Reaction Kinetics of Clustered Impurities

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ABSTRACT
We study the density of clustered immobile reactants in the diffusion-controlled single species annihilation. An initial state in which these impurities occupy a subspace of codimension $\bar{d}$ leads to a substantial enhancement of their survival probability. The Smoluchowski rate theory suggests that the codimensionality plays a crucial role in determining the long time behavior. The system undergoes a transition at $\bar{d} = 2$. For $\bar{d} < 2$, a finite fraction of the impurities survive: $n_I(t) = n_I(\infty) + \text{const} \times \log(t)/\sqrt{t}$ for $d = 2$ and $n_I(t) = n_I(\infty) + \text{const}/\sqrt{t}$ for $d > 2$. Above this critical codimension, $\bar{d} \geq 2$, the subspace decays indefinitely. At the critical codimension, inverse logarithmic decay occurs, $n_I(t) \sim \log(t)^{-\alpha(d,\bar{d})}$. Above the critical codimension, the decay is algebraic $n_I(t) \sim t^{-\alpha(d,\bar{d})}$. In general, the exponents governing the long time behavior depend on the dimension as well as the codimension.

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I. Introduction

The kinetics of diffusion-controlled chemical reactions have attracted much interest recently. For simple homogeneous reaction processes, substantial theoretical knowledge is available [1, 2, 3, 4, 5, 6]. For single species bimolecular reactions it is well known that for \( d \leq 2 \), spatial correlations between reacting particles are important in the long time limit, while for \( d > 2 \) reactants are effectively transparent, and a universal decay of the density occurs. A number of reaction processes, such as the annihilation processes, \( A + A \rightarrow 0 \) [3] and the aggregation process, \( A + A \rightarrow A \) [6] belong to this universality class.

A recent generalization of this process to heterogeneous situations was shown to exhibit a rich array of asymptotic behavior. When the reactants have a polydisperse distribution of diffusion coefficients, non-universal decay kinetics may occur. Such a process is well suited for describing reactions that involve particles with different masses. The case in which a small number of particles move according to one diffusion coefficient and the bulk according to another is especially interesting because of its simplicity. The survival probability of a single “impurity” particle immersed in a background of identical particles, \( n_I(t) \), depends in a nonuniversal fashion on the diffusivity of the impurity. In one dimension, the results are especially intriguing. While for the aggregation process, a mapping to a random walk in three dimensions enables an exact solution [7], for the annihilation process only an approximate theory is available [8]. The survival probability of an immobile impurity particle is equivalent to the fraction of unvisited sites by annihilating random walkers [8]. Additionally, as the annihilation process is equivalent to the \( T = 0 \) Ising model with Glauber dynamics [10], \( n_I(t) \) equals the fraction of “cold” spins, i.e., the number of spins that did not flip up to time \( t \). Numerically, both time-dependent and finite size simulations [8, 11, 12], as well as time series studies [8, 13], suggest that the impurity survival probability follows a non-trivial decay \( n_I(t) \sim t^{-\alpha_I} \), with \( \alpha_I \approx 0.37 \), while the corresponding theoretical exponent for the aggregation case is \( \alpha_I = 1 \). In addition, for trimolecular annihilation, \( A + A + A \rightarrow 0 \) it was found that the impurity decays faster than a power-law but slower than an exponential \( n_I(t) \sim \exp(-\log(t)^{3/2}) \) [9]. Hence, in one-dimension, the impurity decay kinetics are highly sensitive to microscopic details of the reaction process.

