Anomalous kinetics of attractive \( A + B \to 0 \) reactions

Sungchul Kwon, S. Y. Yoon, and Yup Kim

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

(Dated: February 2, 2008)

We investigate the kinetics of \( A + B \to 0 \) reaction with the local attractive interaction between opposite species in one spatial dimension. The attractive interaction leads to isotropic diffusions inside segregated single species domains, and accelerates the reactions of opposite species at the domain boundaries. At equal initial densities of \( A \) and \( B \), we analytically and numerically show that the density of particles (\( \rho \)), the size of domains (\( \ell \)), the distance between the closest neighbor of same species (\( \ell_{AA} \)), and the distance between adjacent opposite species (\( \ell_{AB} \)) scale in time as \( \rho \sim t^{-1/3}, \ell_{AA} \sim t^{1/3}, \text{ and } \ell \sim \ell_{AB} \sim t^{2/3} \) respectively. These dynamical exponents form a new universality class distinguished from the class of uniformly driven systems of hard-core particles.

PACS numbers: 05.40.+j, 82.20.-w

The irreversible two-species annihilation reaction \( A + B \to 0 \) has been intensively and widely investigated as a basic model of various phenomena in physics \( [1, 2] \), chemistry \( [5, 6, 7, 8, 9, 10] \), and biology \( [11, 12] \). The reaction includes two species \( A \) and \( B \) which are initially distributed at random in space. The reaction of opposite species instantaneously takes place with a rate \( k \) when two particles of opposite species encounter on the same site (generally within a reaction radius) during the motion of particles. The reaction forms the third inert species, which is then disregarded in the motion of \( A \) and \( B \).

For the same initial density of \( A \) and \( B \), \( \rho_A(0) = \rho_B(0) \), the mean-field equations predict that \( \rho_A \) and \( \rho_B \) decay linearly in time as \( (kt)^{-1} \). However it turned out that the random fluctuation of the initial number of two species evolves to make a segregation into \( A- \) or \( B- \)rich area \( \ll 1 \). The fluctuation and segregation develop in time, so that the reactions of two opposite species take place only at the boundaries of two adjacent segregated domains. As a result, in sufficiently low dimensions, the effect of fluctuation leads to the anomalous kinetics. That is, the evolution of the density of particles strongly depends on fluctuations, and cannot be derived from mean-field rate equations.

The density decay has been known to depend on the motion of the particles and the mutual statistics of particles. For isotropic diffusions, the density \( \rho_A(t) \) scales in time \( t \) as \( \rho_A(t) \sim t^{-d/4} \) in \( d \)-dimensions \( (d \leq d_c = 4 \) for \( A \)) \( \ll 1 \). The dimension \( d_c \) is the upper critical dimension above which the density decay follows the mean-field rate equations, so \( \rho(t) \sim t^{-1} \) for \( d > d_c \). With the global relative drift of one species, \( \rho_A(t) \) scales as \( \rho_A(t) \sim t^{-(d+1)/4} \) for \( d \leq 3 \). The hard-core (HC) interaction between identical particles is irrelevant to the case of the isotropic diffusion and the relative drift \( \ll 1 \). However when both species are uniformly driven to the same direction, the HC interaction completely changes the asymptotic scaling as \( \rho_A \sim t^{-d/(d+1)/6} \) for \( d < 2 \), \( t^{-d/4} \) for \( 2 < d \leq 4 \), and finally \( t^{-1} \) for \( d > 4 \). Without the HC interaction, \( \rho_A(t) \) decays as \( \rho_A \sim t^{-d/4} \) as in the isotropic diffusion due to Galilean invariance. Recent studies on the reaction under Lévy mixing \( \ll 1 \) and on scale free networks \( \ll 1 \) showed that some mixing mechanisms that homogenizes reactants can suppress the role of the fluctuations.

