Reactive Turbulent Flow in Low-Dimensional, Disordered Media

Michael W. Deem\textsuperscript{1} and Jeong-Man Park\textsuperscript{1,2}

\textsuperscript{1}Chemical Engineering Department, University of California, Los Angeles, CA 90095-1592
\textsuperscript{2}Department of Physics, The Catholic University, Seoul, Korea

We analyze the reactions $A + A \rightarrow \emptyset$ and $A + B \rightarrow \emptyset$ occurring in a model of turbulent fluid in two dimensions. We find the reactant concentrations at long times, using a field-theoretic renormalization group analysis. We find a variety of interesting behavior, including, in the presence of potential disorder, decay rates faster than that for well-mixed reactions.

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I. INTRODUCTION

The behavior of chemical reactions in turbulent flow determines how certain types of chemical reactors function, how combustion occurs in engines, how smog is produced in the atmosphere\textsuperscript{9}, and how certain types of planktonic predators feed in the ocean\textsuperscript{2}. Reactive turbulent flow is usually analyzed by continuum reaction/transport equations for the reactants\textsuperscript{11–13}. We now know, however, that the upper critical dimension in which such mean-field equations fail is two\textsuperscript{4–7}. We provide here the first renormalization group, field-theoretic treatment of reactive turbulent flow in two dimensions.

We consider a low concentration of reactants immersed in an isotropic, turbulent fluid flow. The interplay of reaction, turbulent mixing, and trapping by disorder will be shown to lead to novel kinetics at long times. So as to access the most interesting regime, we will consider a two-dimensional system. At low reactant concentrations, the dynamics of the fluid will not be affected by the kinetics of the reaction. As such, the effect of the turbulence is simply to advect and to mix the reactants.

Our intention is not to derive a theory of turbulence but rather to derive a theory of bimolecular kinetics in the presence of isotropic turbulence and potential disorder. We, therefore, employ the same statistical theory of turbulence conventionally used to study turbulent transport of passive scalars\textsuperscript{14,15}. For a review of this approach, see\textsuperscript{11}. We assume, in particular, that the turbulent fluid which advects the reactants can be modeled as a quenched, random, Gaussian velocity field with the correct statistics. While the fluid velocity streamlines produced by this conventional approach do not satisfy the Navier-Stokes equations, the correct transport properties of the reactants are captured. The correct Kolmogorov energy cascade and Richardson separation laws, for example, are produced. One can imagine using a more detailed model of the fluid mechanics. Avellaneda and Majda have, for example, used statistical flow fields that depend on both space and time to model turbulent transport\textsuperscript{16,17}. On an even more detailed level, one could use statistical flow fields that satisfy the Navier-Stokes equations. Renormalization group theories for flow fields of this type have been derived by Forster, Nelson, and Stephen\textsuperscript{14} and later by Yakhot, Orszag, and coworkers\textsuperscript{15,17}. We settle for the simplest description of the fluid mechanics that captures the essence of turbulent transport. Our results should not be sensitive to this assumption, since the physical processes that appear to dominate the long-time kinetics depend only on the overall transport properties of the fluid. In support of the generality of our results, we note that Deering and West have used mean field theory to analyze the reaction $A + B \rightarrow \emptyset$ in a time-dependent, but spatially uncorrelated, model of isotropic turbulence. Where mean field theory is expected to work (where the renormalized reaction rate does not enter the prediction for the long-time reactant concentration) their results agree with ours.

In this article, we use a field-theoretic approach to analyze reaction kinetics in a model of turbulent fluid flow. A definition of the fluid flow and the reaction kinetics is given in Section II. The reactive turbulence problem is mapped to a field theory that is convenient for analysis in Section III. The long-time behavior of the $A + A \rightarrow \emptyset$ reaction is derived by a renormalization group analysis in Section IV. The long-time behavior of the $A + B \rightarrow \emptyset$ reaction is derived in a similar fashion in Section V. We conclude with a comparison to experimental results in Section VI.

