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Diffusion-limited $A+B \rightarrow 0$ reaction: Correlated initial condition

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We find a time dependence different from that reported previously in the literature for the species concentration in the $A+B \rightarrow 0$ diffusion-limited reaction for dimensions $d<2$ when the A-B pairs are initially correlated. Whereas an uncorrelated initial distribution leads to the well-known decay law $\rho \sim t^{-d/4}$ for $d<4$ and $\rho \sim t^{-1}$ for $d \geq 4$, a correlated initial distribution leads to the decay law $\rho \sim t^{-(d+2)/4}$ for $d<2$ and $\rho \sim t^{-1}$ for $d \geq 2$. The decay is therefore more rapid in the correlated case and the critical dimension for "anomalous" behavior shifts from 4 to 2.

I. INTRODUCTION

Since the original studies of Zeldovich and his coworkers,[1] there has been a great deal of interest in the notion that diffusion-limited $A+B \rightarrow 0$ reactions in sufficiently low dimensions under appropriate conditions lead to spontaneous segregation of species and to associated "anomalous" time dependences and rate laws for the densities of the species.[1-12] Whether or not such "anomalies" occur depends (among other factors) on dimensionality, the initial distribution of the species, and the presence or absence of sources.

In a "batch" reaction an initial distribution of A's and B's is allowed to diffuse and to react upon (suitably defined) contact. In such a reaction there are no sources of A's and B's other than the initial distribution, so that eventually one or the other or both species goes to extinction. The textbook description of this process is based on a quadratic rate law for the overall concentrations $\rho_A(t)$ and $\rho_B(t)$:

$$\dot{\rho}_A(t)=\dot{\rho}_B(t)=-k_g \rho_A(t) \rho_B(t) \ . \tag{1}$$

Here, k_g is the global rate coefficient assumed to be independent of time t and of system size. In recent years, however, it has become clear that there are situations in which k_g may depend on time or, equivalently, on particle density even in the asymptotic ($t \rightarrow \infty$) regime.[7] This dependence is determined by the dimensionality of the medium and by the initial distribution of the species. A time or density dependence of k_g in turn implies a time dependence of the densities that is "anomalous" in the sense that it differs from (decays more *slowly* than) that which would be obtained were k_g constant. In this note we discuss the anomalous time dependence for a particular case for which an incorrect dependence has been reported previously:[2] that of a batch reaction in which the initial A-B distribution is tightly correlated, e.g., a geminate initial distribution.

The time (or density) dependence of k_g or, equivalently, the anomalous time dependence of the densities, can have at least two physical origins. One is the relative spatial distribution of the two species, which in the textbooks is assumed to be uniform (i.e., well stirred) throughout the volume. Any spatial segregation of the species will reduce their effective reaction rate because it reduces the number of contact points between them.[1-4,7,12] Another physical origin of possible anomalies is the particle-particle distribution (regardless of species identification).[12] The textbooks assume a uniformly random (i.e., Poisson) distribution. A deviation from this arrangement can also lead to anomalous behavior: this latter effect is the sole cause of the anomalies that occur in the $A+A$ reaction.[13] In particular, if the particles tend to stay farther apart from one another than in a uniformly random arrangement, the reaction will also be slowed down.

A number of scaling arguments as well as more detailed arguments based on reaction-diffusion models have provided a fairly clear understanding of the behavior of a batch $A+B \rightarrow 0$ reaction when the initial distribution of A's and B's is *random*.[1-4,9] These arguments show that in dimensions up to $d=4$ an initial local excess of one species *grows* in time so that asymptotically the system consists of A- and B-rich regions each of which is of a diffusion-determined size $\sim (Dt)^{d/2}$ (D is the diffusion coefficient, assumed equal for both species). If initially the number of A and B molecules is equal, the scaling arguments show that instead of the classical decay law

$$\rho_A(t)=\rho_B(t) \equiv \rho(t) \sim t^{-1} \tag{2}$$

that would be predicted by Eq. (1) for each of the species, the decay law here for $d \leq 4$ is

$$\rho(t)\sim\sqrt{\rho(0)}(Dt)^{-d/4}\ , \tag{3}$$

implying a rate law

$$\dot{\rho}\propto -\rho^{(d+4)/d} \tag{4}$$

instead of $\dot{\rho}\propto -\rho^2$.

