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Two-species reaction-diffusion system with equal diffusion constants: Anomalous density decay at large times

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We study a two-species reaction-diffusion model where $A+A\rightarrow\emptyset$, $A+B\rightarrow\emptyset$, and $B+B\rightarrow\emptyset$, with annihilation rates λ_0, $\delta_0>\lambda_0$, and λ_0, respectively. The initial particle configuration is taken to be randomly mixed with mean densities $n_A(0)>n_B(0)$, and with the two species A and B diffusing with the same diffusion constant. A field-theoretic renormalization group analysis suggests that, contrary to expectation, the large-time density of the minority species decays at the same rate as the majority when $d\leqslant 2$. Monte Carlo data support the field theory prediction in $d=1$, while in $d=2$ the logarithmically slow convergence to the large-time asymptotics makes a numerical test difficult.

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Fluctuation effects in low-dimensional reaction-diffusion systems have received considerable attention lately [1]. When the dimension d of the system is sufficiently small, below a critical dimension d_c, spatial fluctuations in the particle concentration dramatically influence the large-time behavior of the system. Most strikingly, the large-time scaling exponents and, sometimes, amplitudes of various observables become universal and independent of the microscopic description of the system. Indeed, the quest for possible new universality classes has intensified in recent years, with studies of a variety of models exhibiting fluctuation-dominated kinetics at different levels of complexity. Theoretical advances, together with a growing number of experimentally accessible realizations of low-dimensional reaction-diffusion models—like reaction kinetics of excitons in polymer chains or surface deposition of certain proteins [1]—have further accelerated these studies.

We here consider a generalization of the well-known single-species $A+A\rightarrow\emptyset$ and two-species $A+B\rightarrow\emptyset$ annihilation models [2] by coupling them together and allowing *all* particles to react:

$$A+A\xrightarrow{\lambda_0}\emptyset,\quad A+B\xrightarrow{\delta_0}\emptyset,\quad B+B\xrightarrow{\lambda_0'}\emptyset. \tag{1}$$

The A and B particles are assumed to perform a random walk on a d-dimensional lattice with diffusion constants D_A and D_B, respectively. When two particles meet on the same site they annihilate with probabilities given by the reaction rates λ_0, δ_0, and λ_0' in Eqs. (1). Among a number of possible applications, the model may be used to describe *steric* reaction-diffusion processes [3], with the two species representing the projections of the chemically ''active spots'' of the reactants onto some fixed reference direction [4].

The question we wish to address is how the average particle densities $n_A(t)$ and $n_B(t)$ decay in time when there is an initial imbalance $n_A(0)>n_B(0)$ in the population of the two species. (In an application to a steric reaction-diffusion process, this would correspond to a bias in the initial orientations of the reactants, triggered by some external field [3].) When $\delta_0>\lambda_0,\lambda_0'$ we expect the minority species of B particles to die out before the majority A. This has been confirmed by a field-theoretic renormalization group analysis for the case when $D_A\neq D_B$ [5]: Independent of dimensionality, the minority species was shown to vanish before the extinction of the majority. Here we shall focus on the case when $\lambda_0'=\lambda_0$ and with the diffusion constants tuned to the same value, $D_A=D_B\equiv D$, as would be the proper choice when applying the model to a steric reaction-diffusion process [3]. Since the *effective* time-dependent reaction rates are controlled by the diffusion constants [2], it is interesting to explore whether the case of *equal* diffusion constants could lead to new effects.

To set the stage, let us briefly study the classical rate equations implied by Eqs. (1):

$$\frac{da}{dt}=-(\lambda_0a^2+\delta_0ab),\quad \frac{db}{dt}=-(\lambda_0b^2+\delta_0ba), \tag{2}$$

with a,b the mean-field densities of species A,B, and with initial conditions $a(0)=n_A(0)$ and $b(0)=n_B(0)$.