II. DEFINITION OF REACTIVE TURBULENT FLOW

In our formulation, an isolated reactant undergoes biased Brownian motion in the fluid streamlines, reacting at a given rate with other nearby reactants. In the absence of reaction, the motion of the particles can be described by a Langevin equation:

$$\frac{dx_i}{dt} = \beta D F(x_i) + \eta(t) , \tag{1}$$

where the inverse temperature is given by $\beta = 1/(k_B T)$, and $D$ is the diffusivity. Here the position of particle $i$, $x_i$, undergoes advection due to forces from the fluid flow and diffusion due to forces from the random, thermal motion of the fluid. The random, thermal noise has a correlation determined by the diffusion coefficient:
\[
\langle n_\mu(t)n_\nu(t') \rangle = 2D\delta_{\mu\nu}\delta(t-t') .
\]
We choose the forces coming from the fluid stream lines so that they mimic turbulence. Defining
\[
\langle F_\mu(x)F_\nu(x') \rangle = G_{\mu\nu}(x-x') ,
\] we choose
\[
\hat{G}_{\mu\nu}(k) = \hat{\chi}_{\mu\nu}(k) (\delta_{\mu\nu}k^2 - k_\mu k_\nu) + \hat{\chi}_{uu}(k)k_\mu k_\nu ,
\]
where the Fourier transform of the correlation function is \(\hat{G}_{\mu\nu}(k) = \int d^d x G_{\mu\nu}(x) \exp(i k \cdot x)\) in \(d\) dimensions. Here \(\hat{\chi}_{\mu\nu}(k)\) is the correlation function of the stream function that gives rise to the turbulent fluid flow, and \(\hat{\chi}_{uu}(k)\) is the correlation function of a quenched, random potential, \(u(x)\), which we have included for generality. To mimic turbulence, we choose
\[
\hat{\chi}_{\phi\phi}(k) = \frac{\sigma}{k^{2+\gamma}} , \quad \hat{\chi}_{uu}(k) = \frac{\gamma}{k^{2+\gamma}} .
\]
Isotropic turbulence is modeled by \(\gamma = 8/3\) and \(\gamma = 0\).

Of course, we are interested in reactive, turbulent flow. We consider two different reactions:
\[
A + A \xrightarrow{\lambda_0} \emptyset
\]
and
\[
A + B \xrightarrow{\lambda} \emptyset .
\]
Here \(\lambda_0\) is the conventional reaction rate. We place our reactants on a square lattice, of lattice spacing \(h\). This lattice spacing implies a cutoff in Fourier space of \(\Lambda = 2\pi/h\). Reaction occurs between two particles, at rate \(\lambda_0/h^2\), only when they are on the same lattice site. The diffusion and advection occurs on this same lattice.