In this study, we present a generalization of the isolated impurity problem. We examine the collective effects of “trapped” or equivalently immobile impurities by considering the initial condition in which the immobiles are clustered. For simplicity, the immobiles occupy a subspace of dimension \( d_I \) embedded in a \( d \)-dimensional space. For convenience we introduce the codimensionality \( \bar{d} = d - d_I \). Note that the case \( \bar{d} = d \) corresponds to the isolated impurity problem. We are primarily interested in the relevance of the subspace, if any, to the asymptotic behavior of the survival probability. In
the long time limit, neighboring immobile reactants “shield” each other, and as a result, the immobile reactants decay significantly slower than the background. The subspace becomes more pronounced and consequently, the subspace interface acts as an absorbing boundary to the background. The geometry of the system reduces to a \( d \)-dimensional one. By applying the Smoluchowski rate theory to the background in dimension \( d \) and to the impurity subspace in dimension \( \bar{d} \), theoretical prediction concerning the asymptotic form of the survival probability are made possible. The subspace undergoes a survival-extinction transition at \( \bar{d} = \bar{d}_c = 2 \). Below this critical codimension, a finite fraction of the immobiles survive, while at a higher codimension they decay forever. For \( \bar{d} = 1 \), the approach to the final density is an algebraic one \( n_I(t) - n_I(\infty) \sim 1/\sqrt{t} \) for \( d > 2 \), with a logarithmic correction at \( d = 2 \), \( n_I(t) - n_I(\infty) \sim \log(t)/\sqrt{t} \). At the critical codimension, \( \bar{d} = 2 \), an unusual logarithmic decay occurs \( n_I(t) \sim t^{-\alpha(d,\bar{d})} \), while for \( \bar{d} > 2 \) a dimension dependent decay \( n_I(t) \sim t^{-\alpha(d,\bar{d})} \) occurs as well.

II. The Isolated Impurity Problem

In this section we review the rate equation theory and apply it to the isolated impurity problem. This approach truncates the infinite hierarchy of equations describing the density at the first order. Above the critical dimension, spatial fluctuations are asymptotically irrelevant and thus, this theory is exact. However, this theory can be extended to arbitrary dimension, and is especially attractive due to its simplicity.

In the lattice version of the homogeneous single species annihilation process, particles hop independently with rate \( D_B \) to any one of their nearest-neighbor sites. An attempt to land on an occupied site results in the removal of both particles from the system. Hence, the density, \( n_B(t) \), obeys the following rate equation, \( \frac{dn_B}{dt} \propto -n_{BB} \), where \( n_{BB} \) is the density of pairs of neighboring particles. This approach leads to an infinite hierarchy of rate equations and is of limited practical use. Alternatively, one assumes that the annihilation rate is proportional to the flux experienced by a particle, \( \frac{dn_B}{dt} \propto -jn_B \). This flux can be evaluated by placing an absorbing particle in a diffusing background of density \( n_B \). Since \( j \) is proportional to \( n_B \), the density is described by the following rate equation,

\[
\frac{dn_B}{dt} = -k_{BB}^dn_B^2,
\]

with \( k_{BB}^d \) being the reaction rate. Above the critical dimension \( d_c = 2 \) the reaction rate is constant, and the above theory is exact. Otherwise, the reaction rate is time dependent since the target particle is surrounded by a depletion zone the size of the diffusion length \( \sqrt{Dt} \). In appendix I, we detail a heuristic derivation of the reaction rate in arbitrary dimension using the quasistatic approximation. In general, \( k_{IJ}^d \), the reaction rate between particles of diffusivities \( D_I \) and \( D_J \) has the following long time
form,
\[ k_{IJ}^d \sim \begin{cases} 
A_1 \frac{(D_I + D_J)/t}{t} & d = 1; \\
A_2 (D_I + D_J)/\log((D_I + D_J)t) & d = 2; \\
A_d (D_I + D_J) & d > 2.
\end{cases} \] (2)

Note that both \( k_{IJ}^d \) and \( D_I \) are rates and that \( A_d \) is a dimensionless prefactor. By introducing a modified time variable
\[ z(t) = \int_0^t k_{BB}^d(t')dt', \] (3)
the rate equation simplifies, \( dn_B/dz = -n_B^2 \). The asymptotic solution to this equation is \( n_B \sim 1/z \). Evaluating the modified time variable, \( z \), we arrive at the following asymptotic behaviors of the homogeneous single-species annihilation process,
\[ n_B(t) \sim \begin{cases} 
1/\sqrt{t} & d = 1; \\
\log(t)/t & d = 2; \\
1/t & d > 2.
\end{cases} \] (4)

