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Reaction dynamics controlled by enhanced diffusion

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The reaction schemes $A+B\rightarrow$inert and $A+A\rightarrow A$, controlled by enhanced diffusion, are investigated. The participating particles are assumed to perform Lévy walks with Lévy exponents $1<\gamma\leq 2$. Both theoretical expressions and numerical results are presented. Reaction behaviors are observed which indicate mixing properties. When compared with reactions controlled by Brownian motion we obtain faster processes, new kinetic patterns, and, more importantly, lower, γ-dependent, critical dimensions for the mean-field behavior. The latter suggests erosion of the segregation phenomenon.

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Models of diffusion-controlled reactions $A+B\rightarrow$ inert, $A+A\rightarrow$inert, and $A+A\rightarrow A$, with and without particle sources, have been under extensive investigations in recent years with emphasis on the role of density fluctuations that lead to deviations from the mean-field rate-equations behavior [1–12]. These reaction models are relevant to problems such as exciton-exciton annihilation [13] and diffusion-reaction polymerization [10], and have intimate relationship to some spin models [7] and to the Edwards-Wilkinson interface growth model [14–16].

The various reaction schemes have been studied by direct random-walk techniques [4], by analysis of the corresponding Langevin equation ($A+B$ processes) [9,16,17], and by more specific, mainly one-dimensional methods ($A+A$ processes) [7,10,11]. Both regular and disordered, fractal and amorphous, underlying geometries have been assumed, where the latter show a slowing down of the reaction processes. Pronounced dependence on dimensionality has been observed.

Much attention has been recently drawn to systems that display enhanced diffusion, where the mean-square displacement of a particle grows superlinearly in time [18–24]. Such enhancement has been experimentally observed in a two-dimensional flow in a rotating annulus [25] and in self-diffusion studies in polymerlike breakable micelles [26]. In these cases, as well as in a broad range of numerical studies of dynamical systems, the enhancement has been attributed to Lévy walks, which generalize the simple Brownian motion by extending the central-limit theorem [22,23,27,28].

In this paper, we report on some results of diffusion-controlled reactions under diffusional enhancement on many scales. We introduce Lévy statistics into reaction dynamics, a step which enables us to generalize previously investigated reaction-diffusion schemes by including motional enhancement, and to demonstrate the continuous approach toward the mean-field results. In this sense, the Lévy-walk enhanced reactions present models of simple mixing processes and broadens the scope of applicability of the above mentioned reactions. We show that imposing the Lévy-walk aspect accelerates the reaction process, leads to different reaction patterns, and lowers the critical dimension at which the mean-field behavior sets in.

We will focus on the following reaction schemes: (a) $A+B\rightarrow$inert, with and without sources. This scheme requires, as we will see, the generalization of the Langevin equations to Lévy processes. (b) $A+A\rightarrow$inert and $A+A\rightarrow A$, with and without a source, for which one has to generalize the analysis in terms of the two-body correlation functions [11]. In both cases, we present approximate theoretical results supported by numerical calculations.

During the reaction processes, the particles are considered to move at a constant velocity for randomly chosen event times. The distribution $\psi(t)$ of these event times is assumed to follow a power law $\psi(t)\sim t^{-\gamma-1}$. Here we restrict the range of the power-law exponents to $1<\gamma\leq 2$. Furthermore, we assume a lattice model.

$A+B\rightarrow$ *inert*

An approximate description of this process is given in terms of the linear Langevin equation for the density-difference function $q(\mathbf{r},t)=A(\mathbf{r},t)-B(\mathbf{r},t)$, where $A(\mathbf{r},t)$, and $B(\mathbf{r},t)$ are the A- and B-particle position dependent densities [9,16,17],

$$\partial_t q(\mathbf{r},t)=\hat{L}q(\mathbf{r},t)+\eta(\mathbf{r},t)\ . \tag{1}$$

