# Fast-diffusion mean-field theory for k-body reactions in one dimension

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## ABSTRACT

We derive an improved mean-field approximation for $k$-body annihilation reactions $kA \to$ inert, for hard-core diffusing particles on a line, annihilating in groups of $k$ neighbors with probability $0 < q \leq 1$. The hopping and annihilation processes are correlated to mimic chemical reactions. Our new mean-field theory accounts for hard-core particle properties and has a larger region of applicability than the standard chemical rate equation especially for large $k$ values. Criteria for validity of the mean-field theory and its use in phenomenological data fits are derived. Numerical tests are reported for $k = 3, 4, 5, 6$.

Diffusion limited chemical reactions in low dimensions have attracted much theoretical interest in recent years [1-8]. Indeed, in low dimensions fluctuation effects are more profound; deviations from the mean-field rate-equation behavior have been observed in many cases. Most such studies have been focused on two-body reactions $A + A \to$ products, and $A + B \to$ products, with complications such as particle input and production (fragmentation), etc. [8-9].

The $k$-body decay reactions,

$$kA \to \text{inert} \quad , \tag{1}$$

— the subject of our present work, — have attracted less attention [3]. Indeed, in actual chemical applications the two-body reactions are essentially the only relevant processes. However, recently evidence has been offered that $k$-body reaction kinetics is asymptotically equivalent to the dynamics of empty sites in certain deposition processes with diffusional relaxations. Thus, we find it useful to reexamine the limits of validity of the simplest rate equation corresponding to (1),

$$\frac{dc}{dt} = -\Gamma c^k \quad , \tag{2}$$

where $\Gamma$ is the phenomenological rate constant, while $c$ is the particle concentration.

Our study is limited to one-dimensional ($1d$) reactions for three reasons. Firstly, as already mentioned, fluctuation effects are most profound in $1d$. Secondly, numerical simulations of sufficiently high quality are possible in $1d$, and with modern computer facilities the $k$ values accessible are $k \leq O(10)$. Our numerical results were obtained with $k = 3, 4, 5, 6$. Thirdly, we are going to argue that the rate equation (2) applies only for times which increase with $k$ according to

$$t \gg O\left(e^k/k^2\right) \quad . \tag{3}$$

This expression applies for large $k$ (and $d = 1$); a more accurate estimate is given as relation (6) below. Thus, we are going to develop a modified, improved mean-field theory, following similar ideas advanced for deposition models [10], with a wider range of applicability: $t \gg O(1)$ for all $k = 4, 5, \ldots$. This mean-field theory will be formulated for $1d$ lattice reactions. Implication of our results for $d \geq 1$ will be discussed in the summary paragraphs.

Our "microscopic" dynamical rules are defined as follows. At a given time $t$, let the particle density be $\rho(t) = bc(t)$ measured per site of the $1d$ lattice of spacing $b$. Thus, $\rho$ is dimensionless. We assume that hard-core particles hop on the lattice and annihilate with probability $q$, where $0 < q \leq 1$, in groups of $k$ neighbors. Specifically, we assume that each particle attempts to hop at the rate $H$ per unit time. The hopping direction is selected at random to the left (rate $H/2$) or to the right (rate $H/2$). The latter case is illustrated in Figure 1. The active particle marked **a** attempts to hop to the right. If the neighbor site in the hopping direction is empty, marked by **e** in Figure 1, then the active particle moves one lattice spacing. Otherwise it remains in place. However, after each such hopping attempt, successful or unsuccessful, the active particle **a** can annihilate with probability $q$ with $k-1$ particles *in the direction of the hopping attempt*, provided of course that all the $k-1$ appropriate consecutive lattice sites are indeed already occupied.

These dynamical rules introduce correlations between hopping (diffusion) and reaction. Thus, in fact they are less well described by mean-field theories than systems in which the microscopic diffusion and reaction processes are uncorrelated. However, our rules are more appropriate for mimicing the actual chemical systems in higher dimensions. Indeed, if we consider diffusion as a result of Brownian activation due to surrounding medium, then the same activation should promote the particle cluster to go over the reaction energy barrier.

The mean-field approximation is introduced by assuming that the effect of diffusion is to eliminate all correlations in particle positions. For one-dimensional hard-core particles (without any reactions), such diffusional "decorrelation" occurs for infinite times [4]. For reacting particles the approximation is therefore exact for infinite rate of diffusion as compared to reaction, i.e., in the limit $q \to 0$. In $d = 1$ the fast-diffusion approximation takes on a particularly simple form [10]. Indeed, the particle positions being uncorrelated means that the (normalized) probability to a find gap of $m = 0, 1, 2, \ldots$ lattice spacings between two consecutive particles is

$$\mathrm{Prob}(m) = \rho(1-\rho)^m \quad , \tag{4}$$

independent of the positions of the nearby particles.

