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Reaction front structure in the diffusion-limited $A+B$ model with initially randomized reactants

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Subtle features of the reaction front formation in the $A+B\rightarrow 0$ reaction are reported for the initially random and equal $A+B$ reactant distribution. Three nonclassical parameters (initial linewidth, minimum, and maximum), for each interparticle gap and nearest neighbor distance distributions, are derived, as a function of time, using Monte Carlo simulations. These empirical front measures and their temporal scaling exponents are compared with the previously studied ones for the reactant interparticle distributions.

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I. INTRODUCTION

The $A+B$ bimolecular reaction has been investigated by several groups over the last two decades in great detail [1–16], and the characteristics of the nonclassical behavior of the density of reacting particles, particle distribution functions, and the rate of the reaction, as a function of time, are well understood. However, the reaction front has only been studied for initially separated reactants [4,8,10,12–15]. Here we extend this to initially randomized reactants. Experimentally, there are reaction studies where only the reactant is monitored by fluorescence (e.g., Ref. [16]). There are even situations where the product can be monitored only shortly after creation, e.g., for exciton or electron-hole annihilation, where the product is a photon (e.g. [17]), or for reactions with a product that is a quickly dissipating gas molecule. With today's highly sensitive photon or single molecule detection, it is conceivable that experimental determinations will mimic or test the simulations given here.

In the present work we investigate the positions of the products of the $A+B$ reaction. In this model whenever there is an encounter of one A with one B particle, the two particles react in the usual way, and form the product species, while both the reactants and the products leave the system instantaneously. It is of interest to monitor the locations of the positions where such encounters occur, because it will aid one in monitoring microscopically the reaction mechanism, the formation of the segregated A and B clusters, etc. Thus, we monitor here the exact positions on the lattice where the reactants have reacted during the course of the reactions. These positions are stored in an array in the computer memory, but in no way do they influence the course of the reaction itself. Thus, these array elements are transparent, meaning that they do not participate in the reaction process, and regular A and B reactant particles can diffuse on and over them, and react on them any number of times. They do not diffuse or move in any way, but are stationary.

II. METHOD OF CALCULATIONS

The model reaction $A+B$ is simulated on a 1-dimensional lattice in a fashion similar to previous work. Briefly, A and B particles are randomly distributed on the lattice before the start of the reaction. Then, the particles start to diffuse randomly, and upon encounter A and B particles get annihilated and removed from the system. The remaining particles continue the reaction process in a similar way. We normally monitor the particle density as a function of time. In the present calculation we are interested in the locations of product formation, i.e., the lattice sites where a reaction has occurred. Thus, when a reaction takes place, the exact location of the reaction site is marked. These are the sites where the reaction products are been formed. However, this marking does not affect at all the reaction process. The products do not participate in the reaction but are instantaneously removed from the system. The reaction proceeds for a fixed time (number of steps). We then calculate for each reaction site the nearest neighbor reaction site, and the interparticle spacing (gap) between two reaction sites. For these two quantities we then form their distributions for several different times. For better statistics we perform a large number of realizations, typically 100 000 different realizations, and average the results. We analyze the characteristic features of these distributions as a function of time.

III. RESULTS

In Fig. 1 we plot the distribution of the nearest neighbor distances (NNDD) of the locations of the product formation. Once the reaction locations are recorded, at a fixed time, we simply calculate numerically the nearest neighbor distances for each reaction location. Each such location has strictly only one nearest neighbor (which is, of course, another reaction location), and the distance to it is recorded. This is done for all the locations found at a fixed time, and repeated for several different times. This procedure is the same as was performed in the past for the *reactant* species, i.e., the A-A and the A-B distributions, but here it is done only for the product locations. The x-axis (as in the past) is a normalized quantity, $X=(r-1)/(\langle r\rangle-1)$, where r is the nearest neighbor distance, and $\langle r\rangle$ is the average value of r. The factor of -1 is included because the smallest r value is 1, and thus now $(r-1)=0$. The average value $\langle r\rangle$ is included in order to