Interestingly, these results are asymptotically exact [4, 5], despite the assumptions involved with the rate theory. Moreover, the same results are obtained for the aggregation process \( A + A \to A \) as well. In lower dimensions, the reaction proceeds with a slower rate, since particles are effectively repelling each other. On the other hand, in high dimensions spatial correlations are practically irrelevant and the density decays faster. The critical dimension is characterized by typical logarithmic corrections.

In the impurity problem, the survival probability of a single impurity with diffusivity \( D_I, n_I(t) \), is investigated. Eq. (1) can be generalized to situations with more than one species
\[ \frac{dn_I}{dt} = -k_{BI}^d n_B n_I, \] (5)
with \( k_{BI}^d \) given by Eq. (2). Again, it is useful to rewrite the rate equation in terms of the modified time variable \( z \) defined by Eq. (3), \( dn_I/dz = -(k_{BI}^d/k_{BB}^d)n_B n_I \). Note that in the long time limit the rate ratio approaches a constant that depends only on the diffusivity ratio. By substituting the asymptotic form of the background density \( 1/z \), one finds a purely algebraic dependence of the impurity density \( n_I \sim z^{k_{BI}^d/k_{BB}^d} \) for \( d \neq 2 \). For the case \( d = 2 \) the leading asymptotic correction to the rate ratio is important and a slightly more detailed calculation is needed. Using the aforementioned forms of \( z \) and \( k_{IJ}^d \), we find the following behavior for the impurity density,
\[ n_I(t) \sim \begin{cases} 
t^{-(D_B+D_I)/(8D_B)} & d = 1; \\
t^{-(D_B+D_I)/2D_B} \log(t) & d = 2; \\
t^{-(D_B+D_I)/2D_B} & d \geq 2.
\end{cases} \] (6)
Hence, the diffusivity ratio, $r = (D_I + D_B)/2D_B$, governs the long time kinetics. The logarithmic correction for the case $d = 2$ is characterized by $\gamma = r(1 - \log r)$ \[15\]. For the case $D_I = 0$, the decay exponent equals $1/\sqrt{8} \approx 0.353$ when $d = 1$, and $1/2$ when $d > 2$. While the latter value is exact, the former is only approximate \[8\]. Interestingly, this approximate value is quite close to the observed numerical value 0.37. However, as this approximation is uncontrolled, its accuracy can widely vary, and for the exactly soluble aggregation process, the discrepancy in the exponents is much larger. To summarize, both in the supercritical regime and in the subcritical regime, the decay of the impurities depends on the diffusivity ratio in a nongeneric fashion.

III. Kinetics of Clustered Impurities

The following questions arise naturally from the above theory: Can the presence of neighboring impurities increase the survival probability of an impurity? If yes, to what extent? To answer these questions we start with an initial configuration where impurities occupy a subspace of dimension $d_I$. The codimension $\bar{d}$ can be conveniently defined as $\bar{d} = d - d_I$. For example, when $\bar{d} = 1$, the impurities initially occupy a line in 2D, a plane in 3D, etc. Figure\[\text{fig:initial-configuration}\] illustrates the initial configuration for the case $\bar{d} = 1$ in two spatial dimensions. Note also that the single impurity problem corresponds to the special case $\bar{d} = d$. To preserve the geometrical properties of the impurity subspace as the reaction evolves, we restrict our attention to the case $D_I = 0$.

