Irreversible $nA+mB\rightarrow 0$ reaction of driven hard-core particles

Sungchul Kwon and Yup Kim*

Department of Physics and Research Institute of Basic Sciences, Kyung Hee University, Seoul 130-701, Korea

(Received 2 November 2009; revised manuscript received 19 April 2010; published 8 July 2010)

We investigate the kinetics of general two species annihilation $nA+mB\rightarrow 0$ of driven hard-core (HC) particles with $N=n+m$ in one dimension. With uniform drift velocity, all particles are driven to the right. HC exclusion forbids the interchange of any particles and restricts the number of particles on a site to 0 or 1. The reaction is classified into two classes, the symmetric and the asymmetric reaction. The symmetric reaction means both $nA+mB\rightarrow 0$ and $mA+nB\rightarrow 0$, while the asymmetric reaction means only $nA+mB\rightarrow 0$ for a given (n,m) pair. As N increases, the trains of particles causing the reaction rarely form. Hence, for sufficiently large N, particles are evenly distributed before the reaction, so one expects a crossover N_c above which the kinetics follows the classical mean-field rate equation. We show the existence of N_c and that the kinetics for $N<N_c$ is the same as that of $A+B\rightarrow 0$ of driven HC particles as in the reactions with the isotropic diffusion. However, compared to the isotropic cases, N_c and the kinetics for $N\geq N_c$ are shown to be completely changed by the interplay of the drift and HC exclusion, and strongly depend on the reaction symmetry. We also show that densities decay as $t^{-1/N}$ which cannot be explained by the classical mean-field rate equation. Instead the kinetics is explained analytically by a variant theory.

DOI: 10.1103/PhysRevE.82.011109 PACS number(s): 05.70.Ln, 05.40.−a

I. INTRODUCTION

Interacting particle systems with hard-core (HC) repulsion have long been studied to describe a wide range of phenomena in physics, chemistry and biology [1–5]. In one dimension ($d=1$), HC exclusion severely restricts the motion of particles by forbidding overtaking one another, which results in unexpected and interesting phenomena ranging from anomalous diffusion of a single particle [6,7] to certain types of nonequilibrium absorbing phase transitions [8,9] and the kinetics of irreversible chemical reaction $A+B\rightarrow 0$ [10–12]. In contrast, HC exclusion is believed to be irrelevant in high dimensions ($d>1$) [3] because of overtaking of particles. Especially in reaction-diffusion systems undergoing continuous phase transitions or relaxation to vacuum, density of particles are so low near criticality or annihilation fixed point that the effect of HC exclusion should be too small to be significant even in $d=1$. This belief has been confirmed by recent successes of bosonic field theory on various reaction-diffusion systems [14].

In contrast to reaction diffusions of bosonic particles, external driving fields (drift) can play an important role in reaction kinetics of HC particles. The typical example is two species reaction $A+B\rightarrow 0$ with equal densities of A and B. For isotropic diffusion with random initial distributions with equal densities $\rho_A(0)=\rho_B(0)$, the random fluctuation of the number of initial particles results in segregation of particles into A-rich and B-rich domains [15]. The segregation develops in time and leads to the anomalous density decay in sufficiently low dimensions. The density of each species decays in time t as $\rho_A\sim t^{-d/4}$ for $d<d_c$ and t^{-1} for $d\geq d_c$ with the upper critical dimension $d_c=4$ [15]. On the other hand, for driven HC particles, the interplay of HC exclusion and drift drastically changes the kinetics, i.e. $\rho_A\sim t^{-(d+1)/6}$ in $d<2$ [10–13]. This result is rather surprising because one might naively expect the kinetics of isotropic diffusion by performing Galilean transformation to a zero momentum reference frame. Furthermore, without HC exclusion, the uniform drift does not change the kinetics [16]. Therefore, the interplay of the uniform drift and HC exclusion is crucial for the anomalous kinetics of driven HC particles. However, in $d\geq 2$, the interplay is irrelevant, so the kinetics is the same as that for isotropic diffusion [11]. Hence, the effect of HC exclusion is still restricted in low dimensions $d<2$.

In this paper, as the generalization of $A+B\rightarrow 0$, we study the kinetics of Nth-order two species irreversible reaction $nA+mB\rightarrow 0$ of driven HC particles. The integer n and m indicate the particle number of each species engaged in the reaction and $N=m+n$. From now on we call $nA+mB\rightarrow 0(\mathbf{n},\mathbf{m})$-reaction for the simplicity. We recently showed that the reaction is classified into two classes, the symmetric and the asymmetric reaction [17]. The symmetric reaction means both (n,m) and (m,n) reactions, while the asymmetric reaction means only (n,m) reaction for a given (n,m) pair. The asymmetric reactions with $N>2$ describe various kinds of chemical processes such as the hydriding of uranium and other corrosion reactions [18], chemical reactions in a contaminated atmosphere such as the reaction of nitric oxide with oxygen $2NO+O_2\rightarrow 2NO_2$ [19], catalysis and some pattern formation processes such as Liesegang patterns [20].