### III. FIELD-THEORETIC REPRESENTATION

The quantity of interest is the long-time concentration of the reactants. The presence of the quenched fluid stream lines and the quenched, external potential makes direct analysis of the dynamics rather difficult. Perturbation theory fails due to singularities in the forces at small \(k\). We, therefore, map the above description onto a field theory and analyze the field theory using renormalization group theory. We assume that the concentration of reactants is initially Poisson, with average density \(n_0\). A field theory is derived by identifying a master equation, writing the master equation in terms of creation and annihilation operators, and using the coherent state representation [8,13]. The random potential is incorporated with the replica trick [13], using \(N\) replicas of the original problem. For reaction [8], the concentration of A at time \(t\), averaged over the initial conditions, \(c_A(x,t)\), is given by
\[
c_A(x,t) = \lim_{N \to 0} \langle a(x,t) \rangle ,
\]
where the average is taken with respect to \(\exp(-S_{AA})\),
\[
S_{AA} = \int d^d x \int_0^{t_f} dt \tilde{a}_\alpha(x,t) \left[ \partial_t - D\nabla^2 + \delta(t) \right] a_\alpha(x,t) + \frac{\lambda_0}{2} \int d^d x \int_0^{t_f} dt \left[ 2\tilde{a}_\alpha(x,t) a^2_\alpha(x,t) + \tilde{a}^2_\alpha(x,t) a_\alpha^2(x,t) \right] - n_0 \int d^d x \tilde{a}_\alpha(x,t)
\]
\[
- \frac{\beta^2 D^2}{2} \int dt_1 dt_2 \int_{k_1,k_2,k_3,k_4} (2\pi)^d \delta(k_1 + k_2 + k_3 + k_4) \times \tilde{a}_\alpha(k_1,t_1) \tilde{a}_\alpha(k_2,t_1) \tilde{a}_\alpha(k_3,t_2) \tilde{a}_\alpha(k_4,t_2) \times [k_1 \cdot (k_1 + k_2) k_3 \cdot (k_3 + k_4) \times \hat{\chi}_{uu}(k_1 + k_2)]
\]
\[+ k_1 \times k_2 \times k_3 \times k_4 \hat{\chi}_{\phi\phi}(k_1 + k_2) .
\]
Summation is implied over replica indices. The notation \(\int_k\) stands for \(\int d^d k/(2\pi)^d\). The upper time limit in the action is arbitrary as long as \(t_f \geq t\). We do not dwell on the construction of this field theory. It differs from that for reaction in a random potential field only by the inclusion of the random stream line terms [8,13].

For distinct reactants, reaction [8], a field theory can also be derived. The relevant action has the form
\[
S_{AB} = \int d^d x \int_0^{t_f} dt \tilde{a}_\alpha(x,t) \left[ \partial_t - D\nabla^2 + \delta(t) \right] a_\alpha(x,t) + \frac{\lambda_0}{2} \int d^d x \int_0^{t_f} dt \left[ 2\tilde{a}_\alpha(x,t) a^2_\alpha(x,t) + \tilde{a}^2_\alpha(x,t) a_\alpha^2(x,t) \right] - n_0 \int d^d x \tilde{a}_\alpha(x,t)
\]
\[
- \frac{\beta^2 D^2}{2} \int dt_1 dt_2 \int_{k_1,k_2,k_3,k_4} (2\pi)^d \delta(k_1 + k_2 + k_3 + k_4) \times \tilde{a}_\alpha(k_1,t_1) \tilde{a}_\alpha(k_2,t_1) \tilde{a}_\alpha(k_3,t_2) \tilde{a}_\alpha(k_4,t_2) \times [k_1 \cdot (k_1 + k_2) k_3 \cdot (k_3 + k_4) \times \hat{\chi}_{uu}(k_1 + k_2)]
\]
\[+ k_1 \times k_2 \times k_3 \times k_4 \hat{\chi}_{\phi\phi}(k_1 + k_2) .
\]
The concentrations averaged over initial conditions are given by
\[
c_A(x, t) = \lim_{N \to 0} \langle a(x, t) \rangle
\]
\[
c_B(x, t) = \lim_{N \to 0} \langle b(x, t) \rangle,
\]
where the average on the right hand side is taken with respect to \(\exp(-S_{AB})\). So as to reach the most interesting scaling limit, we have taken the initial average densities to be the same, \(c_A(x, 0) = c_B(x, 0) = n_0\). For simplicity, we have also assumed equal diffusivities of the two species, \(D_A = D_B = D\). Note that the \(A\) and \(B\) particles experience an identical force due to the fluid stream lines but an opposite force due to the quenched, external potential.