II. CORRELATED INITIAL CONDITION

Herein we consider an initial condition in which A-B *pairs* are deposited at random locations in the system—the members of the pair being a distance c apart. We refer to this as a "correlated initial condition", noting that different pairs may interpenetrate. In any volume greater than $O(c^d)$ there are therefore initially an equal number of A's and B's and the scaling arguments based on local fluctuations that can then grow in time no longer apply. Earlier authors have in effect assumed that the initially correlated $A+B\rightarrow 0$ problem leads to the same time dependence as the $A+A\rightarrow 0$ problem.[2,14] For this latter problem a simple random walk argument gives an anomalous time decay for $d<2$. The argument goes as follows:[2] for $d\leq 2$ the random walk of each particle in the system is compact, i.e., a random walker covers essentially every point of a given region before leaving that region. In a time t the typical region so covered has volume $(Dt)^{d/2}$. Unless this volume is empty, the walking particle will be annihilated. Therefore for $d\leq 2$ the density of particles remaining at time t must go as

$$\rho(t)\sim(Dt)^{-d/2} \tag{5}$$

instead of Eq. (2), and the corresponding rate law

$$\dot{\rho}\propto -\rho^{(d+2)/d} \tag{6}$$

now replaces Eq. (1). Note that this argument implies that *each* particle remaining at time t must in effect be isolated from other particles.

We argue that the $A+B$ case even with a correlated initial condition behaves differently than the $A+A$ case,[15] and that in fact the densities in the $A+B$ case for $d<2$ have a time decay that is *faster* than predicted in Eq. (5) but *slower* than the classical t^{-1} behavior.

We begin with a reaction-diffusion model for the local densities $\rho_A(\mathbf{r},t)$ and $\rho_B(\mathbf{r},t)$:[5,6,16]

$$\dot{\rho}_A(\mathbf{r},t)=D\nabla^2\rho_A(\mathbf{r},t)-k_l\rho_A(\mathbf{r},t)\rho_B(\mathbf{r},t) \tag{7}$$

and similarly for ρ_B, where k_l is the time-independent local rate coefficient and D is the diffusion coefficient for both species. It is convenient to deal instead with the difference and sum variables

$$\gamma(\mathbf{r},t)\equiv\tfrac{1}{2}[\rho_A(\mathbf{r},t)-\rho_B(\mathbf{r},t)]\ ,$$
$$\rho(\mathbf{r},t)\equiv\tfrac{1}{2}[\rho_A(\mathbf{r},t)+\rho_B(\mathbf{r},t)]\ . \tag{8}$$

The difference variable satisfies a linear diffusion equation whose solution is easily found to be

$$\gamma(\mathbf{r},t)=\frac{1}{V}\sum_{\mathbf{k}}\int d\mathbf{r}'e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}e^{-Dk^2t}\gamma(\mathbf{r}',0)\ , \tag{9}$$

where V is the system volume. The initial condition for the difference variable is

$$\gamma(\mathbf{r},0)=\tfrac{1}{2}\sum_j[\delta(\mathbf{r}-\mathbf{r}_j^A)-\delta(\mathbf{r}-\mathbf{r}_j^B)]\ , \tag{10}$$

where $\mathbf{r}_j^A$ and $\mathbf{r}_j^B$, $j=1,2,\ldots,N$ denote the initial location of the particles. These initial positions are drawn from an ensemble whose distribution we must specify. We consider the situation where pairs of A-B particles separated by a distance c are placed and oriented randomly, i.e., the probability density for an A-B pair is

$$p(\mathbf{r}_j^A,\mathbf{r}_j^B)=\frac{\Gamma(d/2)}{2V\pi^{d/2}}\int d\Omega\,\delta(\mathbf{r}_j^B-\mathbf{r}_j^A-\mathbf{c})\ , \tag{11}$$

where $\mathbf{c}$ is a vector whose length is c and whose orientation is random, and the integration is over these orientations. The quantities of physical interest are the ensemble averages $\langle\gamma(\mathbf{r},t)\rangle$ and $\langle\gamma(\mathbf{r},t)\gamma(\mathbf{r}',t)\rangle$ over these initial probability densities.