The qualitative behavior of Eq. (2) can be studied by a mapping to a Poincaré sphere [6] with $z=1/a$ and $u=b/a$:

$$\frac{dz}{dt}=\lambda_0+\delta_0u(t),\quad \frac{du}{dt}=(\lambda_0-\delta_0)u(1-u)/z, \tag{3}$$

where u is assumed to be in the interval [0,1]. With $\lambda_0<\delta_0$, Eqs. (3) imply that for $u(0)<1$ and for large times $1/u(t)$ diverges as

$$\frac{1}{u(t)}=\frac{a(t)}{b(t)}\propto t^{\delta_0/\lambda_0-1}\rightarrow\infty,\quad t\rightarrow\infty, \tag{4}$$

when $a(0)>b(0)$. Thus, with λ_0 and δ_0 fixed, the minority species is killed off early, as expected. Note, however, that Eq. (4) suggests that $u(t)$ could saturate to a constant if the effective *diffusion-controlled* reaction rates replacing λ_0 and δ_0 in the presence of fluctuations approach each other asymptotically. To explore this possibility it is convenient to pass to a field-theoretic formulation of the problem.

For this purpose, let us consider the master equation of the system:

$$\frac{d}{dt}P(c,t)=\sum_{c'} R_{c'\to c}P(c',t)-\sum_{c'} R_{c\to c'}P(c,t). \quad (5)$$

Here $P(c,t)$ denotes the probability of a configuration c at time t, and $R_{c'\to c}$ is the transition rate from state c' into c, determined by D, δ_0, and λ_0. We take $P(c,0)$ as a Poisson distribution, with averages denoted by $n_A(0)$ and $n_B(0)$ for A and B particles, respectively. Equation (5) can be translated into a Schrödinger-type equation with a second-quantized Hamiltonian [7], which in the continuum limit turns into a field theory with action S:

$$\begin{aligned} S=\int d^dx\int dt\Bigg[&\sum_{\alpha=A,B}\bar{\phi}_\alpha(\partial_t-\nabla^2)\phi_\alpha \\ &+\sum_{\alpha,\beta=A,B}\lambda_{\alpha\beta}\bar{\phi}_\alpha(1+\bar{\phi}_\beta/2)\phi_\alpha\phi_\beta\Bigg] \\ &-\int d^dx\sum_{\alpha=A,B}n_\alpha(0)\bar{\phi}_\alpha(x,0), \end{aligned} \quad (6)$$

with rescaled time variable $Dt\to t$. The scalar fields ϕ_A and ϕ_B describe the A and B particles with initial densities $n_\alpha(0)$, $\alpha=A,B$, and with the coupling constants $\lambda_{AA}=\lambda_{BB}=\lambda_0$ and $\lambda_{AB}=\lambda_{BA}=\delta_0$ encoding the reaction rates. The action in Eq. (6) faithfully mimics the master equation in Eq. (5), up to terms irrelevant under renormalization. Note that the rate constants become dimensionless when $d=2$ which suggests that $d_c=2$, a result confirmed by standard power counting [8]. Since we are interested in effects from fluctuations, we focus on $d\leqslant 2$ in what follows.

When $d\leqslant 2$ the particle densities can be calculated perturbatively from Eq. (6) as $n_\alpha(t)=\langle\phi_\alpha\rangle_S$ using an ϵ expansion, with the rate constants λ_0 and δ_0 replaced by renormalized rates $g_\alpha(\kappa^{-2})=\kappa^{-\epsilon}\alpha_0/(1+\kappa^{-\epsilon}\alpha_0/g^*)$, with $\alpha=\lambda$ and δ, respectively, and with κ the renormalization scale. Divergent logarithmic terms in the expansion are conveniently grouped together using ‘‘running coupling constants’’

$$g_\lambda(t)=\frac{g^*}{1+(t/t^*_\delta)^{-\epsilon/2}},\quad g_\delta(t)=\frac{g^*}{1+(t/t^*_\lambda)^{-\epsilon/2}}, \quad (7)$$

where $g^*=\Gamma(\epsilon/2)^{-1}(8\pi)^{d/2}$ is the renormalization group (RG) fixed point to which $g_\lambda(t)$ and $g_\delta(t)$ flow under a change of time scale [9]. The running coupling constants in Eqs. (7) are obtained from the Callan-Symanzik equation which expresses the independence of the densities $n_\alpha(t)$ on the choice of κ:

$$\begin{aligned} &n_\alpha(t;g_\lambda(\kappa^{-2}),g_\delta(\kappa^{-2});n_{A,0},n_{B,0};\kappa) \\ &\quad=(\kappa^2t)^{-d/2}n_\alpha(\kappa^{-2};g_\lambda(t),g_\delta(t);\tilde{n}_{A,0}(t),\tilde{n}_{B,0}(t);\kappa), \\ &\qquad\qquad\qquad\qquad \alpha=A,B \end{aligned} \quad (8)$$

with $\tilde{n}_{\alpha,0}(t)=(\kappa^2t)^{d/2}n_{\alpha,0}$.