Here $\hat{L}$ is the operator that constitutes the Lévy process and is defined in Fourier space ($r\rightarrow k$) as $F\{\hat{L}f(r)\}=-c|k|^{\gamma}f(k)$. The regular diffusion limit is recovered when $\gamma=2$ and correspondingly, $\hat{L}$ is the Laplacian. $\eta(\mathbf{r},t)$ is the noise that here denotes the particles source difference, so that $\langle\eta(\mathbf{r},t)\rangle=0$ and $\langle\eta(\mathbf{r},t)\eta(\mathbf{r}',t')\rangle=2\Gamma\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$, and the noise takes the values ± 1. In this analysis, equal numbers of A and B particles at all times are assumed. For the constant source (CS) problem, $\eta_{\rm CS}(\mathbf{r},t)$ represents the rate of adding particles, while in the case of the transient, initial condition (IC) problem, the source exists only initially $\eta_{\rm IC}(\mathbf{r},t)=\eta(\mathbf{r},t)\delta(t)$. We note that Eq. (1) generalizes the

Edwards-Wilkinson growth model [14].

The density of A particles can be shown to obey the inequality $A(t)=\langle A(\mathbf{r},t)\rangle \geq \langle |q(\mathbf{r},t)| \rangle$, which defines a lower bound [1,2]. From earlier studies, one concludes that this lower bound provides a reasonably good description at long times when segregation takes place [9,29]. We are thus interested in calculating the quantity $\langle |q(\mathbf{r},t)| \rangle$. As was shown in Refs. [2] and [15], the moments $\langle [q(\mathbf{r}=0,t)]^m \rangle$ can be obtained from the moment generating function $\langle \exp[\phi q(\mathbf{r}=0,t)] \rangle$. This holds also for enhanced diffusion,

$$\langle \exp[\phi q_{\mathrm{IC,CS}}(\mathbf{r}=0,t)] \rangle = \exp[\tfrac{1}{2}\phi^2 I_{\mathrm{IC,CS}}(t)] , \qquad (2)$$

where the average is taken over all possible realizations of the noise. Equation (2) demonstrates that $q(\mathbf{r}=0,t)$ is Gaussian distributed, thus $\langle |q| \rangle = (2\langle q^2 \rangle / \pi)^{1/2}$. For simplicity, we assume that $A(\mathbf{r},t)$ and $B(\mathbf{r},t)$ are given as number densities, length is given in units of the lattice constant, and time in units τ for moving a lattice constant. $I(t)$ is related to the random-walk autocorrelation function $P_0(t)=P(\mathbf{r}=0,t)$ of the associated diffusion problem [23,24]. For the initial condition case, $I_{\mathrm{IC}}(t)=2A_0P_0(2t)$, where A_0 is the initial concentration of the A particles. We therefore obtain in d dimensions,

$$A_{\mathrm{IC}}(t) \sim C(A_0/t^{d/\gamma})^{1/2} , \quad d/2\gamma \leq 1 , \qquad (3)$$

which for $\gamma=2$ reduces to the regular result [1–4]. For the constant source problem, $I_{\mathrm{CS}}(t)=2\Gamma \int^t P_0(2t')dt'$. Starting from an empty $d=1$ lattice, we find

$$A_{\mathrm{CS}}(t) \sim \begin{cases} \Gamma t , & t < \Gamma^{1-1/\gamma} \\ \Gamma^{1/2} t^{1/2(1-1/\gamma)} , & \Gamma^{-1-1/\gamma} < t < L^{\gamma} \\ \Gamma^{1/2} L^{1/2(\gamma-1)} , & L^{\gamma} < t , \end{cases} \qquad (4)$$

where for early times there is an increase of the density without reactions. The intermediate regime shows an increase under reactions, and finally the stationary state is limited only by the size L of the system. Similar results were obtained in growth models for the width of a surface [14].

Segregations in $A+B$ reactions are the result of density fluctuations that give rise to A-rich and B-rich areas [2–6]. The segregation is considered to take place on a scale $\Lambda(t)$. To obtain an expression for $\Lambda(t)$, we consider the positional correlation function, which for the initial condition problem is related to the propagator by $\langle q(\mathbf{r},t)q(\mathbf{r}',t) \rangle \sim P(\mathbf{r}-\mathbf{r}',2t)$ [9,30]. From the scaling properties of $P(\mathbf{r},t)$, it follows that $\Lambda_{\mathrm{IC}}(t) \sim t^{1/\gamma}$. Similarly, for the constant source problem, one finds that $\langle q(\mathbf{r},t)q(\mathbf{r}',t) \rangle \sim \int^t P(\mathbf{r}-\mathbf{r}',2t')dt'$, indicating an increase of the segregation length $\Lambda_{\mathrm{CS}}(t)$, which is limited only by the size of the system.

