Multiparticle reactions with spatial anisotropy

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We study the effect of anisotropic diffusion on the one-dimensional annihilation reaction $kA \rightarrow$inert with partial reaction probabilities when hard-core particles meet in groups of k nearest neighbors. Based on scaling arguments, mean-field approaches, and random-walk considerations, we argue that the spatial anisotropy introduces no appreciable changes as compared to the isotropic case. Our conjectures are supported by numerical simulations for slow reaction rates, for $k=2$ and 4.

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I. INTRODUCTION

In this work we consider the effect of anisotropy on one-dimensional annihilation reaction processes $kA \rightarrow$inert, with diffusion and hard-core particle interactions. Recent interest in the stochastic dynamics of low-dimensional many-body systems has been largely due to the fact that the mean-field rate equation description applies in many instances not only in high dimensions D but also down to $D=1$ or 2. Thus, in order to observe fluctuation-dominated behavior, one has to consider low-dimensional systems. Specifically, in one dimension (1D), a host of exact solutions, asymptotically exact scaling arguments, and equivalence to other more traditional 1D many-body systems, for instance, Heisenberg spin chains, have been reported [1–15]. Some of these results have experimental relevance [16,17].

A recent work by Janowsky [18] provided an indication that spatial anisotropy in diffusion rates (i.e., unequal hopping probabilities to the left and right on the 1D line) modifies the fluctuation behavior of the annihilation reaction $A+B \rightarrow$inert. In particular, the exponent of the large-time, t, power-law decay of the particle concentration

$$c(t) \sim t^{-\alpha} , \tag{1.1}$$

which applies provided the initial A and B densities are equal, was changed from $\alpha=\frac{1}{4}$ to $\frac{1}{3}$. Janowsky's observation was largely numerical, and we are not aware of any analytical or phenomenological explanation available in the literature.

In order to gain insight into the origins of the asymptotic behavior for anisotropic diffusion, we propose, in the present work, to consider reactions $kA \rightarrow$inert, i.e., k-particle annihilation on the line. The reason for favoring these reactions is that for $k>3$ the asymptotic large-time behavior in the isotropic case is mean field [3,19]. There are several phenomenological arguments for this mean-field behavior, as well as for the fluctuation-dominated behavior for $k=2$ (while the case $k=3$ is marginal). We survey these arguments in Sec. II and propose extensions to the anisotropic case.

We then report, in Sec. III, numerical results for $k=2$ and 4. Both analytical considerations and numerical results suggest that spatial anisotropy has little effect on the overall fluctuation vs mean-field regimes for these reactions. Large-scale numerical simulations indicate that details of the variation of the particle density with time are similar, and allow verification of the exponent predictions. A brief summary is given in Sec. IV.

II. PHENOMENOLOGICAL CONSIDERATIONS

Early arguments [20], yielding the fluctuation-dominated, diffusive behavior, for instance for the reaction $2A \rightarrow$inert, went something like this: the average particle density $c(t)$ at time t implies the average separation of order $1/c$ (in 1D). Given the time t and the diffusion constant (of a single particle) $\mathcal{D}$, the only dimensionless combination is $\mathcal{D}tc^2$, which implies $c \sim (\mathcal{D}t)^{-1/2}$. This approach was further refined in [3]. Indeed, assuming that the fluctuation behavior is universal, i.e., that the initial density $\rho=c(0)$ is "forgotten" at large times, one can write the large-time scaling relation (given here for 1D only)

$$c \simeq \rho F(\mathcal{D}t\rho^2) , \tag{2.1}$$

where the scaling function F is 1 for small arguments but must be power law for large arguments such that the ρ dependence is canceled out:

$$c(t) \simeq \frac{(\text{universal constant})}{\sqrt{\mathcal{D}t}} . \tag{2.2}$$

These arguments are valid provided the initial configuration is random (has no correlations, so that the only length scale is $1/\rho$). Their advantage is that they can be extended to $D>1$ and to some more complicated reactions [3,21]. When compared to the predictions of the mean-field rate equations, they yield the upper critical dimension values. For instance for the $k=2$ reaction considered earlier, one obtains $\alpha=D/2$ and, when compared to the mean-field value $\alpha=1$, the upper critical dimension is identified as $D=2$. The disadvantage of such

scaling approach considerations is that they do not yield any associated approximation scheme for more detailed calculations.