Let us consider a line of impurities in 2D. The presence of nearby static particles can only increase the survival probability of an impurity, and thus, the survival probability is bounded by $n_I \sim t^{-1/2}$, the corresponding result for the single impurity case for $d \geq 2$. However, the background decay $n_B \sim t^{-1}$ is stronger and consequently, the subspace becomes more and more pronounced in the long time limit. Hence, the impurity-background interface is equivalent to an absorbing boundary for the mobile reactants. This absorber is not a perfect one since not all sites are occupied with impurities. However, it is well known that in the long time limit a partial absorber is equivalent to a perfect one. A depletion layer of width $\sqrt{Dt}$ develops around the subspace and the background density profile is strongly suppressed in this depletion zone. As a result, the geometry of the system is drastically altered. A line in 2D reduces to a one-dimensional geometry. In other words, the codimension becomes the relevant dimension. This simple conclusion has a striking effect on the long time kinetics of the impurities.

One possible way to tackle this problem is to describe this spatial inhomogeneity by the reaction-diffusion equation with proper boundary conditions accounting for the impurity interface. However, the leading term in the reaction-diffusion equation is the diffusion term and this approach is equivalent in the long time limit to the quasistatic approximation, or namely, the Smolechowsky rate theory. This theory, appealing in its simplicity, leads to new and interesting behaviors for the clustered impurity problem.
Figure 1: A line of immobile impurities (bullets) in a two dimensional background (circles).

As discussed above, the relevant dimension is the codimension. Thus, we apply the $\bar{d}$-dimensional rate equation to the impurities,

$$\frac{dn_I}{dt} = -k_{BI}^d n_B n_I,$$

(7)

with the reaction rates of Eq. (2). The equation describing the background is left unchanged, and one simply substitutes the density from Eq. (4). In contrast with the previous analysis, introduction of a modified time variable would not simplify the algebra, since the equations involve different dimensions and consequently, different intrinsic time scales. Instead, the impurity survival probability, $n_I(t)/n_I(0)$, is obtained by an integration of the above equation,

$$n_I(t)/n_I(0) = \exp \left( - \int_0^t dt' k_{BI}^d(t') n_B(t') \right).$$

(8)

Since the case $\bar{d} = d$ reduces to the single impurity case (see Eq. (6)), we concentrate on the case $\bar{d} < d$ only. By substituting the proper values for the $d$-dimensional background density and the $\bar{d}$-dimensional reaction rate into Eq. (8), we find the following asymptotic impurity densities,

$$n_I(t) \sim \begin{cases} 
  n_I(\infty) + \text{const} \times \log(t)/\sqrt{t} & \bar{d} = 1 \text{ and } d = 2; \\
  n_I(\infty) + \text{const}/\sqrt{t} & \bar{d} = 1 \text{ and } d > 2; \\
  \log(t)^{-A_d/2A_{\bar{d}}} & \bar{d} = 2 \text{ and } d > \bar{d}; \\
  t^{-A_{\bar{d}}/2A_d} & \bar{d} > 2 \text{ and } d > \bar{d}. 
\end{cases}$$

(9)

This rich behavior follows directly from the annihilation rate, i.e., the integrand in Eq. (8). If $k_{BI}^d(t)n_B(t)$ decays faster than $1/t$, the integral remains finite in the infinite time limit, and a finite fraction of the impurities survive the annihilation process.
Otherwise, the subspace vanishes. For $\bar{d} < 2$, this integrand decays faster than $1/t$, while for $\bar{d} \geq 2$, the integrand is dominated by $1/t$. Consequently, the system exhibits a survival-extinction transition at $\bar{d} = 2$. Below this critical codimension, a fraction of the impurities survive, while they decay indefinitely at a higher codimension.