For isotropic diffusion with homogeneous initial conditions of $m\rho_A(0)=n\rho_B(0)$ for asymmetric reaction and $\rho_A(0)=\rho_B(0)$ for symmetric one, particle density ρ decays as $\rho\sim t^{-\alpha}$. As N increases, the configurations of N particles causing a given reaction rarely form so the reaction is hard to occur. As a result, there exists a crossover N_c above which particles are uniformly distributed and thus the kinetics is described by classical mean-field (CMF) equation

$$d\rho_A(t)/dt=-\rho_A^n\rho_B^m. \tag{1}$$

Therefore, for $N\geq N_c$, ρ decays with $\alpha_{CMF}=1/(N-1)$ by Eq. (1) regardless of the reaction symmetry. However, N_c is

*Corresponding author; ykim@khu.ac.kr

shown to depend on the reaction symmetry [17,21,22]. For the asymmetric reaction, Sasamoto *et al.* applied the field-theoretic renormalization group (RG) method to the reaction [21]. They showed that the kinetics depends on the number of total particles engaged in the reaction, i.e. $N(=n+m)$. They found $d_c=4/(N-1)$ or $N_c=(d+4)/d$ below which the kinetics is fluctuation-dominated and the same as that of (1,1) case ($N=2$), i.e. $\alpha=d/4$. For the symmetric reaction, however, we recently showed $N_c=4$ in $d=1$ and $N_c=3$ in $d\geq 2$ using the microscopic argument of Cornell *et al.* [17,22]. For $N<N_c$, the symmetric reaction also leads to the fluctuation-dominated kinetics of $N=2$ case. We also showed that HC exclusion is irrelevant in $d=1$ for the reactions with the isotropic diffusion as in $N=2$ case regardless of the reaction symmetry [17].

As in $N=2$ case, (n,m)-reactions with $N>2$ also lead to the segregation into A-rich and B-rich domains in $d=1$ [17,21,22]. Since the kinetics of $N=2$ is very sensitive to the motions of particles and HC interaction [10–13,24], it is naturally expected that the kinetics of the reactions with $N>2$ is also affected by the motions and the type of the interaction between particles. In addition, the symmetry of the reaction is also expected to play an important role in determining the kinetics as shown in the reactions with $N>2$ for isotropic diffusion [17,21,22].

In the present work, we investigate the kinetics of (n,m)-reaction of driven HC particles in one dimension. In the model, all particles are driven to the right and HC interaction exists between all particles. For asymmetric reactions, the interplay of HC exclusion and drift completely changes the kinetics. We numerically show that ρ anomalously decays as $t^{-1/N}$ for $N\geq 3$, which cannot be explained by CMF Eq. (1). From a variant analysis, we analytically show $\alpha=1/N$ for $N\geq 3$ for the asymmetric reaction.

On the other hand, for the symmetric reaction, the interplay leaves N_c unchanged, i.e. $N_c=4$ in $d=1$. Hence, for $N<4$, the kinetics is the same as that of (1,1)-reaction of driven HC particles. However, the kinetics for $N\geq 4$ is rather involved. For $N=N_c(=4)$, ρ follows Eq. (1) with $\alpha_{CMF}=1/(N-1)=1/3$. It means that unlike particles are uniformly mixed up for $N=4$. On the contrary, for $N>N_c$, ρ anomalously decays as $t^{-1/N}$ or saturates to a certain value depending on (n,m) pairs of a given N. The dependence of the kinetics on (n,m) pairs for $N>4$ results from whether the symmetric reaction develops the initial segregation of unlike particles or leads to the alternative ordering of unlike particles. We numerically confirm the spatial organization of unlike particles by introducing a simple measure.

We present our results as follows. We introduce the model in detail in Sec. II. Monte Carlo simulation results of the asymmetric and the symmetric reaction are presented in Secs. III and IV respectively. Finally we summarize our findings in Sec. V.

II. MODEL

We introduce the driven HC particle model with N [DHCM(N)] in $d=1$ as follows. All particles are driven to the right. The number of particles at a site is at most one due to HC repulsion between all particles. A randomly selected particle attempts to hop to the right. If the right site is empty, the hopping is accepted. Otherwise, the attempt is rejected. After the hopping attempt regardless of its result, the reaction takes place in the following cases. One considers $N-1$ nearest neighboring sites on the right side of the selected particle. If all N sites including that of the selected particle are occupied, then the reaction occurs according to the reaction symmetry. In the symmetric reaction, if the number of A-particles (n_A) and B-particles (n_B) among the N particles satisfy either ($n_A=n$, $n_B=m$) or ($n_A=m$, $n_B=n$), then the reaction takes places. For the asymmetric reaction, the reaction occurs only if ($n_A=n$, $n_B=m$).

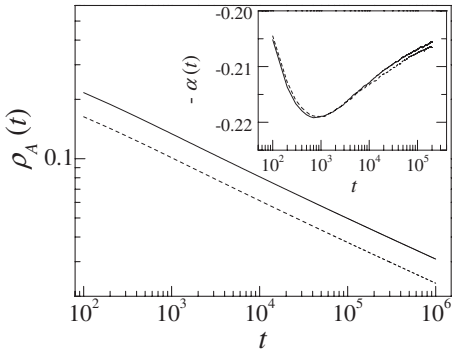

FIG. 1. The asymmetric reaction of $N=5$: The main plot shows the density of A-particles $\rho_A(t)$ of (4,1)-reaction (solid line) and (3,2)-reaction (dashed line). The inset shows the effective exponent $\alpha(t)$ of each line with $b=5$.