In reality in which oppositely charged particles recombine into inert particles such as electron-hole recombinations in photoluminescence \( \ll 1 \) and particle-antiparticle reactions in the early universe \( \ll 1 \), the local attractive interaction between opposite species should be much more important than the global uniform biases. In this paper, we investigate the kinetics of \( A + B \to 0 \) reaction with the attractive interaction between opposite species in one dimension, which may model composite systems of oppositely charged particles much more effectively than the model with the global and uniform drift. When a particle is surrounded by two same species neighbors such as \( BAB \), the central particle (\( A \)) performs random walks. If two opposite species particles surround a particle such as \( AAB \), the central particle (\( A \)) is ballistically driven to its opposite species (\( B \)). As a result, the attractive interaction depends on the local configurations of adjacent particles, and accelerate the reactions of opposite species at the boundaries of segregated domains. However inside segregated domains, each particle has the same neighboring species, so the motion is isotropic diffusion. Hence the situation belongs to neither the relative drift nor the isotropic diffusion. Due to the isotropic diffusion inside domains, the HC interaction should be irrelevant in this case.

With the local attractive interaction in one spatial dimension, we analytically and numerically show, regardless of the existence of the HC interaction, that the density of particles (\( \rho \)), the distance between the closest neighbor of same species (\( \ell_{AA} \)), the size of domains (\( \ell \)), and the distance between adjacent opposite species (\( \ell_{AB} \)) scale in time as \( \rho \sim t^{-1/3}, \ell_{AA} \sim t^{1/3}, \text{ and } \ell \sim \ell_{AB} \sim t^{2/3} \) respectively. These dynamical exponents form a new universality class distinguished from the class of uniformly driven systems of hard-core particles \( \ll 1 \), where the exponents for \( \ell_{AA}, \ell \) and \( \ell_{AB} \) are still controversial. The two features of ballistic and diffusive motions result in pentagonal space-time trajectories of bulk particles (Fig. 1(a)), which allow us to derive the...
asymptotic scaling analytically.

We consider a configuration in which $A$ and $B$ species are randomly distributed on an one dimensional lattice with an equal initial density, $\rho_A(0) = \rho_B(0)$. A randomly-chosen particle performs either isotropic or biased random walks depending on the configurations of neighboring particles. When the chosen particle is surrounded by two same species neighbors such as $AB$, the chosen particle ($A$) performs isotropic random walks. If two opposite species particles surround a particle such as $AAB$, the chosen particle ($A$) is constantly driven to the its opposite species ($B$).

In the region of a length $\ell$, the number of $A$ species is initially $N_A = \rho_A(0)\ell \pm \sqrt{\rho_A(0)}\ell$ and the same for $N_B$. After a time $t \sim \ell^2$, particles travel throughout the whole of the region, and annihilate in pairs. The residual particle number is the number fluctuation in the region so we have the relation $N_A \sim \sqrt{t}$ or $\rho_A \sim 1/\sqrt{t}$ for a given length $\ell$. As the processes evolve, the system becomes a homogeneous collection of alternating $A$-rich and $B$-rich domains. To characterize the structure of segregated domains, we introduce three length scales as in Ref. [5]. The length of the domain ($\ell$) is defined as the distance between the first particles of adjacent opposite species domains [3]. The length $\ell_{AB}$ is defined as the distance between two adjacent particles of opposite species, while $\ell_{AA}(\ell_{BB})$ is the distance between adjacent $A(B)$ particles in a $A(B)$ domain. These length scales asymptotically increase in time as

$$\ell \sim t^{1/z}, \quad \ell_{AA} \sim t^{1/z_{AA}}, \quad \ell_{AB} \sim t^{1/z_{AB}}. \quad (1)$$

With the attractive interaction, as a bulk particle inside single species domains diffuses isotropically until it becomes a boundary particle, its space-time trajectory is pentagonal as shown in Fig. 1(a). These pentagonal trajectories should be self-similar (self-affine) fractal structures, because they should have the scaling symmetry under the scaling transformation $x' = bx$ (space-domain scaling) and $t' = b^2 t$ (time-domain scaling) with $b > 1$ due to the power-law behavior in Eq. (1). A typical base unit of the self-similar pentagonal trajectories of adjacent opposite domains are schematically depicted in Fig. 1(b).

This base unit allows us to calculate a time $\tau$ needed to remove the unit of the space-domain size $\ell$ surrounded by one scale larger ones. Then the size of the larger unit increases by $\ell$ during $\tau$ so we have

$$d\ell/dt \sim \ell/\tau, \quad (2)$$

which gives the dynamic exponent $z$.