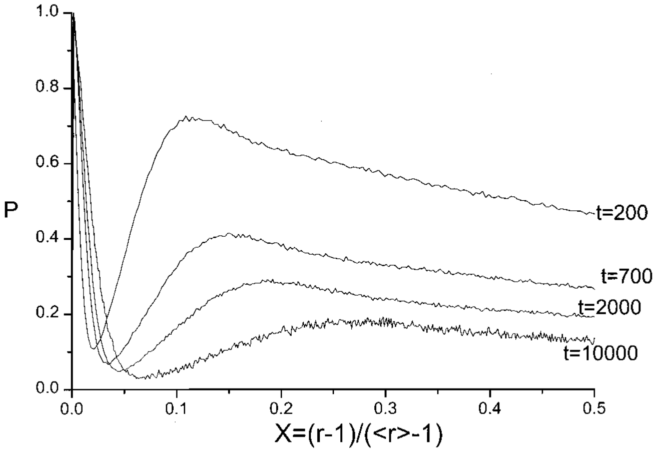

FIG. 1. Nearest neighbor distance distributions (distance is given by r), for the product locations in one-dimensional lattices, for the $A+B$ reaction. The initial A and B particle density is $\rho_0=0.4$ each. The lattice length is $L=100\,000$ sites. The x-axis is the normalized quantity $X=(r-1)/(\langle r\rangle-1)$, where $\langle r\rangle$ is the average value of r. The four curves correspond to four different times in the reaction, $t=200$, $t=700$, $t=2000$, and $t=10\,000$ steps, as marked. The data is average over 100 000 realizations.

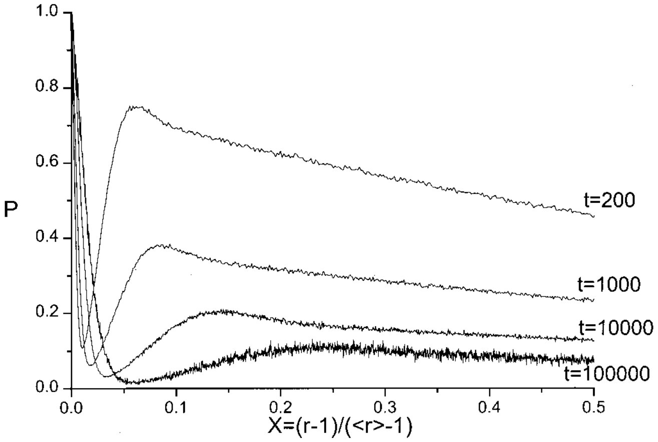

FIG. 2. The interparticle (gap) distributions (the gap distance is given by r), for the product locations in one-dimensional lattices, for the $A+B$ reaction. The initial A and B particle density is $\rho_0=0.4$ each. The lattice length is $L=100\,000$ sites. The x-axis is the normalized quantity $X=(r-1)/(\langle r\rangle-1)$, where $\langle r\rangle$ is the average value of r. The four curves correspond to four different times in the reaction, $t=200$, $t=1000$, $t=10\,000$, and $t=100\,000$ steps, as marked. The data is an average over 100 000 realizations.

have a picture with the same particle density at different times, since as time evolves, there are fewer and fewer particles left and fewer and fewer reaction events (reactions sites/time). In order to *see* the basic effect as it changes with time, we record these reaction locations only for a small time window, and not for the entire time interval. Had we recorded these quantities for the entire time domain, we would have included the contributions from different time regimes, and therefore, different effects, such as the initial random distribution, the later appearing segregated regime, etc. The result would have been quite complicated, and thus we chose in each calculation a small time interval equal to 10% of the total time domain, and record the reactant production locations only during this small window. For example, for the time $t=1000$ steps calculation, we record the locations only at the interval $\Delta t=900-1000$ steps, and ignore the locations of reactions outside this time interval. We observe that each curve goes initially, at small r values, through a sharp minimum, and then rises to a maximum at a longer r value. The locations of the minima (X_{min}) and maxima (X_{max}) clearly move to the right for longer observation times. Also, for longer times there is inherently more noise in the data. This is because there are fewer particles left to react, and therefore the noise is larger. However, the effect is the same at all time regions. We justify the existence of the minimum and the maximum as follows: The location, where the reaction takes place, is strongly dependent on the locations of the reactants. Initially all species are randomly distributed, and therefore we expect to also have randomly distributed locations. However, our time window does not include data from this time regime (see above). It includes data from the last time interval, after reactant segregation has taken place. Thus, as the reaction proceeds and the clusters (‘‘domains’’) of separated A and B species start to form, the reaction locations now are all at the interface region between the two types of clusters. Thus the minimum in the curves samples the length of space between the clusters of opposite species (often called ‘‘gap’’), while the maximum is a measure of the size of the segregated clusters (domains).

In Fig. 2 we show the data for the distributions of the lengths of the gaps between the product locations, a quantity that is somewhat equivalent to the interparticle distances for the A and B reactant particles (as also has been studied in the past). It is simply the length of lattice between the product particles in one dimension (but has no meaning in two or three dimensions, unlike the nearest neighbor distances, a quantity valid in any dimension). Here the x axis is again the quantity $X=r-1/\langle r\rangle-1$, where again r is the gap length, and $\langle r\rangle$ the average gap length. Here r can be 0, since any number of reactions can occur on the same lattice site. We see trends similar to those with the previous quantity, the nearest neighbor distance.