The annihilation event shown in the upper panel of Figure 1 will occur with probability $\rho(1-\rho) \times \rho^{k-2}$, while the event shown in the lower panel will occur with probability $\rho \times \rho^{k-2}$, where we assume that the gap distribution is given by (4). The factors $\rho(1-\rho)$ and $\rho$ are the probabilities to find gaps of size 1 and 0, respectively, while the factors $\rho^{k-2}$ ensure that the next $k-2$ gaps are all 0. Thus the rate of annihilation events *per site* will be the sum of the above probabilities times the fraction of occupied sites, $\rho$, and the overall rate of annihilation per site, $qH$. The decrease in the particle density is therefore described by the relation

$$\frac{d\rho}{dt} = -qkH(2-\rho)\rho^k \quad , \tag{5}$$

where the factor $k$ was introduced because in each annihilation $k$ particles are removed.

The derivation reported above applies for an infinite system. With some more combinatorics, one can also derive the mean-field equation appropriate for a finite system of $N$ lattice sites. This development has not been attempted here.

Having derived the fast-diffusion mean-field approximation, relation (5), for the variation of the particle density, we proceed as follows. We will derive the limits of validity of the mean-field theory, followed by a discussion of how it should be used in actual data fitting. We then report numerical tests for $k = 3, 4, 5, 6$. Two comments are, however, in place at this stage.

Firstly, the precise form of the mean-field approximation depends on the microscopic dynamical rules. Indeed, the factors combining to produce the right-hand side of (5) were obtained by considering the specific annihilation events presented in Figure 1. Any change in the rules may modify the form of (5), although the general proportionality to $\rho^k$ for small $\rho$ will apply because $k$ particles participate in each annihilation. However, our discussion below, of various aspects of the use and limits of validity of the mean-field approximation, applies quite generally.

Secondly, for $\rho << 1$ the form (5) reduces to the rate equation (2) with the rate constant $\Gamma_{\rm bare} = 2qkb^{k-1}H$, where the subscript will be explained later. However, one can show that the precise condition for attaining this regime is

$$t \gg \frac{e^{k-1}}{2qHk(k-1)} \quad . \tag{6}$$

Thus, the simple rate equation (2) fails for times increasing rapidly with $k$, even within the limits of validity of the fast-diffusion approximation (which will be described shortly). It is important to point out, however, that modification of the simplest form (2) needed to extend the time range down to $qHt \gg O(1)$, depends on the precise microscopic dynamical rules.

We now derive the expression for the limits of validity of mean-field theory. Our approach differs from that adopted in [3] and follows instead the ideas developed for deposition processes [10]. The result is however qualitatively the same. Mean-field relations apply in those regimes where the *local* density fluctuations do not dominate the evolution of the reaction, but instead it is controlled by the global variation in various average properties. As the first step, let us consider in what regimes the local density fluctuations are negligible in their effect on the reaction kinetics.

The average distance between two consecutive particles is $b(1-\rho)/\rho$, so that $k$ particles explore diffusively the distance $\ell = kb(1-\rho)/\rho$. Annihilation rate in this length is given (within the mean-field approximation) by

$$\omega = qH(2-\rho)\rho^k \times (\ell/b) = kqH(1-\rho)(2-\rho)\rho^{k-1} \quad , \tag{7}$$

where the factors multiplying $(\ell/b)$ in the intermediate step represent the annihilation rate (per unit time) per site.

Each annihilation event perturbs the density distribution over the distance of order $\ell$, which $O(k)$ particles would explore had there been no annihilation at all. Thus, we expect that for the fast-diffusion approximation to apply the diffusion must smooth out density fluctuations in $\ell$ much faster than the annihilation events occur. Now the time scale for diffusional relaxation, $\tau$, is given by

$$D\tau = \ell^2 = [kb(1-\rho)/\rho]^2 \quad , \tag{8}$$

where $D \equiv b^2H/4$ is the diffusion constant of the particles in the dilute limit.