As only boundary particles of each domain have two opposite species neighbors, the boundary particles ballistically annihilate due to the attractive interaction. It takes a time $\tau_1 = \ell_{AB}$ for two boundary particles to annihilate in the base unit. The second particle from the boundary isotropically diffuses during time $\tau_1$ until the boundary particles annihilate. After the time $\tau_1$, the second particle becomes a boundary particle, and constantly moves to its counterpart during $t_2 = \ell_{AB} + \ell_{AA}$. So it takes time $\tau_2 = \tau_1 + t_2$ in total for the second particle to annihilate. Similarly, the $n$th particle from the initial boundary will annihilate after $\tau_n = \tau_{n-1} + \ell_n$, where $\ell_n = \ell_{AB} + (n-1)\ell_{AA}$ for $n \geq 2$. From the recurrence relation of $\tau_n$, we find

$$\tau_n = n\ell_{AB} + n(n-1)\ell_{AA}/2. \quad (3)$$

As the number of particles in a domain of size $\ell$ is $N_\ell \sim \sqrt{\ell}$, the time $\tau$ needed to annihilate the domain in the base unit is given by

$$\tau_\ell \sim N_\ell \ell_{AB} + N_\ell^2 \ell_{AA} = \quad (4)$$

for $N_\ell \gg 1$. In above calculations, we consider the mean positions of bulk particles, and neglect the increase of $\ell_{AA}(t)$ by diffusions during the annihilation of the base unit. After a smaller unit is completely annihilated by being embodied into larger one, the remainder of particles redistribute over the larger unit increased by the size of the annihilated unit. Hence we approximate $\ell_{AA}(t) = \cdots = \ell_{AA}(t+\tau_n) = \cdots = \ell_{AA}(t+\tau_\ell)$ during the annihilation of the unit.

The scaling of $\ell_{AA}$ is simply $\ell_{AA} \sim \sqrt{t}$ from the relation $\ell_{AA}(t) \sim 1/\rho(t)$. Hence $\ell_{AA}$ scales as $\ell_{AA} \sim t^{1/2z}$ with $z_{AA} = 2z$. On the other hand, the change of $\ell_{AB}$ during $\tau_\ell$ should be of order $N_\ell \ell_{AA}$ because of $N_\ell$ successive annihilations of two opposite particles at boundaries. So we get $d\ell_{AB}/dt \sim \Delta \ell_{AB}/\tau_\ell \sim \ell/\ell_\ell$. With the scaling of $t \sim \ell^2$, we find that $\ell_{AB}$ follows the same scaling as $\ell$, i.e. $\ell_{AB} \sim t^{1/2z}$ with $z_{AB} = z$. Finally using the relations, $\ell_{AA} \sim \sqrt{t}, \ell_\ell \sim \sqrt{\ell}$, and $\ell_{AB} \sim \ell$, we find $\tau_\ell$ from Eq. (4)

$$\tau_\ell \sim \ell^{3/2}. \quad (5)$$

Substituting Eq. (5) into Eq. (2) and integrating the resultant equation, we finally arrive the following scaling...
As a result, we find $z = z_{AB} = 3/2$ with the attractive interaction between opposite species.

From the scaling of $\ell$, $\ell_{AB}$, and $\ell_{AA}$, asymptotic decays of various densities can be extracted. The density of total particles ($\rho = 2\rho_A$), the density of pairs of adjacent same species ($\rho_{AA} = \rho_{BB}$), and the density of pairs of adjacent opposite species ($\rho_{AB}$) scale as

$$\rho \sim t^{-\alpha}, \quad \rho_{AA} \sim t^{-\alpha_{AA}}, \quad \rho_{AB} \sim t^{-\alpha_{AB}}.$$  

(7)

As $\rho$ is order of $\rho \sim 1/\sqrt{t}$, we have $\rho \sim t^{-1/2}$ with $\alpha = 1/2z = 1/3$. $\rho_{AA}$ follows the same scaling of $\rho$ due to $\rho_{AA} \sim 1/\ell_{AA} \sim 1/\sqrt{t}$ so $\rho_{AA} \sim t^{-\alpha}$ with $\alpha_{AA} = \alpha = 1/3$. Finally $\rho_{AB}$ is $\rho_{AB} \sim 1/\ell$, which leads to $\rho_{AB} \sim t^{-1/z}$ with $\alpha_{AB} = 1/z = 2/3$. Using self-similar structures of space-time trajectories and scaling arguments for fluctuations of $\frac{\ell}{\ell_{AA}}$, we find following exponents for the reactions $A + B \rightarrow 0$ with the local attractive interaction between opposite species

$$\alpha = \alpha_{AA} = 1/3, \quad \alpha_{AB} = 2/3, \quad z = z_{AB} = 3/2, \quad z_{AA} = 3.$$  