If we plot the quantity $(r-1)/(\langle r\rangle-1)$ where the *minima* X_{min} and *maxima* X_{max} are located, as time is varied, we receive the plots in Figs. 3 and 4, for the NNDD and gap quantities, respectively. We observe that in log-log axes the locations of both the extrema do scale quite well with time, giving for the NNDD case (Fig. 3) exponent values of $f_{\mathrm{min}}=0.19\pm0.01$, and $f_{\mathrm{max}}=0.31\pm0.01$, and for the gap case (Fig. 4) values of $f_{\mathrm{min}}=0.24\pm0.01$, and $f_{\mathrm{max}}=0.20\pm0.01$.

The third quantity we calculate is the ‘‘initial linewidth’’ (preceding the minimum) of either the NND or the gap. This reduced linewidth L (Fig. 5) is calculated at half height ($P=0.5$), in units of the normalized distance given by the x-axis (from $x=0$ to the next x-value at which $P=0.5$). Like the minimum parameter (X_{min}), it is a measure of the interdomain reaction front. While X_{min} may be related more directly to the interdomain AB gap, L is very similar to the reaction front width (W) parameter used for reactions with initially separated reactants [4,8]. The time exponents are f

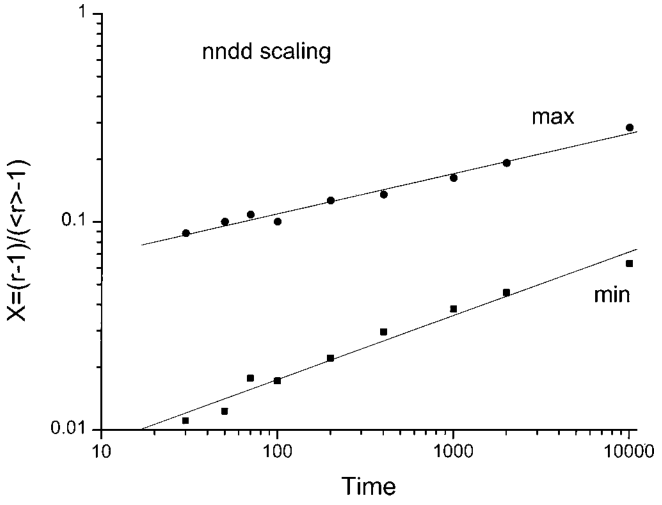

FIG. 3. The location of the minimum and the maximum in Fig. 1, as a function of time. Notice that the *y*-axis units are reduced (normalized) distance *r* units, $(r-1)/(\langle r\rangle-1)$.

$=0.17\pm0.01$ for the $L_{\rm NNDD}$, and $f=0.13\pm0.01$ for the $L_{\rm gap}$.

We note that we do not calculate the long distance decays of the distributions. These would require more extensive simulations but are expected to only give the typical ''tail'' behavior of the hertzian distribution for randomized ensembles.

IV. DISCUSSION

We relate our results to two classes of previous investigations. The first is the $A+B\rightarrow C$ reaction front width W in cases of initially separated reactants A and B. This problem was studied analytically [4,8,10–12], by simulation [8,11,14] and experimentally [13–15]. Depending on the exact situation, the exponent α for $W\sim t^{\alpha}$ has values ranging from zero to $\frac{1}{2}$ for one-dimensional systems. In the mean-field scaling approach [4], asymptotically $\alpha=\frac{1}{6}$. This was also confirmed in some Monte Carlo simulations [14] and experiments [15]. For early times (where the ''diffusion limited'' reaction is practically ''reaction limited'') $\alpha=\frac{1}{2}$, again by simulation [8] and by experiments [13]. When one of the reactants is static, results in one dimension vary from zero to $\frac{1}{4}$ [10–12]. There is no simple relation to our various exponents ranging between $\frac{1}{8}$ and $\frac{1}{4}$. Our exponents are derived at intermediate times and may be characteristic of either ''early'' times, asymptotically long times, or anything in between. Nevertheless, they may serve as guidance for experimental or theoretical work. For instance, it is reasonable that the exponent for the minima could not be asymptotically larger than that of the maxima (otherwise the minima will ''catch-up'' with the maxima).