Employing the mean-field densities from Eqs. (2) in Eq. (8) (*fluctuation-improved mean-field treatment* [5,10]), we obtain

$$u(t)\to u^*=(\Omega-1)/(\Omega+1), \quad (9)$$

where $\Omega^2=1+4\xi^*u_0/(1-u_0)^2$ and $\xi^*=\exp[-8\pi(1/\lambda_0-1/\delta_0)]$, for $d=1$, 2. Thus, at this level of analysis the minority species at large times decays at the same rate as the majority ($u^*\neq 0$). Note also that Eq. (9) implies that $u(d=1,t)>u(d=2,t)$ as $t\to\infty$, suggesting that the survival rate of the minority particles increases with reduced dimensionality.

The fluctuation-improved mean-field analysis (where all tree-level diagrams are summed) takes into account effects from fluctuations via the renormalized coupling constants. However, in order to fully account for fluctuations one has to explicitly consider the loop diagrams. For this purpose it is convenient to expand in the asymptotically small parameter $\eta(t)\equiv g_\lambda(t)-g_\delta(t)$. To one-loop level and to first order in η we thus obtain

$$n_\alpha(t)=\mu_\alpha N(t)[1+\Delta_\alpha(t)],\quad \alpha=A,B. \quad (10)$$

Here $\mu_A=1/(1+u^*)$, $\mu_B=u^*/(1+u^*)$, and $\Delta_A(t),\Delta_B(t)\propto\eta(t)\ln t^{d/2}\to 0$ as $t\to\infty$, and we hence recover the result in Eq. (9) at very large times. The common factor $N(t)$ in Eq. (10) coincides with the density of the single species $A+A\to 0$ model, with $N(t)=\ln t/8\pi t$ in $d=2$ and $N(t)=1/\sqrt{8\pi}t^{-1/2}$ in $d=1$ [10]. The approach of the total density $n_A(t)+n_B(t)$ to that of the single-species model reflects the fact that the equal values of the diffusion-controlled rates in Eqs. (7) at large times make the two species indistinguishable, effectively leaving us with a single-species system. We should here stress that the values of the amplitudes in Eq. (10) have been obtained by ignoring all irrelevant terms (in the RG sense) that could be added to the action in Eq. (6). Since we do not expect the amplitudes to be universal, such terms—if included—could shift the value of u^* in Eq. (9). The scaling form of $n_A(t)$ and $n_B(t)$ on the other hand *is* expected to be universal (considering the generic behavior of this class of problems [2]), and should be insensitive to any left-out irrelevant terms.

To summarize, our RG analysis to the one-loop level suggests that the minority species at large times decays at the same rate as the majority when $d\leqslant 2$. This result—if robust against contributions from higher-order terms in the loop expansion—is quite remarkable and very different from the conventional picture implied by classical rate theory. Unfortunately, due to the difficulty of keeping track of possible ‘‘correction-to-scaling’’ terms [8], the present model (in contrast to the simpler $A+A\to\emptyset$ model) is intractable to standard procedures for assessing higher-loop effects [11]. Therefore, to check the robustness of the result in Eq. (10) we have resorted to a Monte Carlo simulation of the master equation (5) (which in addition provides information on the transient kinetics).