Making diffusion anisotropic modifies the diffusion constant and also introduces another dimensional quantity, the drift velocity. Its effect on the scaling-approach predictions is not clear in general. We note, however, that the scaling approach was mainly used for the $k=2$ reactions for which the drift should not be important. Indeed, in the fluctuation-dominated regime the reaction rate eventually renormalizes to the fast-reaction (so-called diffusion-limited) limit. The interparticle distributions are believed to approach diffusion-dominated forms [13,22–24]. In the drifting reference frame the reaction will be the same with slowed-down diffusion. Thus the results of [18] for the reaction $A+B\rightarrow$inert, which indicate that anisotropic diffusion can modify the fluctuation-dominated behavior, were surprising and they are still largely open to interpretation.

Another mean-field approach was developed in [19]: one uses the uncorrelated form of the interparticle distribution to make predictions of the reaction rates. When combined with phenomenological considerations [19,25] yielding diffusive time-scale estimates, this approach can predict, for instance, that the $k>3$ annihilation reactions are mean field in 1D, while the $k=3$ reactions are marginal, which was recently confirmed numerically and analytically [26], and that the $k=2$ case is fluctuation-dominated. Similar mean-field approximations for 1D correlation quantities were used to study more complicated, mostly two-body, reactions [23,24] in 1D. The advantage of these approaches is that they are associated with specific calculational schemes. The disadvantage of these mean-field approximations [19,23,24] is that they cannot be easily extended to $D>1$. (There are, however, other mean-field formulations not limited to 1D.)

We note that the approach of [19] for instance, only requires that for fast diffusion (i.e., assuming a negligibly slow reaction rate), the particles become uncorrelated. As in [19], here we consider particles diffusing on the line and reacting in groups of k on encounters. However, if less than k particles meet, they interact as hard-core objects. In Fig. 1 we show a snapshot of the stochastic evolution of such an anisotropic process for $k=4$. Further details will be given in Sec. III.

An important observation is that making the diffusion anisotropic does not change the property of the hard-core particle system to loose correlation at large times [4], due to diffusion only (disregarding the reaction). This would suggest that the approximations of [19] should remain valid. The behavior for $k>3$ should be mean field for anisotropic hopping, with $k=3$ marginal, while $k=2$ is non-mean-field (although the arguments of [19] cannot predict the exponent α).

Finally, we consider yet another line of argument based on more local, relative coordinate considerations, similar to those advanced in [11,13,22]. For illustration, let us consider the isotropic-case k-particle annihilation in 1D. We note that when k particles needed for reaction end up as a close group due to diffusion, the memory of this event will be washed away by diffusion provided the random walk in the $k-1$ relative distances is nonrecurrent. Only for the one- or two-dimensional relative-coordinate walk will the encounter likely be repeated with the same particles. Thus local fluctuations are likely to be less important for $k-1>2$, which is consistent with the earlier identification of the borderline value $k=3$ which separates the mean-field and fluctuation-dominated regimes.

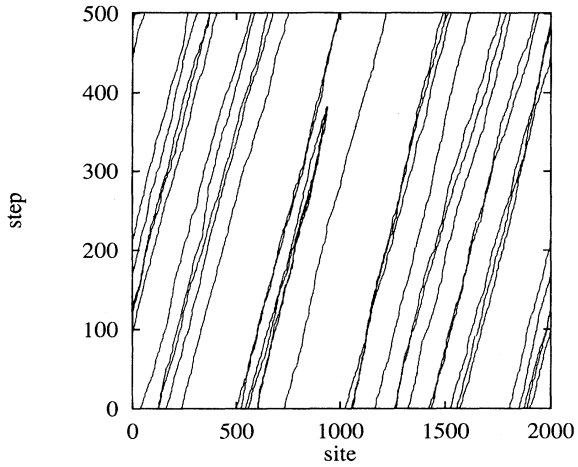

FIG. 1. Snapshot of (a part of) the stochastic evolution for the fully anisotropic reaction-diffusion system $4A\rightarrow$inert. Details of the numerical procedure are described in Sec. III; specifically, the case illustrated was for the reaction probability $q=0.1$.

The advantage of the relative-coordinate argument is that it is local and therefore can easily be applied in $D>1$, etc. However, the locality is also the disadvantage. Indeed, the fluctuation-dominated behavior is generally considered to be a genuinely many-body effect. Few-particle arguments can at best provide hints about the various regimes of behavior.