To perform these averages it is convenient to Fourier transform the initial condition (10):

$$\begin{aligned}\hat{\gamma}(\mathbf{k},0)&=\int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}\gamma(\mathbf{r},0)\\&=\tfrac{1}{2}\sum_j(e^{i\mathbf{k}\cdot\mathbf{r}_j^A}-e^{i\mathbf{k}\cdot\mathbf{r}_j^B})\ .\end{aligned} \tag{12}$$

Random placement of A particles (or B particles) implies that (see the Appendix)

$$\langle e^{i\mathbf{k}\cdot\mathbf{r}_j^A}\rangle=\langle e^{i\mathbf{k}\cdot\mathbf{r}_j^B}\rangle=\delta_{\mathbf{k},0}\ , \tag{13}$$

where the brackets denote an average over the distribution (11). Hence, $\langle\hat{\gamma}(\mathbf{k},0)\rangle=0$ and consequently $\langle\gamma(\mathbf{r}',0)\rangle$ in (9) also vanishes, leading to

$$\langle\gamma(\mathbf{r},t)\rangle=0\ . \tag{14}$$

This condition reflects the fact that the number of A's and B's is equal for all time if it is equal initially.

To calculate the second moment $\langle\gamma^2(\mathbf{r},t)\rangle$ we note that

$$\langle\gamma^2(\mathbf{r},t)\rangle=\frac{1}{V^2}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\langle\hat{\gamma}(\mathbf{k},0)\hat{\gamma}(\mathbf{k}',0)\rangle e^{-(k^2+k'^2)Dt}e^{-i(\mathbf{k}+\mathbf{k}')\mathbf{r}}\ . \tag{15}$$

The correlation function in (15) is in turn given by (see the Appendix)

$$\begin{aligned}\langle\hat{\gamma}(\mathbf{k},0)\hat{\gamma}(\mathbf{k}',0)\rangle&=\frac{1}{4}\Big\langle\sum_j(e^{i\mathbf{k}\cdot\mathbf{r}_j^A}-e^{i\mathbf{k}\cdot\mathbf{r}_j^B})\sum_{j'}(e^{i\mathbf{k}'\cdot\mathbf{r}_{j'}^A}-e^{i\mathbf{k}'\cdot\mathbf{r}_{j'}^B})\Big\rangle\\&=\frac{N}{2}\delta_{\mathbf{k}+\mathbf{k}',0}-\frac{1}{4}\sum_j\langle e^{i(\mathbf{k}\cdot\mathbf{r}_j^A+\mathbf{k}'\cdot\mathbf{r}_j^B)}+e^{i(\mathbf{k}'\cdot\mathbf{r}_j^A+\mathbf{k}\cdot\mathbf{r}_j^B)}\rangle\ .\end{aligned} \tag{16}$$

Evaluating the average in (16) over the distribution (11) and substituting back into (15) gives (see the Appendix)

$$\langle \gamma^2(\mathbf{r},t) \rangle = \frac{\rho_0}{2(8\pi Dt)^{d/2}}(1-e^{-c^2/8Dt}) \rightarrow \frac{\rho_0 c^2 \pi}{2}(8\pi Dt)^{-(d+2)/2} , \tag{17}$$

where $\rho_0 = N/V$ is the initial global density of either species. Note that we can not properly consider the "strictly geminate" case of nearest-neighbor pairs in this continuum formulation since it does not recognize the finite particle size of the reactants. In the limit $c \rightarrow 0$, the difference variable vanishes altogether and there is no segregation because the reactants immediately react before they can begin to diffuse away from one another.