In the simulation calculations, particles are dispersed randomly on the lattice and each particle is assigned with a randomly chosen event time and a direction of motion; typically, 10^6–10^7 particles are considered. The particles are removed from the lattice at first encounter between unlike species. Excluded volume among like particles is neglected. In the case of a source, particles are added randomly to the system with vertical annihilation and with the restriction that the number of A particles is equal to that of B particles at all times.

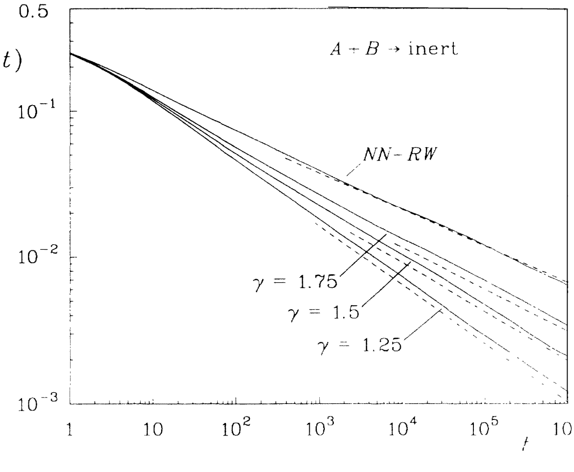

FIG. 1. Time evolution of the density $A_{\mathrm{IC}}(t)$ in the one-dimensional $A+B \rightarrow$inert reaction for nearest-neighbor random walks (NNRW) and for γ-dependent, enhanced diffusion, as indicated. Simulation results are given by full lines; the dashed lines are the predictions according to Eq. (3).

In Fig. 1, we show the densities $A_{\mathrm{IC}}(t)$ as a function of time for various diffusional enhancements and for a nearest-neighbor random walk. The numerical results are compared with the predictions and a satisfactory agreement is obtained. From the above derivations, the prefactors can also be derived. They are explicitly considered in the figure presentations; details will be given elsewhere [30]. In Fig. 2 we show the segregation length $\Lambda_{\mathrm{IC}}(t)$ for the same set of parameters as in Fig. 1. Again, the numerical results follow reasonably well the predicted slopes. Figure 3 refers to the constant source problem. The density increase and the approach to saturation are displayed for the parameters $\gamma=1.5$ and $\Gamma=10^{-3}$ and for several lengths L. The results are displayed in a scal-

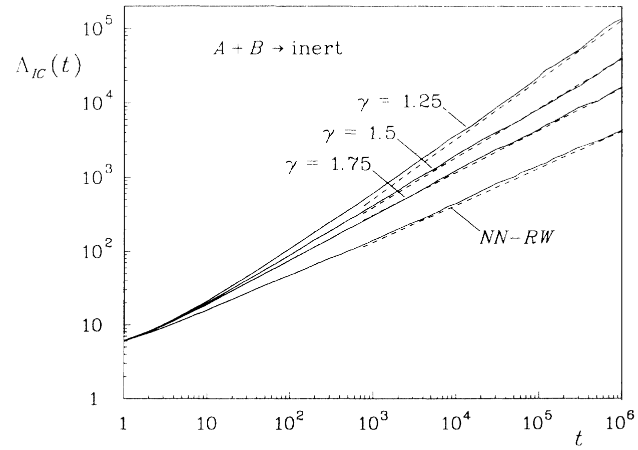

FIG. 2. Segregation length $\Lambda_{\mathrm{IC}}(t)$ as a function of time for the same diffusion-controlled reactions considered for Fig. 1. Full lines give the simulation results and the dashed lines indicate the slopes according to $\Lambda_{IC}(t) \sim t^{1/\gamma}$.