III. ASYMMETRIC REACTION

First, we discuss the numerical and analytical results for the asymmetric reaction. We present Monte Carlo simulation results on a ring with size L up to $N=6$. For homogeneous initial conditions, we randomly distribute particles with initial density $m\rho_A(0)=n\rho_B(0)$, where $\rho=\rho_A+\rho_B$. With $L=1.2\times 10^6$ and $\rho(0)=1.0$, we run simulations up to 10^7 time steps and average $\rho(t)$ over more than 100 independent runs. In addition, as a conventional measure characterizing the special organization of particles, we measure the average length ℓ of a domain containing only like particles defined as the distance between the first particles of two adjacent opposite species domains and the length $\ell_{AA}(\ell_{AB})$ defined as the interparticle distance between two adjacent like (unlike) particles [23]. The lengths algebraically increase in time t as [23]

$$\ell_{AA}\sim t^{1/Z_{AA}},\quad \ell_{AB}\sim t^{1/Z_{AB}},\quad \ell\sim t^{1/Z}. \tag{2}$$

For the fluctuation-dominated kinetics, the segregation of unlike particles occurs and the lengths exhibits different scaling behaviors. For DHCM(2), the exponents of lengths are $Z=3/2$, $Z_{AA}=3$ and $Z_{AB}=8/3$ respectively [11,13]. However, for the normal mean-field kinetics described by the CMF Eq. (1) (CMF kinetics), particles are uniformly mixed up and there is only one length scale of $1/\rho$, i.e. $Z_{AA}=Z_{AB}=Z=1/\alpha$.

Figure 1 shows the density of A-particles $\rho_A(t)$ for the asymmetric (4,1)- and (3,2)-reaction of $N=5$ and the effec-

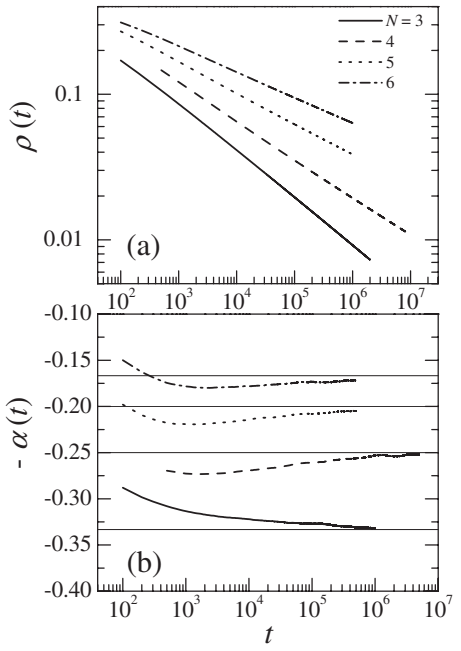

FIG. 2. The asymmetric $(n,1)$-reaction: (a) double logarithmic plot of $\rho(t)$. (b) Semilogarithmic plot of $\alpha(t)$ with $b=2$. Each horizontal line corresponds to $-1/N$.

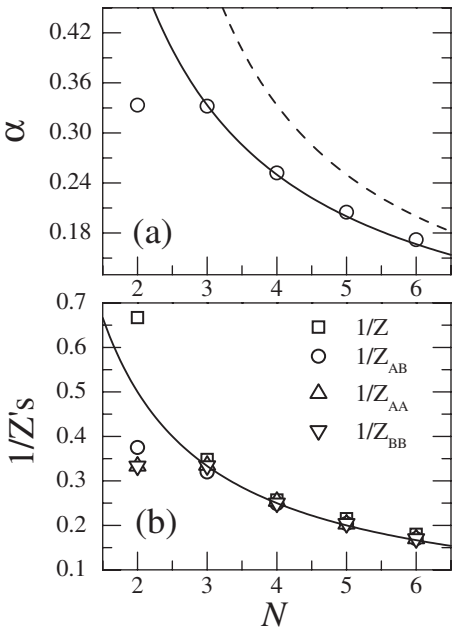

FIG. 3. The asymmetric $(n,1)$-reaction: (a) α (b) $1/Z$'s. The solid line in each panel corresponds to $1/N$-line and the dashed line in (a) represents the line for $\alpha_{CMF}=1/(N-1)$. The error of each data point is smaller than the size of a symbol.

tive exponent $\alpha(t)$ defined as $-\alpha(t)=\ln[\rho_A(bt)/\rho_A(t)]/\ln b$. As shown, $\rho_A(t)$ depends on (n,m) pairs for a given N, but the time-dependence of $\alpha(t)$ of each (n,m) pair is identical. Therefore, as in the isotropic diffusion, the kinetics of DHCM(N) also depends on only N. Since we numerically confirm the same results for various (n,m)-reactions of a given N, we only present the results for $(n,1)$-reaction for simplicity.