Consider now the sum variable defined in Eq. (8). It satisfies the nonlinear reaction-diffusion equation

$$\dot{\rho}(\mathbf{r},t) = D\nabla^2\rho(\mathbf{r},t) - k_l[\rho^2(\mathbf{r},t) - \gamma^2(\mathbf{r},t)] \tag{18}$$

and its ensemble average over the initial distribution of particles is

$$\langle \dot{\rho}(\mathbf{r},t) \rangle = D\nabla^2 \langle \rho(\mathbf{r},t) \rangle - k_l[\langle \rho^2(\mathbf{r},t) \rangle - \langle \gamma^2(\mathbf{r},t) \rangle] . \tag{19}$$

Although we can not solve (18) or (19) exactly, we can infer the leading time dependence of the averages.[6] The diffusion term vanishes since our initial conditions cause $\langle \rho \rangle$ to be independent of absolute position $\mathbf{r}$ for all time and therefore to be the same as the global density $\rho(t)$. We assume that after an initial transient the leading time contribution to $\langle \rho^2 \rangle$ is the square of the leading contribution to $\langle \rho \rangle$. That this assumption does not hold at very early times can be seen clearly by calculating $\langle \rho(0) \rangle^2$ and $\langle \rho^2(0) \rangle$ explicitly from the initial conditions. The former has a finite value while the latter diverges: explicitly, one finds that $\langle \rho^2(0) \rangle = \langle \rho(0) \rangle^2 + \langle \gamma^2(0) \rangle$. We assume (without proof) that this difference between the square of the average and the average of the square, which is a consequence of the initial local-density fluctuations, decays rapidly. Thus, if we set $\langle \rho \rangle \sim t^{-\alpha}$ we can then write (19) schematically (after the initial transient described above) as

$$t^{-\alpha-1} \sim t^{-2\alpha} - t^{-2\mu} , \tag{20}$$

where 2μ is the time exponent of $\langle \gamma^2 \rangle$. At times $t > c^2/8D$ this exponent is given in Eq. (17) as $\mu = (d+2)/4$.

If μ is smaller than unity, then the only way to balance the leading time dependences in (20) at very long times (see below for further discussion on this point) is to set $\alpha = \mu$. If, on the other hand, μ is greater than unity then a balance is achieved by choosing $\alpha + 1 = 2\alpha$, i.e., $\alpha = 1$ (the case $\mu = \alpha = 1$ is the marginal exponent). The former case leads to anomalous (slow) decay of the global density, while the latter is the classical textbook case. Hence, we conclude that at long times

$$\begin{aligned} \langle \rho(\mathbf{r},t) \rangle = \rho(t) &\sim t^{-(d+2)/4}, \quad d \le 2 \\ &\sim t^{-1}, \quad d \ge 2 . \end{aligned} \tag{21}$$

The associated global rate laws are

$$\begin{aligned} \dot{\rho} &\sim -\rho^{(d+6)/(d+2)}, \quad d \le 2 \\ &\sim -\rho^2, \quad d \ge 2 . \end{aligned} \tag{22}$$

These results clearly differ from (5) and (6) when $d < 2$.[17] In particular, in one dimension Eq. (5) predicts a decay of the form $\rho \sim t^{-1/2}$ while we predict $\rho \sim t^{-3/4}$. Recall that the decay law for the $A+B$ reaction when the A's and B's are initially mutually uncorrelated is[1-4] (for $d \le 4$) $\rho \sim t^{-d/4}$ [cf. Eq. (3)] which in one dimension gives $\rho \sim t^{-1/4}$. In our earlier work we introduced a "segregation index" $S = \langle \gamma^2 \rangle / \langle \rho^2 \rangle$; the behavior $S \rightarrow 1$ indicates segregation of the species while $S \rightarrow 0$ indicates its absence [one must be careful with this interpretation at early times when there are still large fluctuations in the local density $\rho(\mathbf{r},t)$]. Our results indicate that segregation of chemical species should be observed asymptotically for dimensions smaller than $d = 2$ and not for higher dimensions. Recall that the critical dimension for segregation in the case of uncorrelated initial conditions is $d = 4$.

The above results were obtained under the assumption that the initial distance c between correlated A-B pairs is fixed. It is perhaps more realistic to assume a distribution of distances with a mean distance c. Our results would not differ in any substantial way from those obtained above (and below) if we had allowed for such a distribution. Therefore this shift in critical dimension must be reflected in any simulation since such correlations are necessarily present.