IV. THE \(A + A \to \emptyset\) REACTION

Let us first consider how turbulence will affect the \(A + A \to \emptyset\) reaction in the absence of potential disorder. Without turbulent mixing, this reaction is diffusion-limited. The concentration decays at long times as \(c_A(t) \sim \ln(t/t_0)/(8\pi Dt)\), with \(t_0 \approx h^2/D\). This decay is slower than the \(c_A(t) \sim 1/(k^* t)\) that would be predicted by simple mean-field kinetics for a well-mixed reaction with effective reaction rate \(k^*\). Turbulence mixes the reactants, tending to eliminate the transport limitation on the reaction rate. As we will see, turbulence will cause the reactant concentration to follow the mean-field result, with \(k^* \leq \lambda_0\).

We analyze the field theory via renormalization group theory. The flow equations in two dimensions, to one loop order, are
\[
\begin{align*}
\frac{d \ln n_0}{d l} &= 2 \\
\frac{d \ln \lambda}{d l} &= -\frac{\lambda}{4\pi D} - g \\
\frac{d \ln g}{d l} &= y - 2g,
\end{align*}
\]
where the dimensionless coupling constant is given by \(g = \sigma \beta^2 \Lambda^{-y}/(4\pi)\). The dynamical exponent is given by
\[
z = 2 - g.
\]
We see that the flow equations lead to a non-zero fixed point for the coupling \(g^* = y/2\). This fixed point is probably exact, if we assume that the reaction does not affect the transport properties.

We determine the long-time decay from the flow equations via matching to short-time perturbation theory. The flow equations are integrated to a time such that \(t(t^*) = t \exp[-\int_0^{t^*} z(t) d\bar{l}] = t_0\). At short times, we find the mean-square displacement of an unreactive particle from \(\langle r^2(t^*), t^* \rangle = 4Dt(t^*)\) and the concentration of reactants from \(c_A(t^*), t^* \rangle = 1/[1/n_0(t^*) + \lambda(t^*)t(t^*)]\). The long-time asymptotic values are given by scaling: \(\langle r^2(t) \rangle \sim e^{2t^*} \langle r^2(t^*), t^* \rangle\) and \(c_A(t) = e^{-2t^*} c_A(t^*, t^*)\). This procedure gives
\[
c_A(t) \sim \left(\frac{1}{2\pi Dy} + \frac{1}{\lambda_0}\right)^{1/2}
\]
where we recognize the mean field result with effective reaction rate \(1/k^* = 1/(2\pi Dy) + 1/\lambda_0\). The mean square displacement is given by \(\langle r^2(t) \rangle \sim 4Dt(t/t_0)^{\gamma/(4-y)}\), which is an exact law in the absence of reaction. As expected, turbulence leads to the well-mixed, mean-field result for the concentration decay, with an effective reaction rate \(k^* < \lambda_0\). We have determined the effective reaction rate as an expansion in the parameter \(y\), which measures the degree of mixing of the fluid. For simplicity, here, and below, we have used used only the fixed point value of \(g\) when integrating the flow equation for \(\lambda(l)\).

What will happen in the presence of a quenched, random potential? We have seen that fluid streamlines increase the mixing of the reactants. We have previously shown that a quenched, random potential in the absence of turbulence leads to a slowing down of the reaction. This occurs because the reaction becomes diffusion-limited at long times, and the random potential leads to sub-diffusion. We might, therefore, expect that the reactant concentration for \(\gamma \neq 0\) will be lower than that for the case of \(\gamma = 0\) for arbitrary \(\sigma\). In fact, a subtle trapping effect due to the potential leads to increased decay rates, above that for \(\gamma = 0\), for some intermediate values of \(\gamma\).