For the asymmetric $(n,1)$-reaction, we plot the total density $\rho(t)$ and its effective exponent $\alpha(t)$ for various N from 3 to 6 in Fig. 2. Together with $\alpha(t)$, we estimate the asymptotic value of α for each N from the scaling plot of ρt^{α} against t and plot in Fig. 3(a). As shown, α's deviate from $\alpha_{CMF}=1/(N-1)$ and intriguingly collapse on $1/N$ line. Figure 4 shows various lengths of $N=3$ and 4 together with effective exponents defined as $1/Z(t)=\ln[\ell(bt)/\ell(t)]/\ln b$ and similarly for the others. For $N=3$, ℓ and ℓ_{AB} exhibit the quite different scaling behavior from those of DHCM(2), i.e. $1/Z=2/3$ and $1/Z_{AB}=3/8$. Furthermore, all $1/Z(t)$'s asymptotically approach to 1/3. Hence, the kinetics of $N=3$ does not belong to DHCM(2), but it is described by a single exponent, i.e. $\alpha=1/Z's=1/3$. For $N=4$, $1/Z(t)$'s also converge to $1/N=1/4$. We also confirm the same behavior of various lengths for $N=5$ and 6. Together with $1/Z(t)$'s, we estimate the asymptotic value of $1/Z$'s from the scaling plot of $\ell t^{-1/Z}$ and similarly for the others. As shown in Fig. 3(b), all length exponents $1/Z(t)$'s also collapse on the line $1/N$ for $N>2$.

As a result, all lengths scale as $1/\rho$, i.e., $Z_{AA}=Z_{AB}=Z=1/\alpha$ for $N>2$. Furthermore, since all the interparticle distances overlap each other as shown in Fig. 4, all particles are distributed with equal interparticle distance for $N>2$. From the same interparticle distances with $Z_{AA}=Z_{AB}=Z=1/\alpha$, one may conclude that the kinetics for $N>2$ shows a mean-field-like aspect that the particles are evenly distributed in the asymptotic time. Physically this result means $N_c=3$ in $d=1$. However, the mean-field behavior for $N>2$ is anomalous because the exponent $\alpha=1/N$ cannot be explained by CMF Eq. (1) which gives $\alpha_{CMF}=1/(N-1)$ due to the uniform mixing of unlike particles. Therefore, unlike particles are not

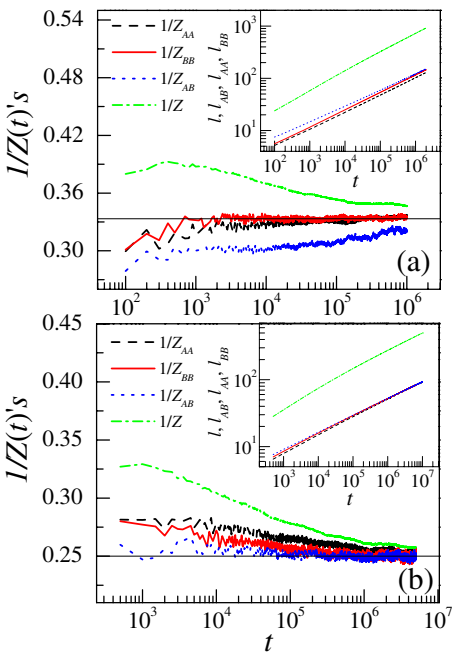

FIG. 4. (Color online) The asymmetric $(n,1)$-reaction: the effective exponent $1/Z(t)$'s with $b=2$ for $N=3$ (a) and $N=4$ (b). The horizontal lines correspond to $1/N$. In each panel, the inset shows various lengths with the same color in the main plot.

uniformly mixed up for $N>2$, which results in the anomalous mean-field kinetics. It implies that in multispecies systems of HC particles, the even distribution of particles does not always guarantee the uniform mixing of unlike particles. To understand such anomalous mean-field kinetics, one should take into account the interplay of three features, i.e., HC exclusion, the asymmetry of the reaction and drift at the same time.

For the effect of HC exclusion, one should consider the development of the segregation of unlike particles from random initial distributions of particles. In pure bosonic models, the initial segregation would disappear in early time due to the fast mixing of unlike particles. However, in $d=1$, HC exclusion forbids the mixing of any particles and thus the initial segregation can persist even for $N \geq N_c$. Furthermore, the asymmetric $(n,1)$-reaction rarely occurs in B-rich domains with few A-particles, so the segregation is naturally preserved by the asymmetric reaction. In driven systems, the segregation by HC exclusion is a crucial feature because it restricts the reaction to occur only at boundary particles of segregated domains.