Mean-field theories can be used provided

$$\omega\tau \ll 1 \quad , \tag{9}$$

which, after collecting all the definitions and relations above, yields

$$\frac{1}{q} \gg [2k(1-\rho)]^3 \rho^{k-3} \quad , \tag{10}$$

where we replaced $\left(1-\frac{\rho}{2}\right)$ by 1 on the right-hand side; this factor is of order 1 in all regimes.

The right-hand side of (10) is plotted in Figure 2 for $k = 2, 3, 4, 5$. Asymptotically, for small densities (i.e., for large times) the mean-field approximation will always fail for $k = 2$. For $k = 4, 5, \ldots$ the mean-field theory provides the correct asymptotic description of the large-time reaction kinetics. The case $k = 3$ is borderline.

The precise nature of the approximation by the mean-field relations must be discussed in greater detail, however. Indeed, strictly speaking the mean-field results are exact only when correlations are absent which in our case corresponds to the limit $q \to 0$, i.e., very slow reaction. For any finite $q$, there are always correlations. For our choice of the dynamics some correlations are in fact easily visualized. For instance, for $q = 1$, the configuration shown in the lower panel of Figure 1 will be never generated dynamically because *all* hopping events forming sequences of $k$ or more particles are followed by reaction events. The only source of large occupied regions will be the unreacted sequences of particles left over from the initial state at time $t = 0$. The gap size distribution (4) cannot be exact for systems with such correlations (which are also partially present for $q < 1$).

More generally, depletion and distortion of two- and multiple-particle correlation functions away from their mean-field values occurs due to correlations in the dynamics. As a result, the mean-field expressions can be used only with *effective*, renormalized (also termed "hydrodynamic") rate parameters, rather than with *bare* (also known as coarse-grained) rate parameter values such as $H$, even in the regimes where they provide the correct functional form of the asymptotic dynamics.

Specifically, we can define the effective rate function

$$R_{\mathrm{eff}}(t) \equiv \frac{1}{qk(\rho-2)\rho^k}\frac{d\rho}{dt} \quad , \tag{11}$$

suggested by the form of the mean-field relation (5). We expect this function to assume constant values, say $R$, in all the asymptotically mean-field regimes, where $R \neq H$. Since fast reaction tends to decrease the probability of small interparticle gaps, we expect the renormalized rate parameter $R$ to satisfy $R \leq H$, with equality for $q \to 0$.

In our derivation of the criterion (10) for the applicability of the mean-field theory, we used the length scale $\ell = kb(1-\rho)/\rho$ which becomes small for $\rho \to 1$. A conclusion suggested by Figure 2, that the mean-field relations apply for $\rho \simeq 1$, is valid only in a state well equilibrated diffusively. Thus, for initial densities of order 1, our criterion can be used only for *random initial particle distribution*, or for nonrandom distributions which only involve correlations over lengths smaller than $kb[1-\rho(0)]/\rho(0)$.

Thus, there are two possibilities for the mean-field expression to apply for short times, provided that the initial distribution is sufficiently random. If the $\rho(0)$ and $q$ values are such that the inequality (10) is well satisfied to the right of the "hump" of the curves $k \geq 4$ in Figure 2 (or to the right of the full curves for $k = 2, 3$), then the effective rate parameter $R_{\mathrm{eff}}(t)$ will be initially more or less constant. However, this constant value need not be the same as the one attained for large times, to the left of the "hump," for $k = 4, 5, \ldots$, and in fact we expect it to be larger than the $t = \infty$ value. If, however, the initial density is sufficiently small, or $1/q$ sufficiently large, then the whole density variation may fall in the low-density regime (for $k \geq 4$), in which case the mean-field relation with the effective $R$ value replacing $H$, will apply for all times.

The rate function $R_{\mathrm{eff}}(t)$ should therefore decrease monotonically with time. If the initial density is close to 1, and the distribution random, then the rate function will have a distinct plateau for short times, with values approaching $H$ for $\rho(0) \to 1$. For large times the rate function will decrease to the asymptotic mean-field renormalized rate parameter value $R$, provided $k = 4, 5, \ldots$. If the initial density is sufficiently small, or $1/q$ sufficiently large, then this large time behavior will in fact set in for short times as well.

For $k = 2$ the mean-field theory breaks down asymptotically for sufficiently large times, see Figure 2. The rate function then decreases to 0 according to the power law $\sim 1/\sqrt{t}$, as follows from results available in the literature [2,5-7]. Generally for reaction kinetics with identical particles, the nature of deviation from the mean-field behavior for large times can be related to the problem of repeated meetings of $k$ random walkers; see, e.g., [7]. However, presently all such mathematical results are limited to two-body reactions. For short times and fast diffusion, the $k = 2$ system can have certain mean-field like properties which, however, fade away as time increases. This behavior has been observed numerically for reactions [11] and for related deposition models [12].