The flow equations that result in the presence of the random potential are
\[
\begin{align*}
\frac{d \ln n_0}{d l} &= 2 \\
\frac{d \ln \lambda}{d l} &= -\frac{\lambda}{4\pi D} + 3g_\gamma - g_\sigma \\
\frac{d \ln g_\gamma}{d l} &= y - 2g_\sigma \\
\frac{d \ln g_\sigma}{d l} &= y - 2g_\sigma,
\end{align*}
\]
where the dimensionless coupling constants are given by \(g_\gamma = \gamma \beta^2 \Lambda^{-y}/(4\pi)\) and \(g_\sigma = \sigma \beta^2 \Lambda^{-y}/(4\pi)\). The dynamical exponent is given by
\[
z = 2 + g_\gamma - g_\sigma.
\]
These flow equations lead to fixed points for the couplings \(g_\gamma^* = y/2\) and \(g_\sigma^* = (\gamma/\sigma) y/2\). The flow diagram for the couplings is shown in Figure. Including higher order diagrams in the flow equation leads to a bending of the fixed line, more strongly for larger \(\gamma/\sigma\), with the coupling flows remaining linear.
The maximum rate of decay occurs for $3\gamma > \sigma$, in which case we have
\[
c_A(t) \sim \frac{1}{4\pi D(g_\sigma^* - 3g_\gamma^*)} + \frac{1}{\lambda_0} \frac{t}{t_0}
\times \left( \frac{t}{t_0} \right)^{-2g_\gamma^*/(2+g_\gamma^*-g_\sigma^*)}, \quad (3\gamma < \sigma). \tag{17}
\]
For strong potential disorder with $3\gamma > \sigma$, there is a finite fixed point value $\lambda^* = 4\pi D(3g_\gamma^* - g_\sigma^*)$, and we have
\[
c_A(t) \sim \frac{1}{\lambda^* t} \left( \frac{t}{t_0} \right)^{(g_\gamma^*-g_\sigma^*)/(2+g_\gamma^*-g_\sigma^*}, \quad (3\gamma > \sigma). \tag{18}
\]
The maximum rate of decay occurs for $3\gamma = \sigma$, in which case we have
\[
c_A(t) \sim \frac{\ln(t/t_0)}{8\pi(1-y/6)D} t^{-y/(6-y)}, \quad (3\gamma = \sigma). \tag{19}
\]
In all cases, the mean square displacement is given by
\[
\langle r^2(t) \rangle \sim 4Dt(t/t_0)^{(g_\gamma^* - g_\sigma^*)/(2-g_\gamma^* + g_\sigma^*)}.
\]

Examining the asymptotic decay laws (17)-(18), we see that a small amount of potential disorder added to the turbulent fluid mixing leads to an increased rate of reaction. As the potential disorder is increased, eventually the rate of reaction decreases. The exponent of the concentration decay is shown in Figure 2. This result is rigorously valid for small $y$ and finite values of $\gamma$ and $\sigma$. For finite values of $y$, we expect qualitatively similar behavior.

How can potential disorder, which tends to slow down the diffusing reactants, lead to an increased rate of reaction? The potential disorder creates regions of low energy, which tend to attract reactants. The local density of reactants in these deep energy wells is significantly higher than the average density. The reaction rate in these regions, therefore, is higher than would be predicted by mean-field theory based upon the average density. The turbulent mixing flows continuously replenish the reactants in these wells as the reaction occurs. In this way, a reaction rate significantly higher than that for a perfectly well-mixed system arises.

V. THE $A + B \rightarrow \emptyset$ REACTION

We now turn to the $A + B \rightarrow \emptyset$ reaction. In this case, the $A$ and $B$ reactants are attracted to different regions of space by the external potential, and so there is no mechanism for super-fast reaction.