To perform the simulation we have used an *improved minimal process algorithm* [12]: At each time step a lattice site, say, i, is picked at random (out of L possible sites), and a table of statistical weights $w_\alpha^{(i)}$ for the possible processes

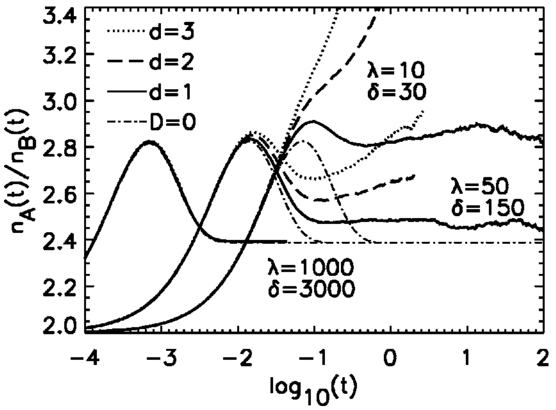

FIG. 1. Density ratio $n_A(t)/n_B(t)$ obtained from a numerical simulation of the master equation (5) in $d=1$, 2, and 3 on a 10^6, $10^3\times10^3$, and $10^2\times10^2\times10^2$ lattice, and numerical solution of Eq. (5) in the limit of $D=0$ (''decoupled-site problem''). The fixed parameter values are $D=1s^{-1}$, $n_{A,B}(0)=2,1$ particles/site. The reaction rates λ_0 and δ_0 are given in units of the diffusion constant D.

π_α, $\alpha=1,\ldots,M$, at this site is constructed, with π_M a ''null process.'' The weights are defined as cumulative probabilities: $w_\alpha^{(i)}=\Sigma_{\beta=1}^{\alpha}R_\beta^{(i)}/Q$, with $Q=\Sigma_{\alpha=1}^{M}R_\alpha^{(i)}$, where $R_\alpha^{(i)}$ denotes the rate for π_α. Here Q is the total rate which is kept the same for all sites by properly adjusting the rates $R_M^{(j)}$, $j=1,\ldots,L$, for the null processes. After selecting a random number $0\leqslant r<1$ that process π_α is carried out for which $w_{\alpha-1}^{(i)}\leqslant r<w_\alpha^{(i)}$ ($w_{-1}^{(i)}\equiv 0$), and time is incremented by $t\to t+1/LQ$.

Figure 1 shows results for the density ratios $n_A(t)/n_B(t)$ from simulations in one, two, and three dimensions. Initially the system is homogeneous with randomly mixed A and B particles, with $n_A(0)>n_B(0)$. At early times a typical minority particle is then surrounded by several A's, and is therefore likely to be killed off. As seen in Fig. 1, this is indeed the case: in all dimensions the density ratio grows initially. However, for sufficiently large rates there is a *recovery effect*: After the initial growth the density ratio drops — the minority species finds a way to recover. (Here and in the following ''recovery'' is understood in relative terms. The number of minority particles still decays in time but the ratio of majority to minority densities decreases in favor of the minority). As seen in Fig. 1 the large-time behavior of the curves depends on the dimensionality as well as on the values of the reaction rates. For $\delta_0=3\lambda_0=150$ the $d=3$ curve takes off after the recovery phase, in agreement with the classical mean field result Eq. (4). This is in striking contrast to the $d=1$ curve which saturates to a plateau, as predicted by the one-loop RG result in (10). The eventual fate of the $d=2$ curve is more difficult to foretell since the convergence to the asymptotic scaling regime in $d=2$ is logarithmically slow [11]. Unfortunately, with available techniques it is hard to push the $d\geqslant2$ simulations reported in Fig. 1 much beyond $\log_{10}(t)\approx0.5$ where the number of particles becomes too small to obtain a reliable statistics. Turning to the $\delta_0=3\lambda_0=30$ runs, the $d=1$ curve again saturates to a plateau, while the $d=2$ and $d=3$ curves take off even before a peak has developed. For this case it may be harder to argue that the $d=2$ curve may eventually also saturate, although it cannot be excluded considering the slow convergence. Note that the RG prediction of an enhanced survival rate in low dimensions is confirmed for this choice of reaction rates as well: the $d=1$ curve falls below that for $d=2$. The runs with very large reaction rates $\delta_0=3\lambda_0=3000$ produce curves which collapse onto a single curve, spuriously suggesting a plateau in all dimensions: In $d=3$, however, large reaction rates impede the crossover to the mean field asymptotics, and we expect the $d=3$ curve to take off at a time not accessible with our simulation. On the other hand, we do expect the $d=1$ curve to stay flat (considering the generic behavior for smaller rates), while the asymptotics of the $d=2$ curve is again hard to predict due to the logarithmically slow convergence to the scaling region.