The decay laws obtained above are valid at long times. It is interesting to consider the behavior of the density at earlier times and the times at which crossover from one decay law to another takes place for dimensions $d < 2$. It is particularly interesting to observe the effect of the correlation distance c on these properties.

At early times (more precisely given below) the kinetics of the system are "classical" (regardless of the precise statistical distribution of reactants) since there has not yet been an opportunity for the system to sample this distribution. Thus, at early times $\rho \sim (k_l t)^{-1}$ (provided $k_l t > \rho_0^{-1}$). As time increases, one of two sequences of behavior takes place depending on the parameter values. If c is sufficiently large (or ρ_0 sufficiently small) then a crossover to the decay $\rho(t) \sim t^{-d/4}$ characteristic of a system with uncorrelated initial conditions occurs next, to be followed subsequently by a crossover to the behavior (21). The intermediate range appears here because for sufficiently large correlation distances it takes the system some time to note the presence of a correlation between A-B pairs. If, on the other hand, the correlation distance c is too small (or the initial density ρ_0 too large) then a direct crossover from the classical behavior to that found in (21) takes place (which for $d \geq 2$ implies entirely classical behavior).

The conditions for these various possible kinetic behaviors and the corresponding crossover times are found by balancing the contributions to Eq. (19). The three-regime case occurs if

$$\frac{c^{4-d}\rho_0 k_l^2}{128\pi^{d/2}D^2} > 1 \ . \tag{23}$$

If the condition (23) is satisfied, then a crossover from $\rho \sim t^{-1}$ to $\rho \sim t^{-d/4}$ occurs at

$$t \sim \left[\frac{4(8\pi D)^d}{k_l^4 \rho_0^2} \right]^{1/(4-d)} \ . \tag{24}$$

The subsequent crossover to the decay law $\rho(t) \sim t^{-(d+2)/4}$ for $d<2$ or back to $\rho(t) \sim t^{-1}$ for $d \geq 2$ occurs at the later time

$$t \sim c^2/8D \ . \tag{25}$$

Note that with increasing c, this last crossover is postponed and in the limit $c \rightarrow \infty$ it does not occur at all since the problem then reduces to that of an uncorrelated initial distribution of reactants.

If Eq. (23) is not satisfied, then the $t^{-d/4}$ regime is bypassed and for $d<2$ there is a direct crossover from t^{-1} behavior to Eq. (21) which occurs at the crossover time

$$t \sim \left[\frac{256(8\pi)^d D^{(d+2)}}{k_l^4 c^4 \rho_0^2} \right]^{1/(2-d)} \ . \tag{26}$$

This crossover thus gets postponed as c decreases and disappears entirely when c vanishes, in agreement with the fact that the "source term" $\langle \gamma^2 \rangle$ then vanishes.

At first glance our prediction (21) may appear counterintuitive. In particular, it would appear that the $A+B$ decay should, if anything, be *slower* than the $A+A$ decay because in the latter *all* the unreacted particles try to isolate themselves from one another, while in the former only dissimilar particles do, and hence there are fewer reactive interfaces in the $A+B$ case (unless the dimension is at least 2, in which case both reactions behave classically and hence are indistinguishable from one another). The $A+B$ decay is in fact the slower one as long as the time is not yet long enough for the reactants to sense the correlation distance c. On the other hand, whereas there can be large empty gaps in the $A+A$ case, the regions over which the fluctuations in the species that cause "anomalous" kinetic behavior in the $A+B$ case are limited by the correlation length.