The flow equations for this case are
\[
\begin{align*}
\frac{d\ln n_0}{dt} & = 2 \\
\frac{d\ln \lambda}{dt} & = -\frac{\lambda}{4\pi D} - (g_\gamma + g_\sigma) \\
\frac{d\ln g_\gamma}{dt} & = y - 2g_\gamma \\
\frac{d\ln g_\sigma}{dt} & = y - 2g_\sigma.
\end{align*}
\tag{20}
\]
The dynamical exponent is given by
\[
z = 2 + g_\gamma - g_\sigma. \tag{21}
\]

We first consider the case of no external potential. If, in addition, there is no turbulent flow, the $A$ and $B$ reactants segregate into distinct regions in space. This segregation leads to a severely diffusion-limited reaction at long times. The concentration decays as $c_A(t) = c_B(t) \sim n_0/(8\pi^2Dt)^{1/2}$. Allowing for turbulent mixing, we expect the reaction to become more well-mixed, with less segregation and faster reaction. In fact, there will be a transition to a region that is reaction limited for strong enough mixing flows.
Specifically, for weak mixing we have the reaction will be in the reaction-limited regime. In the transport-limited regime, we use $c_A(t^\ast, l^\ast) = 1/[1/n_0(t^\ast) + \lambda(t^\ast)t(l^\ast)]$, as before.

For weak fluid mixing, the reaction will be in the transport-limited regime, whereas for strong fluid mixing, the reaction will be in the reaction-limited regime. Specifically, for weak mixing we have

$$c_A(t) \sim \left( \frac{n_0}{8\pi^2Dt} \right)^{1/2} \left( \frac{t}{t_0} \right)^{-y/(8-2y)}, \quad (y < 2, \gamma = 0).$$

(22)

For strong mixing, we have

$$c_A(t) \sim \left( \frac{1}{2\pi Dy} + \frac{1}{\lambda_0} \right)^{1/2} \left( \frac{t}{t_0} \right)^{\gamma/\sigma}, \quad (y > 2, \gamma = 0).$$

(23)

The exponent of this decay is shown in Figure 4. Note that for isotropic turbulence ($y = 8/3$), the reaction is always in the reaction-limited regime in two dimensions.

Potential disorder will slow down the reaction, both because reactants are attracted to different regions of space and because the transport of reactants to each other is slowed. Our one-loop flow equations predict that in the transport-limited regime

$$c_A(t) \sim \left( \frac{n_0}{8\pi^2Dt} \right)^{1/2} \left( \frac{t}{t_0} \right)^{(g_0^\ast - g_0^\gamma)/(4-2g_0^\ast + 2g_0^\gamma)}, \quad (g_0^\ast + g_0^\gamma < 1),$$

(24)

where, as before, we have $g_0^\ast = y/2$ and $g_0^\gamma = (\gamma/\sigma)y/2$. In the reaction-limited regime, we have

$$c_A(t) \sim \left[ \frac{1}{4\pi D(g_0^\ast + g_0^\gamma)} + \frac{1}{\lambda_0} \right] \left( \frac{t}{t_0} \right)^{2g_0^\ast/(2-g_0^\ast + g_0^\gamma)}, \quad (1 < g_0^\ast + g_0^\gamma < 2).$$

(25)

The exponent of this decay is shown in Figure 4. The effective reaction rate in Eq. (25), however, may contain corrections higher order in $y$.

### VI. CONCLUSION

Experiments to test our predictions for isotropic turbulence, Eqs. (14) and (23), would be relatively simple to perform. The behavior of the prefactor would be the quantity of interest. Reaction conditions of the type that we consider could be realized in reactions between ionic species confined to two-dimensional fluid films that are surrounded by spatially-addressable electrodes or media with ionic disorder that is not equilibrated. The electrodes or disordered media are necessary to generate a potential with the required, singular correlation function. The required isotropic turbulence can be generated in the standard fashion. Fluid flows less strong than isotropic turbulence ($y < 8/3$) could be observed in regions of developing turbulence.

A recent experiment by Paireau and Tabeling has seen an enhancement of the effective reaction rate between ions in a chaotically-mixed, two-dimensional, fluid with attractors [21]. In this experiment only the prefactor to the reactivity was enhanced. The decay exponent remained at unity because the disorder was technically irrelevant. We are unaware of experiments, to date, that can test our predictions for technically relevant disorder, Eqs. (17)-(19) and (24)-(25).

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