For $k = 3$, — the borderline case, — it is likely that the rate function vanishes logarithmically for large times, $\sim 1/\log t$, though we are not aware of any published results to substantiate this expectation. However for any data set for $k = 3$, taken over several decades of $t$, the mean-field relations can be phenomenologically used with the effective rate parameter $R > 0$. The marginal logarithmic vanishing of the rate function is difficult to observe numerically.

Our Monte Carlo data were obtained for $k = 3, 4, 5, 6$, on lattices of sizes 2000 with periodic boundary conditions. Each data set was averaged over 50 independent runs, all with random initial conditions. A few runs, order 10, were also made for $k = 10$. We replace $H$ by $R$ in the mean-field approximation (5) and all relations that derive from it. The Monte Carlo time steps were selected to have the microscopic hopping attempt rate $H = 1$. Thus we expect the effective rate values to satisfy $R < 1$. Our typical numerical results are illustrated in Figures 3-6.

Integration of the mean-field relation yields the function $t(\rho)$ as follows,

$$q2^k kR\,[t(\rho)-t_0] = I(\rho) - I(\rho_0) + \ln\frac{2-\rho}{2-\rho_0} \quad , \tag{12}$$

where

$$I(\rho) \equiv -\ln\rho + \sum_{j=1}^{k-1} \frac{2^j}{j\rho^j} \quad , \tag{13}$$

provided that mean-field theory applies for times $t \geq t_0$, with the corresponding density $\rho_0 = \rho(t_0)$. As exemplified by Figures 3-6, our data eventually reached the large-time behavior not sensitive to the initial density. This observation suggests that the large-time value $R$ only depends on $q$, but not on $\rho(0)$. Thus, we used this large time data to fit the $R$ value from the relation (12) in which the terms which are of order 1 for small densities were discarded,

$$Rt \simeq I(\rho)/q2^k k \quad . \tag{14}$$

These curves are shown by dashed lines in Figures 4 and 6, while in Figures 3 and 5 they were too close to other lines (solid lines marked 0.8) to be shown. On a double-logarithmic plot, variation of the trial $R$ value corresponds to translation of the dashed line along the $\log t$ axis. Thus, we only obtain the estimates of $\log R$. The accuracy of the resulting $R$ values is at best semiquantitative.

The values of the large-time asymptotic rate constant, $R$, are summarized in Table 1. The overall trend is as expected from our heuristic discussion of the validity of the mean-field approximation. The effective rates $R/H$ approach 1 for small $q$, while for $q \simeq 1$ the mean-field relation applies with substantially renormalized values $R < H$. Numerical data for several decades in $t$ cannot be used to detect logarithmic terms for $k = 3$. However, the $k = 3$ estimates of $R$ in Table 1 are markedly lower than their $k > 3$ counterparts with the same $q$.

The dashed lines in Figures 3 and 5, defined by (14), deviate in two ways from similar relations predicted by the simpler rate equation (2) with $\Gamma = 2qkb^{k-1}R$ (which are not shown in the figures). Firstly, the curves differ for short times. A more interesting observation is that for larger times, i.e., for smaller $\rho$ values, the dashed lines in Figures 3 and 5 look nearly straight. However, their slope is somewhat steeper than the prediction of the asymptotic rate equation (2): slope $-1/(k-1)$. Indeed, this deviation is quite small for $k \leq 6$. It becomes more profound as $k$ increases, as was found in our preliminary, limited-statistics runs for $k = 10$ as well as in Monte Carlo simulations [13] of related deposition models up to $k = 10$. Of course, asymptotically the slope slowly approaches the rate-equation value, for times defined by (6).

Statistical noise in our data precluded direct estimation of the rate function (11) because evaluation of the time derivative turns out to be particularly sensitive to statistical fluctuations. However, we used the $R$ values estimated for large times (Table 1) and the initial values $\rho(0)$ to draw mean-field curves (12) corresponding to different initial densities. As expected, the short-time behavior of the data is fitted well only for small $\rho(0)$; the quality of the fit improves as $q \to 0$. These properties are illustrated in Figures 3-6 (solid curves). They were shared by all our data sets listed in Table 1. As discussed earlier, the mean-field theory either fails for short times or applies with the effective rate constant larger than $R$, unless the initial density and $q$ are both sufficiently small. Only in the latter case the fixed-$R$ mean-field approximation extends down to $t = 0$.