III. SUMMARY OF RESULTS

We have examined the effects of a finite correlation length in the initial distribution of A-B pairs on the kinetics of the $A+B\rightarrow 0$ reaction. Whereas an uncorrelated initial distribution leads to the well-known decay law $\rho \sim t^{-d/4}$ for $d<4$ and $\rho \sim t^{-1}$ for $d \geq 4$, a correlated initial distribution leads to the decay law $\rho \sim t^{-(d+2)/4}$ for $d<2$ and $\rho \sim t^{-1}$ for $d \geq 2$. The decay is therefore more rapid in the correlated case (even more rapid than for an $A+A\rightarrow 0$ reaction) and the critical dimension for "anomalous" behavior shifts from 4 to 2. If the correlation distance is sufficiently large, the new more rapid decay law is preceded by the slower decay of the form $t^{-d/4}$ until the reactants sense the finite correlation distance. We estimate the crossover time for the onset of the new decay law and find that it diverges in the limit of a vanishing correlation distance and also in the limit of an infinite correlation distance. In the former case the members of each correlated pair land so close together that there are never any fluctuations in the species densities. The kinetics is then always classical and there is no transition to anomalous behavior. In the opposite limit, i.e., when the correlation length diverges, the problem reduces to the case of the uncorrelated initial distribution and the decay law is that appropriate to the latter case, never crossing over to a more rapid one.

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APPENDIX: EVALUATION OF AVERAGES

In this Appendix we perform in some detail the averages indicated in the text. In general, the wave vectors $\mathbf{k}$ are a discrete set that must be chosen to satisfy the appropriate boundary conditions. For periodic boundary conditions

$$\mathbf{k} = \frac{2\pi}{V}\mathbf{n} \ , \tag{A1}$$

where $\mathbf{n}$ is an n-tuple of integers. The wave vectors become continuous in the limit of an infinite volume, i.e., when the length scale of the system is larger than any other length scale of the problem.

Consider first the averages in Eq. (13). The random placement of the A particles (or B particles) leads to the distribution

$$p(\mathbf{r}_j^A) = p(\mathbf{r}_j^B) = \frac{1}{V} \tag{A2}$$

for each j. The averages in (13) then are

$$\langle e^{i\mathbf{k}\cdot\mathbf{r}_j^A} \rangle = \langle e^{i\mathbf{k}\cdot\mathbf{r}_j^B} \rangle = \frac{1}{V}\int_V d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \underset{V\rightarrow\infty}{=} \delta_{\mathbf{k},0} \ , \tag{A3}$$

where $\delta_{\mathbf{k},0}$ is the Kronecker delta. We thus find that $\langle \hat{\gamma}(\mathbf{k},0) \rangle = 0$ and subsequently Eq. (14), reflecting the equality of numbers of A's and B's.

Next we consider the averages needed for the calculation of second moments. In particular, consider the average appearing on the right side of Eq. (16):

$$\langle \hat{\gamma}(\mathbf{k},0)\hat{\gamma}(\mathbf{k}',0)\rangle = \tfrac{1}{4}\left\langle \sum_{j}(e^{i\mathbf{k}\cdot\mathbf{r}_j^A}-e^{i\mathbf{k}\cdot\mathbf{r}_j^B})\sum_{j'}(e^{i\mathbf{k}'\cdot\mathbf{r}_{j'}^A}-e^{i\mathbf{k}'\cdot\mathbf{r}_{j'}^B})\right\rangle . \tag{A4}$$

We separate these contributions into the two terms

$$\langle \hat{\gamma}(\mathbf{k},0)\hat{\gamma}(\mathbf{k}',0)\rangle = \tfrac{1}{4}\sum_{j}\langle e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_j^A}+e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_j^B}\rangle - \tfrac{1}{4}\sum_{j}\langle e^{i(\mathbf{k}\cdot\mathbf{r}_j^A+\mathbf{k}'\cdot\mathbf{r}_j^B)}+e^{i(\mathbf{k}'\cdot\mathbf{r}_j^A+\mathbf{k}\cdot\mathbf{r}_j^B)}\rangle . \tag{A5}$$

The average in the first two terms is carried out exactly as in Eq. (A3) and each yields a Kronecker delta which is multiplied by N due to the sum over j:

$$\frac{1}{4}\sum_{j}\langle e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_j^A}+e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_j^B}\rangle = \frac{N}{2}\delta_{\mathbf{k}+\mathbf{k}',0} . \tag{A6}$$