Since the hard-core constraint is short range, it should have no effect when the particles are well separated, in the dilute limit. Therefore, the recurrence or nonrecurrence properties in the relative coordinates will be the same for isotropic or anisotropic diffusion (as long as no finite-size effects are present, i.e., as long as the particles cannot interact "around" the system for periodic boundary conditions, for instance). In fact, for $k=2$ we anticipate small or no changes as compared to the isotropic case. Our numerical results (Sec. III) have verified this expectation and also indicated a similar property for $k=4$.

III. NUMERICAL RESULTS

The specific details of the hard-core interaction and annihilation reactions, used in our numerical simulations, are given below. We note, however, that the conclusions regarding the asymptotic large-time behavior are generally expected to be universal. The numerical results reported were large scale, computer resource demanding, which was the main reason for considering only the cases $k=2$

(non-mean-field) and $k=4$. The latter provides the simplest example of the clean mean-field behavior already well studied for the isotropic diffusion [19].

At time $t=0$, each site of the one-dimensional lattice with periodic boundary conditions is occupied with probability $c(0)=\rho$ by identical hard-core particles. The particles perform a biased random walk between nearest-neighbor lattice sites. At a given time t one of the $N(t)$ particles present in the system is picked at random. Let j denote its lattice site location. This particle hops to the site $j+1$ (or $j-1$) with probability h (or $1-h$) provided the target site is vacant, otherwise it remains in place. After each successful hopping attempt, the active particle can annihilate with probability $q \leq 1$ with $k-1$ consecutive particles located *in the direction of the hopping*, i.e., on sites $j+2,\ldots,j+k$ (or $j-2,\ldots,j-k$), provided of course that all the $k-1$ corresponding neighboring sites were already occupied. If the target site $j+1$ (or $j-1$) was already occupied, so that the hopping event did not take place, the active particle at j may still annihilate (with probability q) with $k-1$ particles at sites $j+1,\ldots,j+k-1$ (or $j-1,\ldots,j-k+1$), provided they were all occupied. This rule, involving annihilation with particles in the direction of the hopping attempt, successful or unsuccessful, introduces correlations between hopping and reaction which has some similarity with the actual chemical reactions in $D>1$; see [19].

Each successful annihilation reduces the total number of particles present in the system by k. The numerical procedure allows for N such hopping with reaction attempts per each time unit. Thus only after N attempts is the time increased by 1, and the particle number $N(t+1)$ is recalculated. This methodology is particularly efficient for dilute regimes and sets up a well-defined time scale since on average each particle is selected once per unit time. Of course, the results are only meaningful for sufficiently large system sizes so that $N(t) \gg k$ holds for all times t studied. (Strictly speaking, a low reaction probability is also required when the particle density is of order 1.)

Our Monte Carlo simulations confirm the general theoretical expectations for $k=2$ and 4. Results for the density, $c(t)$, are illustrated in Fig. 2. In order to investigate any changes due to anisotropy of hopping in the large-time asymptotic regime, we studied the case $h=0.5$, compared to the maximal anisotropy $h=1$. In fact, large-scale simulations up to 10^8 time steps, starting with random, homogeneous initial particle distribution with densities $\rho=0.25$, 0.5, and 0.8, indicate that no such differences are present, even for rather slow reactions $q \ll 1$ (our numerical values were as low as 0.001). Moreover, the evolution of the particle concentration for $h=1$ closely follows the density of the isotropic case for all times. For *instantaneous* reactions ($q=1$) of *two* particles this result was shown to be rigorous [15,27].

For slow annihilation rates the case $k=2$ exhibits a regime of the mean-field-like behavior ($c \sim t^{-1}$), followed by a crossover to the fluctuation-dominated asymptotic power law ($c \sim t^{-1/2}$). This is illustrated by the $q=0.01$ data in Fig. 2(a). These data were averaged over 200 independent Monte Carlo runs for periodic lattices of

