Diffusion-controlled binary reactions in low dimensions: Refined simulations

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Refined Monte Carlo simulations have been performed on the diffusion-controlled $A+B\rightarrow 0$ and $A+A\rightarrow 0$ reaction on two- and three-dimensional critical percolation clusters and in one dimension. For comparison, we also tested the single random walker S_N (number of distinct sites visited in N steps). Effects of excluded volume, time counting, random number generators, averaging procedures, and boundary conditions have been tested and found to be within our simulation uncertainties. However, finite-size and finite-time effects are important, as well as the initial particle density and the number of runs. All the $A+A$ and S_N data agree with the well-known scaling predictions, i.e., the time exponent is $d_s/2$, where d_s is the spectral (fracton) dimension. The same is true for $A+B$ reactions in one dimension (the exponent being 1/4). Finally, for the $A+B$ reactions on two- and three-dimensional critical percolation clusters, our refined data are consistent with the classical Kang and Redner [Phys. Rev. Lett. **52**, 944 (1984)] scaling result as well as the bounds (given in more recent work) involving other fractal dimensions.

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INTRODUCTION

Nonclassical reaction kinetics, like anomalous diffusion, has been receiving great interest for well over a decade [1–14]. Due to renewed interest in this problem [15–17] we come back here to the simplest diffusion-limited binary reactions ($A+A\rightarrow 0$ and $A+B\rightarrow 0$) performed on fractal and one-dimensional lattices. In particular, we study the $A+B\rightarrow 0$ reaction on critical percolation clusters, using them as representative random fractal lattices. The emphasis is on the relation of the reaction time exponent to the various fractal dimensions.

For $A+A$ as well as for symmetric (equidensity) $A+B$ reactions one can express the long-time reaction coefficient k as

$$k\sim t^{h},\quad t\rightarrow\infty \tag{1}$$

where the heterogeneity exponent [6,13] arises due to the nonhomogeneity of the particle distribution. We note that classically this distribution is always homogeneous (Poissonian), giving $h=0$. Alternatively, one expresses the density of the surviving particles as

$$\rho\sim t^{-\alpha},\quad t\rightarrow\infty \tag{2}$$

where $\alpha=1-h$. We note that classically, of course, $\alpha=1$ and that for $A+A$ reactions α is often called f. The traditional expression can be written as

$$\rho^{-1}-\rho_0^{-1}=k_0 t^{\alpha}, \tag{3}$$

where the subscript 0 refers to $t=0$. While this expression holds rigorously only classically (where $\alpha=1$ and $k_0=k$) it has been found to be a reasonable approximation for finite as well as infinite times [18]. However, strictly speaking α is constant only for $t\rightarrow\infty$ but, in general, it is a weak function of time, and is treated this way in our present simulation work.

The asymptotic ($t\rightarrow\infty$) value of α (and h) has been of much interest recently [15–17]. The now accepted value for nonclassical (nonconvective) reactions in Euclidean spaces is $\alpha=f=\min(d/2;1)$ for $A+A$ reactions and $\alpha=\min(d/4;1)$ for $A+B$ reactions [3,4] where d is the dimension (possibly with logarithmic corrections at the critical dimensions, 2 and 4, respectively). For fractal spaces this has been modified [6–10] such that d is replaced by d_s, the spectral (fracton) dimension. However, very recently, the expression $\alpha=\min(d_s/4;1)$ for $A+B$ reactions has been questioned and a more elaborate scheme has been suggested [15,17], involving other fractal dimensions, in addition to d_s. For instance, for $d_s<1$ and $t\rightarrow\infty$, it has been argued [17] that

$$\frac{d_s}{2}\left[1-\frac{d_s}{2}\right]\leq\alpha\leq\frac{d_s}{2}\left[1-\frac{d_s}{2d_f}\right],\quad t\rightarrow\infty \tag{4}$$

where d_f designates the traditional fractal dimension or possibly a fractal chemical dimension [12,19]. We note [19] that the traditional expression for $d_s<1$, i.e., $\alpha=d_s/4$, is consistent with Eq. (4) but it is much more restrictive.