Interestingly, the approach to the final density, $n_I(t) - n_I(\infty) \propto \log(t)/\sqrt{t}$ for a line in 2D ($\bar{d} = 1$) is reminiscent of the single impurity decay in 2D. These cases differ in that $n_I(\infty)$ does not vanish for the clustered case. They also differ in their logarithmic correction. The critical case is characterized by inverse logarithmic decay since the annihilation rate is proportional to $1/\log^2(t)/dt$. Both the critical case and the supercritical regime follow a power-law with the exponent, $\alpha(d, \bar{d}) = A_d/2A_d$. Thus, both decays depend on the dimension as well as the codimension. Only in the extreme case, $\bar{d} = d$, corresponding to the single impurity case, $A_d$ cancels out and a universal decay is expected, $n_I \sim t^{-1/2}$. Generally, a detailed calculation for the prefactors is necessary in order to find the various decay exponents. Since the decay in the clustered case $\bar{d} < d$ is slower than in the isolated case $\bar{d} = d$, we learn that the prefactor $A_d$ is an increasing function of the spatial dimension $d$. This observation is consistent with the fact that the initial reaction rate is given by $k^I(t = 0) = 2(D_t + D_I)z_d$, with $z_d$ the number of neighboring sites in $d$-dimensions. Indeed, $z_d$ is an increasing function of $d$. Above the critical dimension $d = 2$, the effective reaction rate depends weakly on time. Hence, the assumption $A_d \propto z_d$ leads to an approximate value for the decay exponent $\alpha(d, \bar{d}) \cong z_d/2z_d$. For a simple square lattice one has the $z_d = 2d$ or $\alpha(d, \bar{d}) \cong \bar{d}/2d$. Note also that this approximation improves as the dimension and the codimension increase.

The above results can be easily generalized to arbitrary dimensions. Such a generalization is nontrivial only when the temporal nature of the reaction rate is dimension dependent, or namely, below the critical dimension. Using the reaction rates of Eq. (A3), we evaluate the immobile impurity densities,

$$n_I(t) \sim \begin{cases} 
  t^{-d/2+1/d/2} & \bar{d} < 2 \text{ and } d = \bar{d}; \\
  n_I(\infty) + \text{const} \times t^{-(d-\bar{d})/2} & \bar{d} < 2 \text{ and } \bar{d} < d < 2; \\
  n_I(\infty) + \text{const} \times \log(t)t^{-(2-d)/2} & \bar{d} < 2 \text{ and } d = 2; \\
  n_I(\infty) + \text{const} \times t^{-(2-\bar{d})/2} & \bar{d} < 2 \text{ and } d > 2; \\
  t^{-1/2}\log(t)^{(1+\log 2)/2} & \bar{d} = 2 \text{ and } d = 2 \\
  \log(t)^{-A_d/2A_d} & \bar{d} = 2 \text{ and } d > \bar{d}; \\
  t^{-A_d/2A_d} & \bar{d} > 2 \text{ and } d \geq \bar{d}.
\end{cases} (10)$$

To summarize, the impurity subspace survives only when $\bar{d} < 2$ and $d > \bar{d}$. The behavior for $d < 2$ is influenced by the background density behavior $n_B \sim t^{-d/2}$. As a result, the approach towards the limiting density is algebraic with a vanishing decay
exponent \((d - \bar{d})/2 = d_I/2\), for the case \(\bar{d} \lesssim d < 2\). It will be interesting to see how well the above results compare with Renormalization Group studies in the vicinity of the critical codimension \(\bar{d} = 2 - \epsilon\).

For completeness, we briefly discuss the early time behavior of the system. We focus on the case where all lattice sites are initially occupied, such that \(n_B(0) = n_I(0) = 1\). Following the above discussion, the initial background-background reaction rate is given by \(k_{BB}^d(t = 0) \approx 2Dz_d\). From Eq. (1), the background density is found

\[
n_B(t) \approx (1 + 2Dz_dt)^{-1} \quad t \to 0.
\]

On the other hand, only interfacial sites contribute to annihilation of impurities, and as a result \(k_{BI}^d = D(z_d - z_{d-\bar{d}})\). By substituting this rate and the early time background density into Eq. (5), the impurity density is calculated in the early time regime,

\[
n_I(t) \approx (1 + 2Dz_dt)^{\beta(d, \bar{d})} \quad t \to 0.
\]

The above exponent, \(\beta(d, \bar{d})\), equals the reaction rate ratio \(\beta(d, \bar{d}) = (z_d - z_{d-\bar{d}})/2z_d\). This exponent should not be regarded as an asymptotic one, since it is relevant only for a short time. In addition to the dimension dependence, the early time behavior depends on the lattice structure as well. As the reaction process evolves, such details become irrelevant, and the general asymptotic behavior is recovered. Note that there is no sign of a critical codimensionality in the early stages since the system is still \(d\)-dimensional. After waiting a sufficiently long time, the geometry changes, and the codimension governs the kinetics.