Since we expect that the persistence of the segregation is one of the important features determining the kinetics, it is necessary to numerically confirm the spatial organization of unlike particles. As a simple measure for the spatial organization of unlike particles, we consider a ratio ρ_p/ρ, where ρ_p is the total pair density of adjacent unlike particles, $\rho_p=\rho_{AB}+\rho_{BA}$. Similarly, $\rho_{AA}(\rho_{BB})$ is the pair density of adjacent $A(B)$ particles. Then, ρ_A is written as $\rho_A=\rho_{AA}+\rho_p/2$ and similarly for ρ_B with $\rho=\rho_{AA}+\rho_{BB}+\rho_p$. For the random distribution of unlike particles with $m\rho_A=n\rho_B$, one readily finds $\rho_A=\frac{n+m}{n}\rho_{AA}$ and $\rho_B=\frac{n+m}{m}\rho_{BB}$ using the approximation of $\rho_{AB} \approx \rho_A\rho_B$. Then, with $\rho=\frac{n+m}{n}\rho_A$, one gets for the uniform mixing of unlike particles

$$\frac{\rho_p}{\rho}=\frac{2nm}{(n+m)^2}, \tag{3}$$

which is the criterion for the other spatial organizations. On the other hand, when the segregation occurs, ρ_p scales with the domain size ℓ as $\rho_p \sim 1/\ell$ by the definition of the domain. Therefore, ρ_p is smaller than that of the random distribution and thus we require $\rho_p/\rho < \frac{2nm}{(n+m)^2}$ for the persistence of the segregation. In Fig. 5, we plot $\frac{2nm}{(n+m)^2}\rho$ and ρ_p for N up to 5. As shown, $\rho_p < \frac{2nm}{(n+m)^2}\rho$ holds for $N \geq 3$ as expected. Therefore, HC exclusion preserves the initial segregation of unlike particles, which develops in times for the asymmetric reaction with $N \geq 2$.

When the segregation occurs, the uniform drift restricts the reaction to occur at the boundary particles of segregated domains defined as interfaces. We define a AB-interface as the leftmost B-particle in B-domain located at the right side of A-domain such as the underlined B particle in $(AAA\cdots\underline{B}BB)$ configuration. Similarly, a BA-interface is defined as the leftmost A-particle in A-domain. For isotropic diffusion, since the reaction occurs in the middle of the two interfaces, the reaction probability is proportional to $\rho_A^n\rho_B \sim \rho^N$. However, in driven case, the reaction always includes an interface, so the reaction probability is proportional to ρ_A^n at AB-interface and $\rho_B\rho_A^{n-1}$ at BA-interface. As a result, the restriction by the interplay of the segregation and drift reduces the degree of the reaction probability by one, i.e., ρ^{N-1}, which results in the anomalous exponent $\alpha=1/N$.

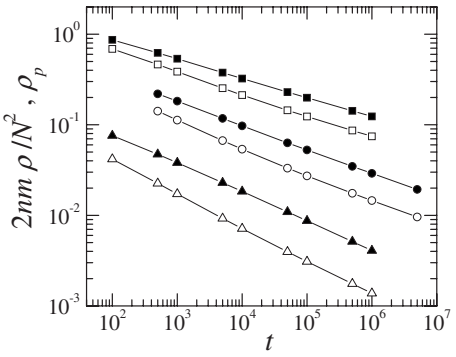

FIG. 5. The asymmetric $(n,1)$-reaction: plot of $\frac{2nm}{N^2}\rho$ (filled symbols) and ρ_p (open symbols) for $N=3$ (triangle), 4 (circle), 5 (square), respectively. The line between data is a guide to the eyes.

On the other hand, the asymmetric reactions preferentially occur at AB-interfaces due to the drift. At BA-interfaces, however, the asymmetric reactions are relatively hard to occur. It can be understood from the following mean-field argument. Let define p_{AB} and p_{BA} as the probability of $(n,1)$-reactions at AB- and BA-interfaces respectively. As mentioned above, one expects $p_{AB}=\rho_A^n$ and $p_{BA}=\rho_B\rho_A^{n-1}$ by the restriction. Then the relative probability of the reactions at AB-interfaces defined as $R=p_{AB}/p_{BA}$ is given as $R=\rho_A/\rho_B=n$, where $\rho_A=n\rho_B$ for the asymmetric reactions. Therefore, as N increases, the reactions mainly occur at AB-interfaces and BA-interfaces become more and more insensitive to the reactions. As a result, particles tend to be evenly distributed near the BA-interface before the reactions occur. It eventually causes the uniform particle distribution over the whole system even for $N=3$.

To quantify the above arguments for $N_c=3$ and $\alpha=1/N$, we consider the velocity $v_{AB}=d\ell_{AB}/dt$, which is the difference of velocities of two adjacent boundary particles. Since the reaction always occurs at an interface and particles are evenly distributed for $N \geq N_c$, (n,m)-reaction occurs at the AB-interface with rate $\rho_A^n\rho_B^{m-1} \sim \rho^{N-1}$. Hence, one gets $v_{AB} \sim \rho^{N-1} \sim \ell_{AB}^{1-N}$, where we use $\ell_{AB} \approx \ell_{AA} \sim 1/\rho$ for $N \geq N_c$. Finally, one finds $\ell_{AB} \sim t^{1/N}$ and $\rho \sim t^{-1/N}$ for $N \geq N_c$.

IV. SYMMETRIC REACTION

We simulate the symmetric $(n,1)$-reaction for various N up to 6 for homogeneous initial distributions with $\rho_A(0)=\rho_B(0)$. We set L as 1.2×10^6 for $N=3$ and 10^5 for the others. We run simulations up to $t=10^7$ for $N=3$ and $t=5\times10^5$ for the others. We average densities and various lengths with more than 500 independent runs. In the asymmetric reaction, the mean-field analysis shows $\alpha=1/N$ for $N \geq N_c$, provided that the initial segregation persists. Hence, for $N \geq N_c$, the kinetics should depend on whether the symmetric reaction preserves and develops the segregation or not.