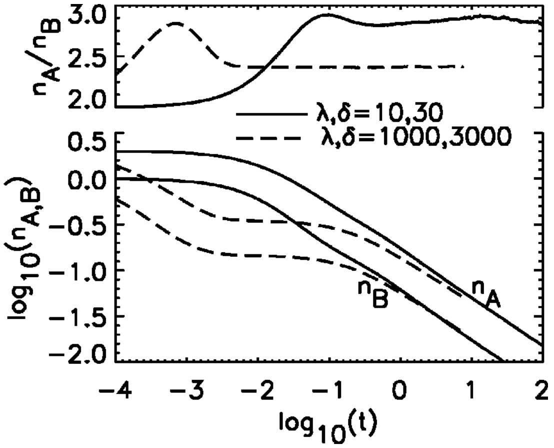

FIG. 2. Plot of individual densities (bottom) together with density ratios $n_A(t)/n_B(t)$ (top) in $d=1$ obtained from simulations.

The buildup of a density-ratio peak with a subsequent ''recovery phase'' in the early stage of the kinetics (for sufficiently large rates) is made transparent by solving the master equation (5) with the diffusion constant D set to zero (i.e., with an ensemble of decoupled single-site problems [13]). The hatched curves in Fig. 1 represent the corresponding density ratios for very large and small reaction rates. Initially the dominant $A+B\to\emptyset$ reactions on the different sites cause a fast rise of $n_A(t)/n_B(t)$ (*peak formation*). After some time this process gets exhausted with single B particles left at a finite fraction of the sites. The $A+A\to\emptyset$ reactions on the remaining sites now become dominant, causing a depletion of A particles (*recovery phase* for B particles). As this process in turn gets exhausted one is left with a constant ratio $n_A(t)/n_B(t)$ (*plateau*). As seen in Fig. 1, for small rates the early-time decoupled-site kinetics gets perturbed by diffusion of particles from neighboring sites, which leads to an enhanced mixing of A and B particles and hence a steeper rise of the density-ratio curve. Still, in $d=1$, the curve eventually saturates to a plateau. This plateau, however, is of a very different origin from that of the decoupled-site problem with no diffusion. This is strikingly shown in Fig. 2 where we have plotted the individual densities in $d=1$ for large and small rates, with the corresponding density ratio curves inserted at the top. In both cases the individual densities are seen to decay *after the plateau has formed.* Note in particular that the decoupled-site plateau for large rates (with no decay of the individual densities) persists only in the time interval $-2.5\leqslant\log_{10}(t)\leqslant-1$. At later times effects from diffusion set in, without, however, visibly distorting the plateau. Note

