii) a power-law correlation with the exponent $0 < \beta < 1$. The system was assumed to be ergodic.

Using this setup and these assumptions, we have analytically shown that concentration deviations start to play an important role on the system dynamics as an incomplete mixing regime emerges. During this regime the concentrations decay at a slower rate compared to the well-mixed case. In particular, we have shown how the initial correlation structure of the concentration affects the late time behavior of the system, and demonstrated the difference between the influence of short-range correlation structures and long-range (power-law) correlation. For short range structures we demonstrated that the concentrations scale like $t^{-1/4}$ in the Fickian case, and scale like $t^{-\frac{1}{2\alpha}}$ in the super-diffusive case (where $1 < \alpha < 2$ is the fractional dispersion exponent), which is entirely consistent with previous studies. The novel aspect is that we show that for the long-range correlation structure, the concentration scales as $t^{-\frac{\beta}{2\alpha}}$ (where $0 < \beta < 1$ is the power-law correlation exponent), which can scale somewhere between t^0 and $t^{-\frac{1}{2}}$ depending on the value of α and β . This work serves to once again highlight as has often been done in the anomalous transport community that qualitatively similar anomalous kinetics can arise for a multitude of reasons and that one should not infer underlying processes from purely upscaled information.

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