(8)

Intriguingly and incidentally $\rho(t)$ decays with the same exponent $1/3$ as that of the uniformly driven hard-core particles $\frac{11}{12}$, in which the driven motion of a single species domain was argued to be described by the noisy Burgers equation $\frac{11}{12}$. However for the attractive interaction case, the $1/4$ decay of $\rho(t)$ comes from the interplay of isotropic diffusions inside domains and ballistic annihilations at boundaries. For scalings of inter-domain distances and others, our results of (8) are completely different from those of $\frac{12}{11}$, where $\ell \sim t^{7/12}, \ell_{AB} \sim t^{3/8}$, and $\ell_{AA} \sim t^{1/3}$. Hence we conclude that the local attractive interaction between opposite species forms a new universality class of irreversible $A + B \rightarrow 0$ reactions.

To see the validity of our analytic results, we now want to report the simulation results for the model with the attractive interactions. With equal initial density of $\rho_A(0) = \rho_B(0)$, $A$ and $B$ particles distribute randomly on a lattice of size $L$. In the simulations we consider both hard-core (HC) particles and the particles without the HC interactions, which we call the bosonic particles. In the model with HC particles there can be at most one particle of a given species on a site. In the bosonic model there can be many particles of the same species on a site. As we shall see, the simulation results are independent of the HC interactions.

All the simulations are done on the one-dimensional chains with the size up to $L = 3 \times 10^6$ and the initial densities are always taken as $\rho_A(0) = \rho_B(0) = 0.2$. We average $\rho(t)$, $\rho_{AA}(t)$, and $\rho_{AB}(t)$ up to $10^5$ time steps over 7200 independent runs. In Fig.2, we plot the densities and their effective exponents defined as

$$-\alpha(t) = \ln[\rho(t)/\rho(t/2)]/\ln 2,$$  

(9)

and similarly for others. As you can see in Fig. 2, the data for HC particles (Fig.2(a)) are almost identical to those for bosonic particles (Fig.2(b)). While $\alpha_{AB}$ still shows larger fluctuations for both HC particles and bosonic particles, $\alpha$ and $\alpha_{AA}$ nicely converge to the same value. We estimate $\alpha = 0.33(1)$, $\alpha_{AA} = 0.33(1)$, and $\alpha_{AB} = 0.68(2)$ for both HC and bosonic models, which agree well with the predictions (8).

To estimate the dynamic exponent $z$, we measure the densities for various $L$ from $2^{14}$ up to $2^{18}$. With the scaling assumption

$$\rho(L,t) \sim t^{-\alpha} f(t/L^z),$$  

(10)

and the estimate $\alpha = 0.333$, we observe the best data collapse at $z = 1.50(2)$ which also agree well with the prediction of (8) as shown in Fig. 3.

For the time dependence of average distances defined in Eq. (1), we measure $\ell$, $\ell_{AA}$, and $\ell_{AB}$ under the same measurement conditions as those of densities. The effec-
The anomalous density decay of $t^{-1/3}$ appear to belong to the same universality class as uniformly driven systems of hard-core particles, which was argued to be described by noisy Burgers equations\cite{11}. However our system is not in the same universality class as the uniformly driven system, because scaling behaviors of basic distances are different from each other\cite{12}. The difference can infer from the underlying mechanisms. In our model, isotropic diffusions inside domains lead to Galilean invariance of domains so the hard-core interaction has no effects on the reactions. Furthermore there is no global bias to one direction which change the kinetics of hard-core particles. Only boundary particles feel bias to opposite species, which is the essential physical factor and distinguishes our model from the models in Refs.\cite{1,5,6}. We conclude that the attractive interaction between opposite species is the key feature of the new universality class characterized by exponents in Eq. (8), and it is another path to the anomalous density decay of $t^{-1/3}$.

This work is supported by Korea Research Foundation Grant No. KRF-2004-015-C00185

\begin{thebibliography}{9}
\bibitem{3} N. G. van Kampen, Stochastic processes in Physics and Chemistry (North-Holland, Amsterdam, 1981).
\end{thebibliography}