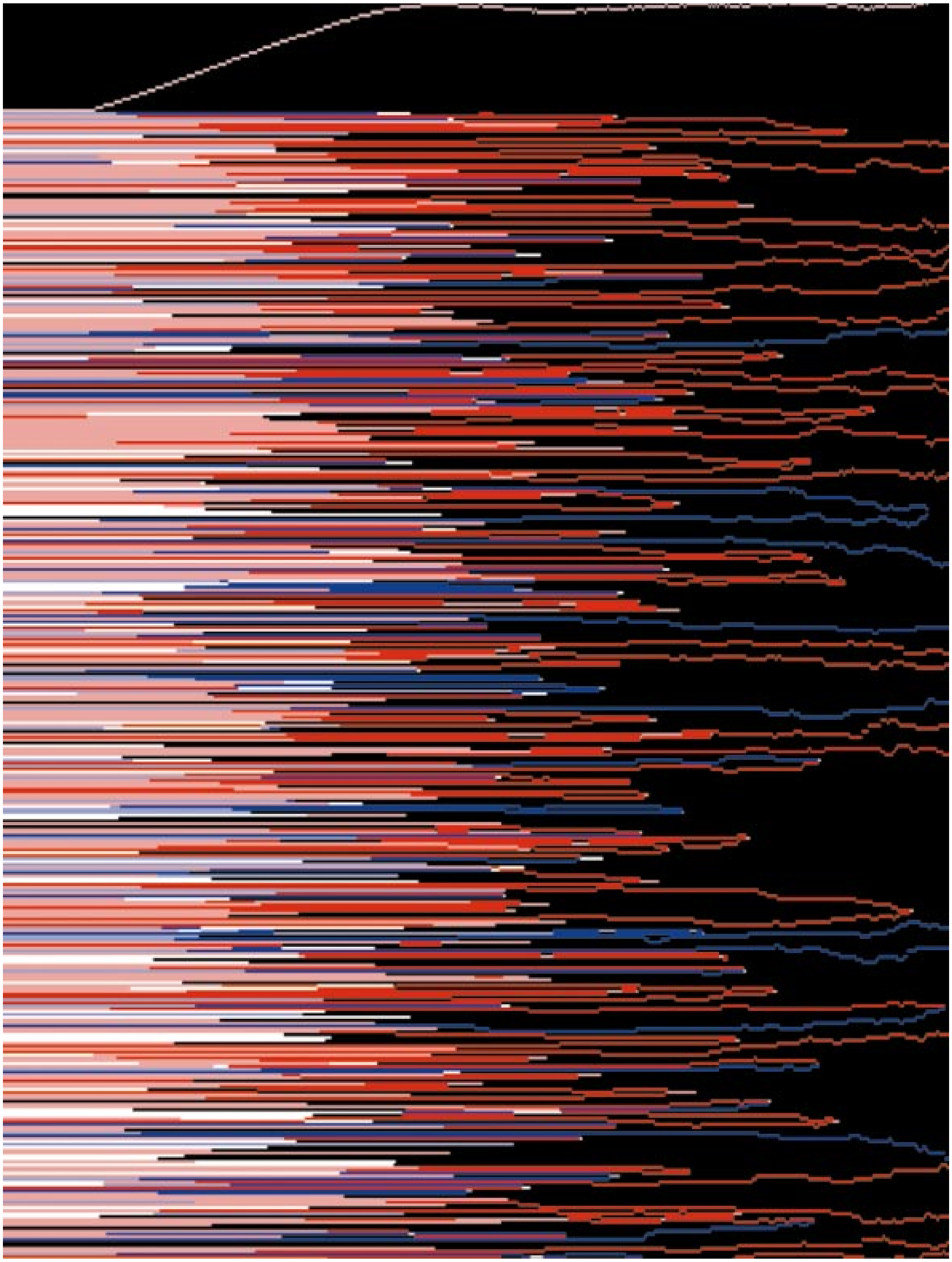

FIG. 3. (Color) ''Cartoon'' of the $d=1$ kinetics. Time runs horizontally, with 300 lattice sites represented along the vertical axis. At the top the corresponding density ratio is plotted for comparison. The reaction rates are $\lambda_0, \delta_0 = 10,30$. Red (blue) color denotes that a majority of particles belong to the $A(B)$ species. White indicates the same number of A's and B's on a lattice site, with intermediate cases covered by intermediate colors. Black color denotes an empty site.

also that although the asymptotic curves come very close to each other, they do not collapse onto a single curve, in agreement with the one-loop RG result: The total density $n_A(t)+n_B(t)$ in (10) is universal, whereas the individual components are not.

It is instructive to look at a Monte Carlo ''cartoon'' of the kinetics in $d=1$, as plotted in Fig. 3. The ''recovery phase'' (for B particles) is visible as dense red ropes of A particles terminating in black (empty sites), with the remaining particles diffusing as single threads colored red (A particles) or blue (B particles). Remarkably, at large times these threads self-organize spatially in such a way as to keep the density ratio at a constant value. By a comparison to the $A+B\rightarrow 0$ model [11] one observes that the tendency for domain formation in the present model is much weaker: A and B particles appear to be rather well mixed asymptotically. This makes the anomalous density decay even more intriguing, suggesting that the average A-A and A-B distances are correlated asymptotically so as to precisely compensate for the smaller number of A-B pairs (with endangered B particles) as compared to A-A pairs.

To conclude, we have studied a two-species reaction-diffusion model where the particle densities exhibit an anomalous behavior at large times: The spatial self-ordering of the two species allows the minority population to persevere, with the asymptotic density ratio (of majority to minority species) kept at a constant value. This apparent ‘‘non-Darwinian’’ kinetics is entirely driven by fluctuations in the diffusion-controlled regime, typical for a system of reduced dimensionality. A perturbative RG analysis suggests that the same remarkable behavior is present also in two dimensions, although this is still to be verified by independent methods. Details and extensions will be published elsewhere [11].

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