First, we consider the criterion for the possible spatial organizations of unlike particles. For the random distribution

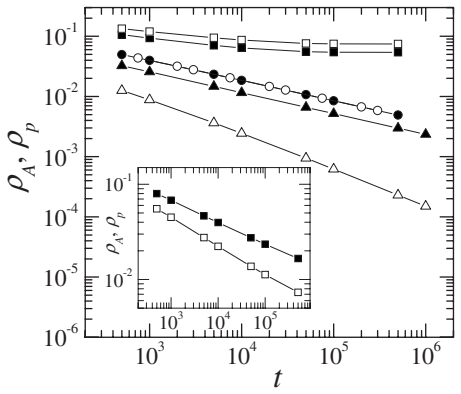

FIG. 6. The symmetric $(n,1)$-reaction: plot of ρ_A (filled symbols) and ρ_p (open symbols) for $N=3$ (triangle), 4 (circle), 5 (square) respectively. Inset shows (3,2)-reaction with the same symbols. The line between data is a guide to the eyes.

of unlike particles with $\rho_A=\rho_B$, we find $\rho_p/\rho=1/2$ (or $\rho_p/\rho_A=1$) from Eq. (3). Hence, for the segregation of unlike particles, we require $\rho_p/\rho<1/2$ (or $\rho_p/\rho_A<1$). On the other hand, for $\rho_A=\rho_B$, the alternative ordering of unlike particles such as $ABAB$ is also possible. For the complete alternative ordering, we have $\rho_p/\rho=1$ due to $\rho_{AA}=\rho_{BB}=0$.

In Fig. 6, we plot ρ_A and ρ_p for N up to 5. For $N=3$, $\rho_p/\rho_A<1$ indicates the persistence of the segregation of unlike particles. On the other hand, we find $\rho_p/\rho_A=1$ for $N=4$. Hence, the symmetric $(n,1)$-reaction leads to the uniform mixing of unlike particle for $N=4$. As a result, the kinetics for $N=4$ is the CMF kinetics of Eq. (1) and thus $N_c=4$. It means that the kinetics for $N=3$ is fluctuation-dominated and the same as that of DHCM(2). Figure 7 shows the effective exponents $1/Z(t)$'s of various lengths for $N=3$ and 4. Since we confirm $\ell_{AA}=\ell_{BB}$ for $N=3$ and $\ell_{AA}=\ell_{BB}=\ell_{AB}$ for $N=4$, we only plot one length among overlapped lengths for clarity. For $N=3$, the domain length ℓ exhibits a quite different scaling behavior from the others. From the scaling plot of $\ell/t^{1/Z}$ and similarly for the others, we estimate $1/Z_{AA}=0.354(5)$, $1/Z_{AB}=0.37(1)$, and $1/Z=0.63(1)$, which agree well with those of DHCM(2), $1/Z_{AA}=1/3$, $1/Z_{AB}=3/8$, and $1/Z=2/3$ as expected. We also estimate $\alpha=0.345(5)$ from the scaling plot ρt^{α}. Therefore, we confirm the DHCM(2) kinetics for $N=3$. For $N=4$, ℓ_{AA} and ℓ exhibit the same scaling behavior, i.e. $Z_{AA}=Z$. We estimate $1/Z_{AA}=1/Z=0.34(1)$ and $\alpha=0.340(1)$ from the scaling plots which agree with $\alpha_{CMF}=1/(N-1)=1/3$. Hence, we confirm the CMF kinetics for $N=4$ and $N_c=4$ for the symmetric reaction as in the isotropic diffusion.

For $N=5$, however, ρ_A and ρ_p eventually converge to certain values after some transient time (Fig. 6). We find $\rho_p/\rho\approx 0.7$ for $N=5$. We also confirm $\rho_p/\rho\approx 0.6$ for $N=6$ (not shown). As a result, the symmetric $(n,1)$-reaction leads to the alternative ordering of most unlike particles for $N>4$ because of $1/2<\rho_p/\rho<1$. The alternating ordering of unlike particles for $N>4$ can be understood from the following argument. The symmetric $(n,1)$-reaction occur at both types of interfaces due to the drift. However, the reaction annihilates trains of like particles with big size $n(\sim N)$ at all interfaces. After the exhaustion of such big size trains, the reaction cannot occur anymore at interfaces, and the resultant particle-distributions should be alternatively ordered configurations like $(\cdots ABAB\cdots)$ containing only the trains of size less than n. Therefore, the alternative ordering is intrinsically natural for the symmetric $(n,1)$-reaction rather than the uniform mixing for large N. The uniform mixing for $N=4$ can be thought as the result of the competition between the processes of the segregation and the alternative ordering.