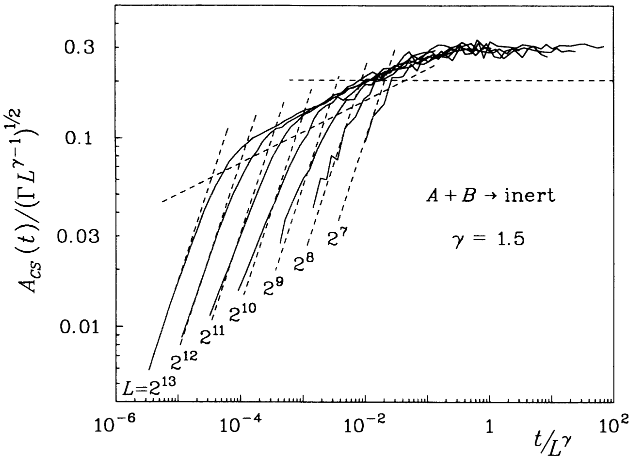

FIG. 3. Growth and saturation of the density $A_{\mathrm{CS}}(t)$ for the same diffusion-controlled reactions considered for Fig. 1, but with a source. Full lines give the simulation results in the scaling representation for various system sizes L, as indicated. The dashed lines are the predictions according to Eq. (4).

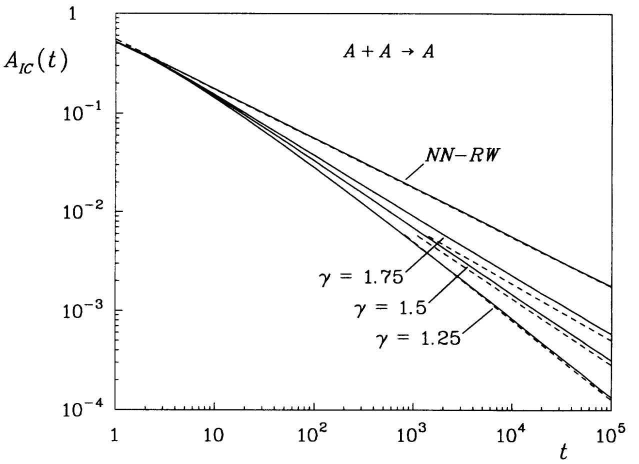

FIG. 4. Time evolution of the density $A_{\mathrm{IC}}(t)$ in the $A+A \rightarrow A$ reaction for NNRW and for γ dependent, enhanced diffusion, as indicated. Simulation results are given by full lines. The dashed lines are the predictions according to the powers of Eq. (7).

ing representation to strengthen the impression of the crossover behavior to saturation.

From the above analysis, we conclude that the enhanced diffusion, when introduced into reactions controlled by diffusion, manifests itself in a number of ways. As expected, the reaction is accelerated so that for the transient (IC) problem the decay is faster and the size of the segregated areas grows faster. Moreover, while in the simple diffusion case the critical dimension at which the classical rate-equation approach is applicable is $d_c=4$ [1–4], here, due to the enhancement, the critical dimension is reduced to $d_c=2\gamma$. Correspondingly, the segregation, which slows down the reaction, is expected to disappear at dimensions lower than $d=4$. In the case of a constant source and regular diffusion, segregation occurs in $d=1$, is marginal for $d=2$ (critical dimension), and is absent above $d_c=2$ [9]. Under enhancement conditions, with $1<\gamma<2$, the reaction is again accelerated and the marginal dimension, above which no segregation occurs, is lowered.

A + A → A, → inert

We now focus on the $A+A \rightarrow$ inert and $A+A \rightarrow A$ reactions. These processes were shown to be very similar to each other in their density decay and in their source strength dependence [10,11]. The situation is somewhat more complicated when the interparticle distances are considered, since the corresponding distance distributions $\rho(r,t)$ do not belong to the same universality class for the two kinds of processes. In the generalization to enhanced diffusion, we concentrate on the $A+A \rightarrow A$ process in $d=1$ and follow the work in Ref. [11], which relates the decay pattern to the average interparticle distance. The interparticle distances are governed by the probability to move a distance r subject to the boundary condition of an adsorbing origin [11]. We make use of the method of images for the derivation of an approximate form; a critical discussion of the limitations of the method will be presented elsewhere [30]. We obtain