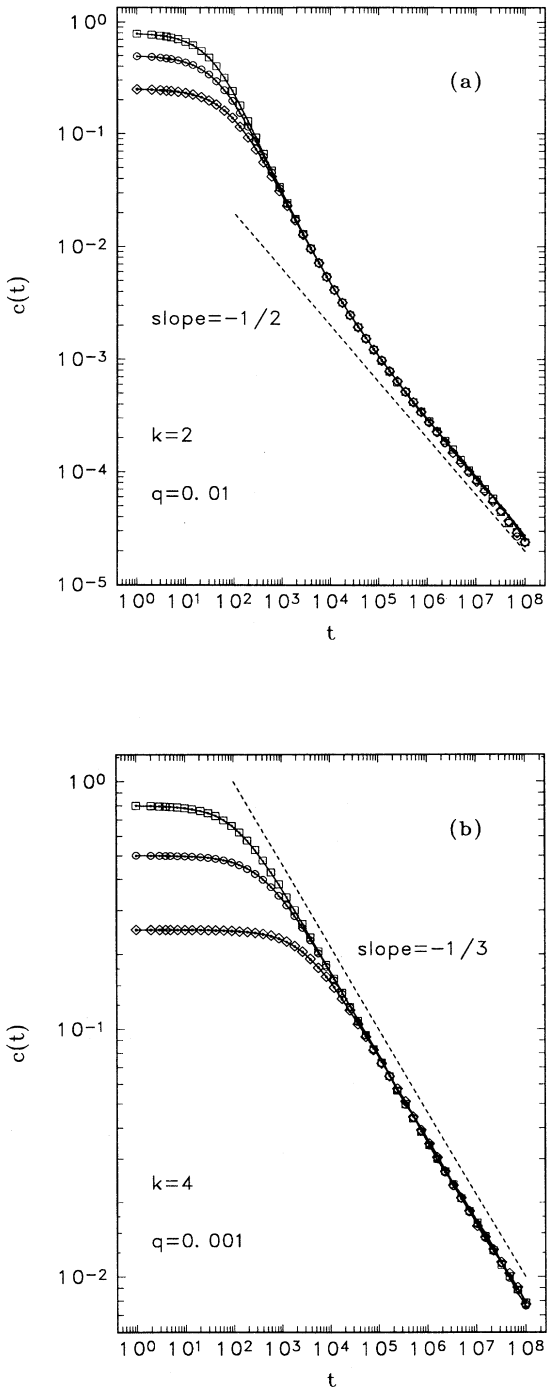

FIG. 2. Macroscopic density $c(t)$ obtained numerically starting from the random particle distribution with the initial concentrations $\rho=0.25$, 0.5, and 0.8. The open symbols correspond to the fully anisotropic hopping ($h=1$). The small dots joined by solid lines denote the isotopic-hopping results ($h=0.5$). (a) Data for $k=2$ and reaction probability $q=0.01$, averaged over 200 Monte Carlo runs, for a periodic lattice of 6×10^4 sites. (b) Results for $k=4$ and $q=0.001$, for 2×10^3 lattice sites, averaged over 200 runs. The dashed lines indicate the asymptotic slopes corresponding to the predicted power-law behavior described in the text.

6×10^4 sites. Although finite-size effects were not severe, rather large lattice sizes were necessary to explore large-time behavior while keeping the particle number $N(t)$ large, as discussed earlier. The mean-field regime became more pronounced as q decreased. For instance, for $q=0.001$ (not shown here) it extended over more than three decades in the t variable.

However, the asymptotic behavior of the $k=2$ reaction-diffusion system is always fluctuation dominated, $\alpha=\frac{1}{2}$, and the anisotropy introduces no detectable changes in the density. Interestingly, the initial density is forgotten before the onset of the mean-field-regime behavior (and of course the initial short-range correlations are completely washed away in the fluctuation-dominated asymptotic limit). This property is shared by the $k=4$ results; see Fig. 2(b).

For $k=4$ the asymptotic behavior was found to be mean field for both isotropic and anisotropic hopping. The density variation of the fully anisotropic case ($h=1$) was in close numerical agreement with the results obtained for isotropic hopping ($h=0.5$), and therefore it can be described accurately by the mean-field rate-equation calculation scheme given in [19]. Since the asymptotic particle concentration decay is now slower ($c\sim t^{-1/3}$), smaller lattice sizes can be used to investigate the behavior for large times. For instance, the $q=0.001$ data shown in Fig. 2(b) represent average over 200 runs, for a periodic lattice of 2×10^3 sites.

IV. DISCUSSION

Generally, our simulations have confirmed the phenomenological considerations regarding the asymptotic particle density, presented in Sec. II. However, the observation that the data for the isotropic and anisotropic cases are so close numerically for all times and q values has not been explained adequately.