If there is no A-B correlation in the initial distribution of reactants, then the last two terms in (A5) contribute only if $\mathbf{k}$ and $\mathbf{k}'$ are zero, i.e.,

$$\langle \hat{\gamma}(\mathbf{k},0)\hat{\gamma}(\mathbf{k}',0)\rangle_{\text{uncorrelated}} = \frac{N}{2}(\delta_{\mathbf{k}+\mathbf{k}',0}-\delta_{\mathbf{k},0}-\delta_{\mathbf{k}',0}) \tag{A7}$$

and Eq. (15) in the infinite volume limit then gives

$$\langle \gamma^2(\mathbf{r},t)\rangle = \frac{N}{2V(2\pi)^d}\int d\mathbf{k}\, e^{-2k^2Dt} = \frac{N}{2V(8\pi Dt)^{d/2}} \tag{A8}$$

as in Eq. (17) when $c\to\infty$. On the other hand, a correlated initial condition with the probability density (11) leads to the following contribution:

$$\begin{aligned}\tfrac{1}{4}\sum_{j}\langle e^{i(\mathbf{k}\cdot\mathbf{r}_j^A+\mathbf{k}'\cdot\mathbf{r}_j^B)}\rangle &= \frac{\Gamma(d/2)}{2V\pi^{d/2}}\int d\mathbf{r}_j^A\int d\mathbf{r}_j^B\int d\Omega\,\delta(\mathbf{r}_j^B-\mathbf{r}_j^A-\mathbf{c})e^{i(\mathbf{k}\cdot\mathbf{r}_j^A+\mathbf{k}'\cdot\mathbf{r}_j^B)}\\ &= \frac{\Gamma(d/2)}{2\pi^{d/2}} - \sum_{j} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_j^A}\int d\Omega\, e^{i\mathbf{k}'\cdot\mathbf{c}}\\ &= \frac{\Gamma(d/2)}{2\pi^{d/2}} N\delta_{\mathbf{k}+\mathbf{k}',0}\int d\Omega\, e^{i\mathbf{k}\cdot\mathbf{c}} .\end{aligned} \tag{A9}$$

Each of the last two terms in (A5) contributes equally, and when substituted into (15) lead to the negative contribution in Eq. (17).

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[1] A. A. Orchinnikov and Y. B. Zeldovich, Chem. Phys. **28**, 215 (1978), and references therein.

[2] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).

[3] V. Kuzovkov and E. Kotomin, Phys. Status Solidi B **105**, 789; **108**, 37 (1981); Chech. J. Phys. B **35**, 541 (1985).

[4] K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985).

[5] K. Lindenberg, B. West, and R. Kopelman, Phys. Rev. Lett. **60**, 1777 (1988).

[6] B. J. West, R. Kopelman, and K. Lindenberg, J. Stat. Phys. **54**, 1429 (1989).

[7] R. Kopelman, Science **241**, 1620 (1988).

[8] D. ben-Avraham and C. R. Doering, Phys. Rev. A **37**, 5007 (1988).

[9] S. Kanno, Progr. Theor. Phys. **79**, 721 (1988); **79**, 1130 (1988).

[10] E. Clément, L. M. Sander, and R. Kopelman, Phys. Rev. A **39**, 6455 (1989).

[11] M. Bramson and J. L. Lebowitz, Phys. Rev. Lett. **61**, 2397 (1988); **62**, 694 (1989).

[12] P. Argyrakis and R. Kopelman, J. Phys. Chem. **93**, 225 (1989).

[13] R. Kopelman, J. Stat. Phys. **42**, 185 (1986).

[14] D. ben-Avraham, Philos. Mag. B **56**, 1015 (1987).

[15] Note that in one dimension with reactants of finite size the kinetics of the strictly alternating sequence . . . *ABABAB*. . . is of course identical to the kinetics of the $A+A\to 0$ reaction. In our continuum formalism it has no meaning to talk about such a strictly alternating sequence.

[16] Zh. Yi-Chang, Phys. Rev. Lett. **59**, 1726 (1987); **60**, 1885 (1988).

[17] Since our results emerge from a reaction-diffusion equation, they are justified only for integer dimensions. It is common (although not necessarily correct) practice to assume that such results are also valid for noninteger d.