**IV. Conclusions**

We have studied the kinetic behavior of simple subspaces of immobile reactants in the annihilation process \(A + A \rightarrow 0\). Asymptotically, such an inhomogeneity leads to a change in the geometry of the system, and the codimension becomes the relevant parameter. The Smolechowsky theory shows that a transition from survival to extinction takes place at \(\bar{d} = 2\). For \(\bar{d} < 2\), and \(d > \bar{d}\), a finite fraction of the impurities survive, while for \(\bar{d} \geq 2\) the impurity subspace eventually vanishes. Furthermore, the asymptotic behavior of the impurity density depends on the dimension as well as the codimension.

This study suggests that the rate theory can be extended to heterogeneous situations. Moreover, a time-dependent reaction equation is equivalent in the long time limit to the detailed reaction-diffusion equation. The success of this theory is remarkable especially considering its simplicity. It will be interesting to apply the same mechanism to more complicated processes, such as multispecies reactions.
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Appendix A. The Quasistatic Approximation

The reaction rate, $k^d_{I,J}$, can be found by evaluating the flux $j$ experienced by an absorbing test particle of radius $R$ due to a diffusing background of concentration $c_0$. Hence, the diffusion equation $\partial c/\partial t = D \nabla c$ is solved under the initial conditions $c|_{t=0} = c_0$ and the absorbing boundary condition $c(r)|_{r=R} = 0$. Although an exact solution can be obtained, we present a simpler approximate technique. Since the length scale governing the diffusion process is $\sqrt{Dt}$, one assumes that the absorber does not affect the background density at distances larger than $\sqrt{Dt}$. Inside this depletion zone the Laplacian term dominates the spherically symmetric diffusion equation,

$$Dr^{1-d} \frac{\partial}{\partial r} r^{d-1} \frac{\partial c(r)}{\partial r} = 0, \quad R < r < \sqrt{Dt}. \quad (A1)$$

The quasistatic approximation imposes an additional time-dependent boundary condition $c|_{r=\sqrt{Dt}} = c_0$. The concentration profile is readily obtained for $R < r < \sqrt{Dt},$

$$c(r,t) \simeq \begin{cases} c_0 \left( \frac{(r/R)^{2-d} - 1}{((\sqrt{Dt}/R)^{2-d} - 1) \log((\sqrt{Dt}/R)^{2-d})} \right) & d < 2; \\
\frac{c_0 \log(r/R)}{\log(\sqrt{Dt}/R)} & d = 2; \\
\frac{c_0 \left(1 - (r/R)^{2-d}\right)}{1 - ((\sqrt{Dt}/R)^{2-d})} & d > 2. \end{cases} \quad (A2)$$

Above the critical dimension $d_c = 2$, $c(r,t)$ approaches a limiting density profile. The reaction rate is given by the calculating the total flux seen by the test particle $j = DS_d R^{d-1} \partial c/\partial r$, with $S_d$ the surface area of the $d$-dimensional unit sphere. We quote the leading asymptotic term of the reaction rate, $k^d = j/c_0$,

$$k \propto \begin{cases} D^{d/2} t^{d/2-1} & d < 2; \\
D/\log(Dt) & d = 2; \\
DR^{d-2} & d > 2. \end{cases} \quad (A3)$$

In case where the target diffusivity $D_T$ is nonzero, the effective diffusion constant is $D + D_T$. We derived the continuum rates, however, the lattice counterparts can be conveniently obtained by setting $R \equiv 1.$

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