In summary, we analyzed the applicability of a mean-field approximate equation accounting for the hard-core particle dynamics, to chemical reactions in $1d$. Some of our conclusions are generally valid for $d \geq 1$; these include the fact that difficulties with the simplest rate equations for large $k$ are not inherent to mean-field approximations and can be repaired by accounting for the hard-core interactions, although our explicit results were limited to the one-dimensional case.

Another well known general feature illustrated by our $1d$ studies, is that mean-field theories break down in those cases when local fluctuations dominate the dynamics of the reaction. Classification of borderline $d$-values at and below which the mean-field theory breaks down for multiparticle-input reactions $k_1A_1 + k_2A_2 + k_3A_3 + \ldots \to$ inert, etc., by scaling agruments, can be found in [3,14].

However, even in the regimes where the local fluctuations are irrelevant asymptotically, the $1d$ model studies emphasize the fact that mean-field theories can only be applied as "effective" asymptotic approximations, with renormalized, "hydrodynamic" rate parameters. Our study further suggests that with careful choice of a mean-field equation, one-parameter data fits work quite adequately for large times and in some cases describe the behavior down to $t = 0$.

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## TABLE

**Table 1.** Large time estimates of the phenomenological mean-field rate constant $R \leq H$, based on Monte Carlo data up to $t = 10^6 H^{-1}$. Due to statistical noise in the data, the values $R/H$ shown are semiquantitative; no reliable error limits can be offered. (The $q = 0.001$ Monte Carlo run was only for $k = 3$. Limited-statistics results for $k = 10$, up to times $tH = 10^7$, were also obtained, but no reliable $R$ estimates can be offered.)

| | $k = 3$ | $k = 4$ | $k = 5$ | $k = 6$ |
|---|---|---|---|---|
| $q = 1$ | 0.05 | 0.13 | 0.18 | 0.2 |
| $q = 0.1$ | 0.3 | 0.5 | 0.6 | 0.6 |
| $q = 0.01$ | 0.7 | 0.9 | 0.9 | 0.9 |
| $q = 0.001$ | 0.96 | —— | —— | —— |

## FIGURE CAPTIONS

**Fig. 1.** The active particle **a** attempts to hop to the right. The upper panel shows a configuration in which the attempt is successful: the particle will move to the empty site **e**. The lower panel shows a blocked configurations. In both cases, the $k-1$ lattice sites in the direction of the hopping attempt are occupied ($k=5$ here). Thus, all $k$ particles shown will annihilate with probability $q$.

**Fig. 2.** The function defined by the right-hand side of the inequality (10), shown for $k = 2, 3, 4, 5$.

**Fig. 3.** Numerical data for $k = 6$ and $q = 1$, with the initial densities $\rho(0) = 0.8$ ($\circ$), 0.5 ($\triangle$), 0.2 ($\square$). The solid lines, labeled by the $\rho(0)$ values, represent the mean-field relation (12) with the large-time $R$ value, forced to obey the initial condition $\rho = \rho(0)$ at $t = 0$.

**Fig. 4.** Numerical data for $k = 6$ and $q = 0.01$, with the initial densities $\rho(0) = 0.8$ ($\circ$), 0.5 ($\triangle$), 0.2 ($\square$). The solid lines, labeled by the $\rho(0)$ values, represent the mean-field relation (12) with the large-time $R$ value, forced to obey the initial condition $\rho = \rho(0)$ at $t = 0$. The dashed line indicates the large-time asymptotic expression (14) used to fit the $R$ value.

**Fig. 5.** Numerical data for $k = 3$ and $q = 0.1$, with the initial densities $\rho(0) = 0.8$ ($\circ$), 0.5 ($\triangle$), 0.2 ($\square$). The solid lines, labeled by the $\rho(0)$ values, represent the mean-field relation (12) with the large-time $R$ value, forced to obey the initial condition $\rho = \rho(0)$ at $t = 0$.

**Fig. 6.** Numerical data for $k = 3$ and $q = 0.001$, with the initial densities $\rho(0) = 0.8$ ($\circ$), 0.5 ($\triangle$), 0.2 ($\square$). The solid lines, labeled by the $\rho(0)$ values, represent the mean-field relation (12) with the large-time $R$ value, forced to obey the initial condition $\rho = \rho(0)$ at $t = 0$. The dashed line indicates the large-time asymptotic expression (14) used to fit the $R$ value.

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