A primary motivation for this work has been to test whether this restrictive form ($\alpha=d_s/4$) may be relaxed in favor of Eq. (4). Furthermore, this presented an opportunity to check on several other important points: (1) The analytical arguments [3,8,14] concern continuum

spaces rather than lattices and point particles, with no excluded-volume effects. Most simulations [1,2,4,7,9] are not only on lattices but also employ excluded volumes, i.e., no multiple occupancy of any site. We thus compare results between excluded-volume and multiple occupancy simulations. (2) The way the time is measured differs; our method (e.g., Ref. [18]), lets or even forces all particles to move within a single time step while others [7,9] move one particle at each step and then normalize for the number of particles surviving at that time. (3) Different averaging procedures can be employed, i.e., using in expression (3) either $\langle\rho\rangle$, $\langle\rho^{-1}\rangle$ or $\langle\alpha\rangle$. The latest approach (the right one?) is equivalent to calculating $\langle\log_{10}(\rho^{-1}-\rho_0^{-1})\rangle$, plotting it versus $\log_{10}(t)$ and taking the slope. (4) Checking finite-size effects [20]. (5) Are modern computer simulation facilities adequate to deal with the above subtle distinctions?

In addition to simulations of $A+B\rightarrow 0$ on critical percolation clusters (two and three dimensions), we also present simulations on one-dimensional lattices, where all theories are in agreement (i.e., $\alpha=1/4$). This enabled us to deal with points (1)–(5) above without the theortical complication [Eq. (4)]. Furthermore, we also simulated the reaction $A+A\rightarrow 0$ on all three kinds of lattices (one-, two-, and three-dimensional critical percolation clusters), as well as the single random walker S_N, the average number of distinct sites visited in N steps. The latter property is free of theoretical complications as well as of considerations (1)–(3) above. It is well known that $f=d_s/2$ for $A+A$ reactions and that $S_N\sim N^f$ asymptotically. It is also believed that these exponents are very sensitive to the quality of random number generators, etc.

The simulations enable us to reach some interesting conclusions, especially with respect to the $A+B$ reactions on fractals. It appears that points (1)–(3) contribute little within the uncertainty of these simulations (1–2 %). Moreover, it appears that the older result ($\alpha=d_s/4$) holds, within the uncertainty. This means that the upper and lower limits in (4), giving the wide range of α, may be correct but largely irrelevant extremes.

METHOD OF COMPUTATIONS

All computer simulations are carried out according to the conventional methods paying attention to the specific model used [12,21]. The lattice sizes are considerably larger than previously utilized: The linear dimensions are as follows: for one-dimensional lattices, $L=2$ million sites; for two dimensions $L=2000$; and for three dimensions $L=160$. The reactions on the fractal percolating clusters are performed using binary lattices exactly at the critical threshold, where we have used $p_c=0.5931$ for two dimensions, and $p_c=0.3117$ for three dimensions. The largest cluster is isolated using the cluster multiple-labeling technique (CMLT) [22]. Due to the inherent uncertainty of the exact location of the critical point we also tried an alternate p for the two-dimensional lattices: $p_c=0.5927$. It turns out that the values of the exponents presented here do not depend on such minute details of the system, as the changes are within the computational uncertainties. The initial densities for all reactions were such that most of the available lattice sites were occupied, i.e., 80% of these sites.

The details of the reaction mechanism are as follows: A certain initial particle population is placed at random on the lattice. We distinguish two cases here: In the first case no two particles are allowed to occupy the same site, the model being an analog of the continuum excluded-volume case. In the second case any number of particles may occupy any given site. In the case of the $A+A$ reaction the particles have no label, while in the case of $A+B$ each particle is designated as either an A or B particle. For the $A+B$ case at $t=0$ and at any later time it is always in a state of equidensity, i.e., $\rho_A=\rho_B$. Diffusional motion is simulated by forcing each particle to perform a random walk with steps leading to its nearest-neighbor sites only. When a particle is not permitted to make a move (e.g., when it collides with the perimeter of the percolating cluster, or when an A particle attempts to move to a site occupied by another A particle in the $A+B$ reaction) then we use the so-called "blind-ant" option [1,12,21] meaning that time advances in the usual way, as if a move were made. The parameter of time is also calculated in two different methods. In the first method one reaction step is considered to be a full cycle of moving all particles that happen to be present at any given instance, regardless of any reactions that may take place. In the second method, after each particle moves, the reaction clock advances by $1/N$ steps, where N is the number of particles present at that instance. Even though these two methods are fairly close, strictly speaking they produce different results. A reaction is considered to take place when during the random walk, two particles occupy the same lattice site, at which point both reaction particles are removed from the system. We