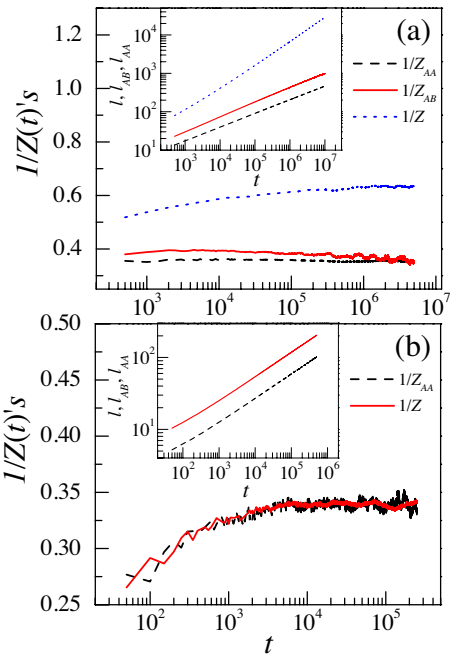

FIG. 7. (Color online) Lengths and $1/Z(t)$'s for the symmetric $(n,1)$-reaction. (a) $N=3$ and (b) $N=4$. The main plots show the effective exponents $1/Z(t)$'s with $b=2$. Insets show the corresponding lengths.

On the contrary, the (n,m)-reactions with $n\simeq m$ can occur even in the alternatively ordered state, and the alternative ordering is removed by the reaction. Then the segregation should persist because of the interplay of HC exclusion and the drift as in the asymmetric reaction. Hence, we expect the anomalous mean-field kinetics of $\alpha=1/N$ and $Z's=1/\alpha$ for $n\simeq m$ for $N>4$. For the symmetric (3,2)-reaction $(N=5)$, we confirm $\rho_p/\rho_A<1$ (Inset of Fig. 6). We estimate $\alpha=0.215(5)$ from the scaling plot, which is consistent with $1/N$ as expected. Therefore, for (n,m) pairs with $1<m\lesssim n$, the symmetric reaction also exhibits the anomalous kinetics with $\alpha=1/N$ for $N>4$, provided that the reaction does not drive the system into the alternatively ordered configurations forbidding the reaction.

V. SUMMARY

In summary, we investigate the kinetics of $nA+mB\rightarrow 0$ reaction of driven hard-core (HC) particles in one dimension. With uniform drift velocity, all particles are driven to the right. HC exclusion forbids the interchange of any particles and restricts the number of particles on a site to 0 or 1. We call the reaction as (n,m)-reaction with $N=n+m$. The reaction is classified into two classes, the symmetric and the

asymmetric reaction [17]. The symmetric reaction means both (n,m)- and (m,n)-reactions, while the asymmetric reaction means only (n,m)-reaction for a given (n,m) pair. Since the interplay of the uniform drift and HC exclusion changes the kinetics of $A+B\rightarrow 0$ [10], the kinetics with $N>2$ is also expected to be affected by the interplay.

However, as N increases, the trains of particles causing the reaction rarely form. Hence, for sufficiently large N, particles are evenly distributed before the reaction, so one expects a crossover N_c above which the kinetics follows the classical mean-field (CMF) Eq. (1). For $N<N_c$, the kinetics is that of the $N=2$ case. For isotropic diffusion [17], N_c depends on the reaction symmetry, i.e. $N_c=4$ for the symmetric reaction and $N_c=5$ for the asymmetric one. Similarly, for the driven systems, we show the existence of N_c and that the kinetics for $N<N_c$ is the same as that of the driven HC model with $N=2$. However, we show that N_c and the kinetics for $N\geq N_c$ are completely changed by the interplay of the drift and HC exclusion, and strongly depend on the reaction symmetry.

For the asymmetric reaction, we numerically find $N_c=3$. However, the kinetics for $N\geq 3$ cannot be described by the CMF Eq. (1). For $N\geq 3$, particles are evenly distributed, but densities anomalously decay as $t^{-\alpha}$ with $\alpha=1/N$ instead of the expected mean-field value, $\alpha_{CMF}=1/(N-1)$. On the other hand, for the symmetric reaction, we find the same N_c as that of the isotropic diffusion, i.e., $N_c=4$ at which the kinetics follows the CMF equation. However, for $N>N_c$, the kinetics exhibits completely different behavior according to (n,m) pairs of a given N. For $(n,1)$-reaction with $N>4$, a density ρ eventually saturates to a certain value. However, for other (n,m) pairs of a given N, e.g., (3,2) for $N=5$, ρ decays as $t^{-1/N}$ without the saturation as in the asymmetric case.

The anomalous kinetics for $N>N_c$ results from the interplay of HC exclusion and uniform drift. HC exclusion preserves the local segregation of unlike particles due to random initial distributions. When the segregation develops in time by the reaction, the uniform drift restricts the reaction to occur at the interface defined as the leftmost particle in a segregated domain. As a result, the interplay leads to the slower density decay than the expected CMF one. From a variant analysis based on the segregation and the even distribution, we analytically show $\alpha=1/N$ regardless of the reaction symmetry.