Our dynamical rules introduce correlations between hopping and reaction; however, they are more appropriate to describe actual chemical systems. Specifically, the partial reaction probability rates $q<1$ might be interpreted as the result of an effective potential that particles must overcome in order to annihilate. Thus collisions between particles (due to diffusion) should promote the particle cluster to go over the reaction energy barrier. Although these correlated processes are less well described by mean-field calculation schemes, for $k>3$ the use of this methodology is still justified within the fast-diffusion regime ($q\ll1$) where the role of such correlations becomes irrelevant both in the isotropic and anisotropic cases. It is worth pointing out, however, that for $k=2$ and $q=1$ the decoupling between annihilation and diffusion allows for an exact solution of the macroscopic particle concentration which is independent of the hopping anisotropy. To the best of our knowledge, no way of solving the case $k=2$ is presently known either with partial annihilation rates or hopping-reaction correlations.

Finally, our numerical results were only for systems with periodic boundary conditions. It is well established that *pair correlations* in hard-core (nonreacting) particle systems with *anisotropic diffusion* are extremely sensitive to boundary conditions. It is also expected that anisotropic diffusion might introduce significant changes in the form of *unequal-time* correlation functions (not studied in our present simulations). Specifically, for $k=2$ and $q=1$ exact analyses are feasible using fermionic techniques. Thus we hope that the present work will set the stage for further studies of the anisotropic multiparticle reactions.

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[1] M. Bramson and D. Griffeath, Ann. Prob. **8**, 183 (1980).
[2] D. C. Torney and H. M. McConell, J. Phys. Chem. **87**, 1941 (1983).
[3] K. Kang, P. Meakin, J. H. Oh, and S. Redner, J. Phys. A **17**, L665 (1984).
[4] T. Liggett, *Interacting Particle Systems* (Springer-Verlag, New York, 1985).
[5] A. A. Lushnikov, Phys. Lett. A **120**, 135 (1987).
[6] V. Kuzovkov and E. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).
[7] J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988).
[8] D. J. Balding and N. J. B. Green, Phys. Rev. A **40**, 4585 (1989).
[9] J. G. Amar and F. Family, Phys. Rev. A **41**, 3258 (1990).
[10] Z. Racz, Phys. Rev. Lett. **55**, 1707 (1985).
[11] M. Bramson and J. L. Lebowitz, Phys. Rev. Lett. **61**, 2397 (1988).
[12] C. R. Doering and D. ben-Avraham, Phys. Rev. A **38**, 3035 (1988).
[13] D. ben-Avraham, M. A. Burschka, and C. R. Doering, J. Stat. Phys. **60**, 695 (1990).
[14] V. Privman, J. Stat. Phys. **69**, 629 (1992).
[15] The equivalence of adsorption-desorption processes, reaction-diffusion systems, and spin-chain dynamics has been explored by M. D. Grynberg, T. J. Newman, and R. B. Stinchcombe, Phys. Rev. E **50**, 957 (1994); M. D. Grynberg and R. B. Stinchcombe, *ibid.* **49**, R23 (1994); M. Barma, M. D. Grynberg, and R. B. Stinchcombe, Phys. Rev. Lett. **70**, 1033 (1993); R. B. Stinchcombe, M. D. Grynberg, and M. Barma, Phys. Rev. E **47**, 4018 (1993); G. M. Schütz, J. Stat. Phys. **79**, 243 (1995); M. D. Grynberg and R. B. Stichcombe, Phys. Rev. Lett. **74**, 1242

(1995).
[16] R. Kopelman, C. S. Li, and Z.-Y. Shi, J. Lumin. **45**, 40 (1990).
[17] R. Kroon, H. Fleurent, and R. Sprik, Phys. Rev. E **47**, 2462 (1993).
[18] S. A. Janowsky, Phys. Rev. E **51**, 1858 (1995).
[19] V. Privman and M. D. Grynberg, J. Phys. A **25**, 6575 (1992).
[20] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984); Phys. Rev. A **30**, 2833 (1984).
[21] S. Cornell, M. Droz, and B. Chopard, Phys. Rev. A **44**, 4826 (1991).
[22] C. R. Doering and D. ben-Avraham, Phys. Rev. A **38**, 3035 (1988).
[23] J. C. Lin, C. R. Doering, and D. ben-Avraham, Chem. Phys. **146**, 355 (1990).
[24] V. Privman, C. R. Doering, and H. L. Frisch, Phys. Rev. E **48**, 846 (1993).
[25] V. Privman and M. Barma, J. Chem. Phys. **97**, 6714 (1992).
[26] D. ben-Avraham, Phys. Rev. Lett. **71**, 3733 (1993); P. L. Krapivsky, Phys. Rev. E **49**, 3223 (1994); B. P. Lee, J. Phys. A **27**, 2533 (1994).
[27] V. Privman, J. Stat. Phys. **72**, 845 (1993).