$$\begin{aligned}\rho(r,t) &\simeq \int_0^{\infty}[P(r-x,2t)-P(r+x,2t)]\rho_0(x)\,dx\\ &\simeq -2\partial_r P(r,2t)A_0^{-1}\,, \end{aligned}\tag{5}$$

where $P(r,t)$ is the propagator introduced for the $A+B$ case and $\rho_0(r)$ is the initial interparticle distance distribution. Equation (5) is considered to hold at asymptotically long times for which the typical interparticle distance in the initial realization is small compared to actual length scale. From the above equation, we obtain for the time dependent density [11],

$$A_{\mathrm{IC}}(t) \simeq -2A_0\int_0^{\infty}\partial_r P(r,2t)\,dr = A_0 P_0(2t)\,, \tag{6}$$

which leads to

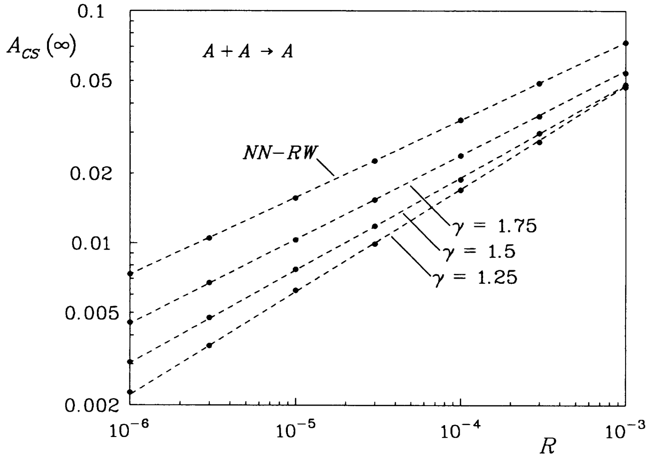

FIG. 5. Saturation concentration $A_{\mathrm{CS}}(\infty)$ for the same diffusion-controlled reactions considered in Fig. 4, but with a source. The numerical results are given by the dots as a function of the source rate R; the dashed lines give the predicted slopes according to Eq. (9).

$$A_{\mathrm{IC}}(t)\sim C A_0 t^{-1/\gamma} \; . \tag{7}$$

In the case of regular diffusion, this result coincides with that of Refs. [4,7,11]. Furthermore, the result of Eq. (7) can also be obtained from a Smoluchowski type of approach, which relates the density $A_{\mathrm{IC}}(t)$ to $S(t)$; the average number of new sites visited by a particle is $A_{\mathrm{IC}}(t)\sim[S(t)]^{-1}$ [4]. From this point of view, enhanced diffusion appears to explore space more efficiently than Brownian motion, a property of importance for reactions.

From Eq. (7), we can derive in approximate effective rate equation when a source R is included [11],

$$\partial_t A_{\mathrm{CS}}(t)\simeq -K A_{\mathrm{CS}}^{1+\gamma}(t)+R \; . \tag{8}$$

For stationary conditions, Eq. (8) yields an expression for the dependence of the concentration on the source strength,

$$A_{\mathrm{CS}}(\infty)\sim R^{1/(\gamma+1)} \; , \quad 1<\gamma\leq 2 \; . \tag{9}$$

We have simulated the $A+A\rightarrow A$ process along the procedure introduced for the $A+B\rightarrow$inert process, but with only one particle discarded when two particles meet. In Fig. 4, we show, in analogy to Fig. 1, the densities $A_{\mathrm{IC}}(t)$ as a function of time for various diffusional enhancements and also for nearest-neighbor random walks with constants taken from Ref. [30]. One notices that the numerical results are in satisfactory agreement with the predictions. Figure 5 refers to the constant source problem at saturation with the densities displayed as functions of the source strength R. The numerical results follow reasonably the power-law prediction of Eq. (9).

In summary, we have investigated the effects of enhanced diffusion on a family of diffusion-controlled reactions by incorporating Lévy walks into the diffusional process. For all reaction schemes we have studied, the enhancement acts as a model "stirrer," which accelerates the reactions on all scales and reduces the effects of segregation relative to the Brownian motion case.

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