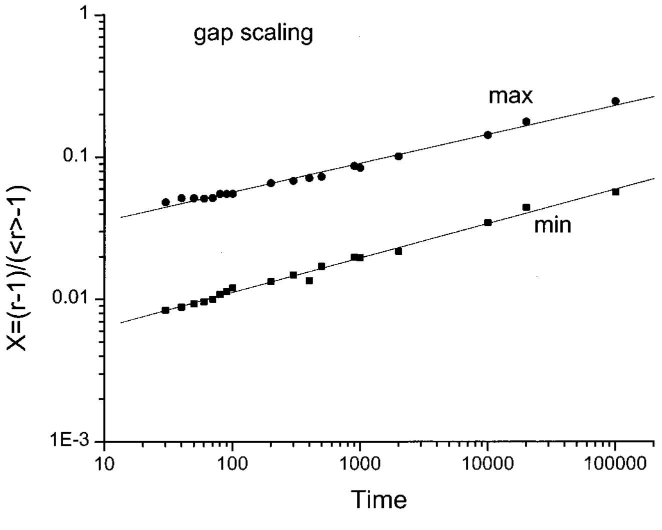

FIG. 4. The location of the minimum $X_{\rm min}$ and the maximum $X_{\rm max}$ in Fig. 2, as a function of time. Notice that the *y*-axis units are reduced (normalized) distance *r* units, $(r-1)/(\langle r\rangle-1)$.

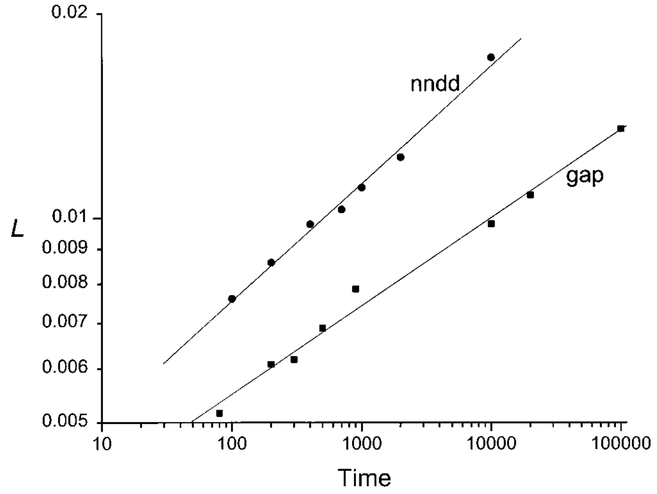

FIG. 5. Scaling of the reduced linewidth *L*, as a function of time, for the data of Figs. 3 and 4.

A comparison is now made with previous work on the same $A+B$ model, i.e., with initially random reactant distribution [5–7,9,18]. For simplicity, we limit ourselves to $d=1$ (one dimension). This previous work emphasized segregated domain sizes [9,14,19], gaps and NNDD [5–7,9]. Relevant to our present work are the *A*-*B* gaps (and NNDD), as well as the domain sizes. We expect the product formation sites to be limited to the gaps between *A* and *B* domains. Thus, the ''initial linewidth'' *L* should be smaller than such gaps. We also expect our $X_{\rm min}$ to be statistically larger (slightly?) than the *A*-*B* gap. Furthermore, we interpret the broad, distributed $X_{\rm max}$ as a rough measure of the domain sizes. The picture is roughly: $\ldots AAAAAACCCBBBBBBBCCCCAAAAAA\ldots$. We note that the *C* sites denote ''recent past'' locations of *A*-*B* annihilation sites. According to Leyvraz and Redner [7,9], the *AB* gaps grow with exponent $\frac{3}{8}$ $(d=1)$, while the domain sizes time scaling [1,2] is assumed to go with exponent $\frac{1}{2}$, asymptotically. In comparison, all our ''product'' or front exponents are significantly smaller than $\frac{3}{8}$. We note that scaling results in these problems are very sensitive to subtle changes, i.e., when one reactant species is immobile [8–10,12]. Finally, we note that in a random ''classical'' system, the

NNDD or gap distribution should be hertzian (i.e., exponential in $d=1$), showing no L, no $X_{\min}$ and no $X_{\max}$.

V. CONCLUDING REMARKS

Three pairs of measures and their time exponents have been calculated for the product formation sites in an elementary $A+B$ reaction with initially randomized reactants. The reaction front structures differ significantly from the random, hertzian NNDD or the Poissonian gap distributions of classical reaction kinetics fronts (where none of our three measures even exist). We can only qualitatively relate our results to other measures of $A+B$ reactions (A or B domains and AB gaps and nearest neighbor distances), as well as to previous work on reaction front measures in the case of initially separated reactants.

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