The persistence of the segregation is one of the important features determining the kinetics for $N\geq N_c$. As a simple measure of the spatial organizations of unlike particles, we consider a ratio ρ_p/ρ, where ρ_p is the total number of pairs of adjacent unlike particles, $\rho_p=\rho_{AB}+\rho_{BA}$. For the asymmetric reactions with $m\rho_A=n\rho_B$, we analytically show $\rho_p/\rho=2nm/(n+m)^2$ for the uniform distributions of unlike particles. For the persistence of the segregation, one requires $\rho_p/\rho<2nm/(n+m)^2$. For the symmetric reactions with $\rho_A=\rho_B$, one requires $\rho_p/\rho=1/2$ for the random distribution of unlike particles. For the other organizations, we find $\rho_p/\rho<1/2$ for the segregation of unlike particles, and $\rho_p/\rho=1$ for the complete alternating ordering of unlike particles.

For the asymmetric reaction, we numerically confirm $\rho_p/\rho<2nm/(n+m)^2$ for $N>2$. Hence, we numerically show that the segregation is developed in time by the asymmetric reaction for any N. On the other hand, for the symmetric $(n,1)$-reactions, we numerically confirm $2\rho_p=\rho$ for $N_c=4$ and $1/2<\rho_p/\rho<1$ for $N>4$. Therefore, we show that the symmetric $(n,1)$-reactions lead to the uniform distribution of unlike particle for $N=4$ and the alternative ordering of most unlike particles for $N>4$ in which the reaction cannot occur anymore. However, since the other (n,m) pairs can react even in alternatively ordered configurations, densities are expected to decay without the saturation for other (n,m) pair of $N>4$. For (3,2) pair for $N=5$, we numerically confirm $\rho>2\rho_p$ and $\rho\sim t^{-1/N}$ again. Therefore, the symmetric reactions also develop the segregation for $N>4$ which leads to the anomalous kinetics, provided that the reaction does not drive the system into the alternatively ordered configurations forbidding the reaction. The uniform mixing for $N=4$ can be thought as the result of the competition between the processes of the segregation and the alternative ordering.

Since we mainly understand the kinetics of (n,m)-reactions via simulations and a variant theory, we have no theoretical prediction for N_c of driven HC particles. Hence, for more systematic and quantitative understandings, e.g., d_c as a function of N and its dependence on the reaction symmetry, we need an analysis of systematic theoretical formalisms such as field-theoretic formalisms for HC systems [12].

ACKNOWLEDGMENTS

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MEST) (Grant No. 2009-0052659) and by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (Grant No. KRF-2007-313-C00279).

[1] E. J. Harris, *Transport and Accumulation in Biological Systems* (Buttterworth Scientific, London, 1960).
[2] J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and other Microporous Solids* (Wiley, New York, 1992).
[3] S. Havlin and D. Ben-Avraham, Adv. Phys. **36**, 695 (1987); (Academic, London, 1995), Vol. 17.
[4] C. Dekker, Nat. Nanotechnol. **2**, 209 (2007).
[5] M. A. Lomholt, T. Ambjörnsson, and R. Metzler, Phys. Rev. Lett. **95**, 260603 (2005).
[6] E. Barkai and R. Silbey, Phys. Rev. Lett. **102**, 050602 (2009).
[7] S. N. Majumdar and M. Barma, Phys. Rev. B **44**, 5306 (1991).
[8] D. Helbing, D. Mukamel, and G. M. Schütz, Phys. Rev. Lett. **82**, 10 (1999).
[9] S. Kwon, J. Lee, and H. Park, Phys. Rev. Lett. **85**, 1682 (2000).
[10] S. A. Janowsky, Phys. Rev. E **51**, 1858 (1995); **52**, 2535

(1995).
[11] I. Ispolatov, P. L. Krapivsky, and S. Redner, Phys. Rev. E **52**, 2540 (1995).
[12] S.-C. Park, D. Kim, and J.-M. Park, Phys. Rev. E **62**, 7642 (2000); S.-C. Park and J.-M. Park, *ibid.* **71**, 026113 (2005); F. van Wijland, *ibid.* **63**, 022101 (2001).
[13] S. Kwon and Y. Kim, Phys. Rev. E **75**, 021122 (2007).
[14] U. C. Täuber, M. Howard, and B. P. Lee, J. Phys. A **38**, R79 (2005).
[15] K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985).
[16] V. Privman, A. M. R. Cadihe, and M. L. Glasser, J. Stat. Phys. **81**, 881 (1995).
[17] S. Kwon and Y. Kim, Phys. Rev. E **79**, 041132 (2009).
[18] J. R. Kirkpatrick, J. Phys. Chem. **85**, 3444 (1981).
[19] G. N. Pandey, *Environmental Science and Technology* (Anmol Publications PVT, LTD, India, 1998).
[20] S. Cornell and M. Droz, Phys. Rev. Lett. **70**, 3824 (1993); J. Magnin, Eur. Phys. J. B **17**, 673 (2000), and references therein.
[21] T. Sasamoto, S. Mori, and M. Wadati, Physica A **247**, 357 (1997).
[22] S. Cornell, M. droz, and B. Chopard, Physica A **188**, 322 (1992).
[23] F. Leyvraz and S. Redner, Phys. Rev. A **46**, 3132 (1992).
[24] S. Kwon, S. Y. Yoon, and Y. Kim, Phys. Rev. E **73**, 025102(R) (2006); **74**, 021109 (2006).