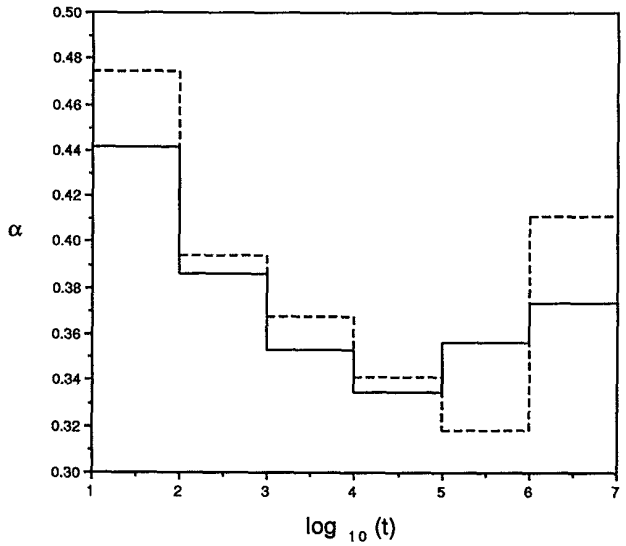

FIG. 1. The exponent α as a function of time (averaged for each time decade) for the $A+B$ reaction on critical percolation clusters. Solid line, two-dimensions (2000×2000, 5 runs averaged, $\rho_0=0.4$ for each A and B, cyclic boundary conditions, excluded volume). Dashed line, three dimensions ($160\times 160\times 160$, 5 runs averaged, $\rho_0=0.4$ for each A and B).

monitor the particle density as a function of time, for times ranging up to 10 million steps. We note that the UNIX random number generators RAN and RAND were used and compared (see below).

RESULTS

In Fig. 1 we plot the value of the exponent α as a function of time (the number of steps) for the two- and three-dimensional $A+B$ reactions at the percolation threshold. The α average value is calculated for each logarithmic time decade and plotted for the intervals shown. We notice that, while at $t<1000$ steps α is considerably above the expected value of $1/3$, it approaches this value in the range of $t=10^5$ steps, and then deviates to higher values (due to finite-size effects—we show below that α also may not be meaningful at this long t).

In Fig. 2 we do the same for the one-dimensional $A+B$ reaction. Here the expected value is $1/4$. We also plot here the results of the model where any number of particles may occupy a given site (nonexcluded volume), and notice that the two cases are very similar, indicating that not much difference exists between these two models within our present simulation uncertainties.

Figure 3 presents the data for $A+A$ reaction in two- and three-dimensional percolation clusters, together with the results for the number of sites visited by a single randomly moving particle on the same clusters. The expected value here in all cases is half the spectral dimension, $\alpha=f=d_s/2=2/3$, and we see that this value is approached asymptotically (before the onset of finite-size effects).

Figure 4 gives the results for the $A+A$ reaction for one-dimensional lattices. Here we have also plotted the data from the second model of time keeping for the course of the reaction, and we only notice some slight

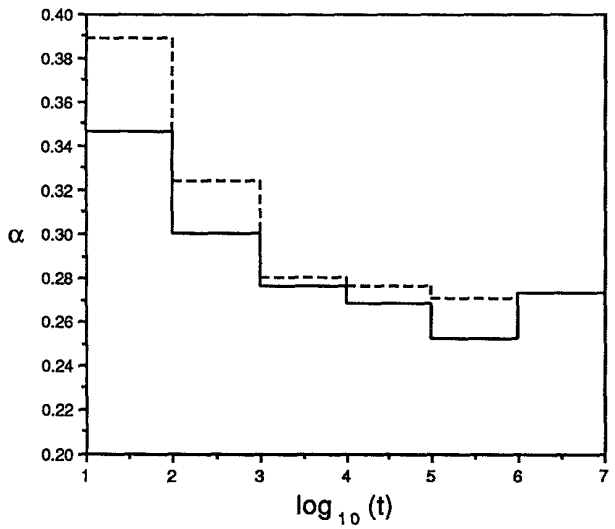

FIG. 2. The exponent α as a function of time (average for each decade) for the one-dimensional $A+B$ reaction. Lattice size $L=100\,000$ sites, $\rho_0=0.4$ for each A and B, 10 runs averaged, cyclic boundary conditions. Solid line, excluded-volume case. Dashed line, any number of particles may occupy any given site.

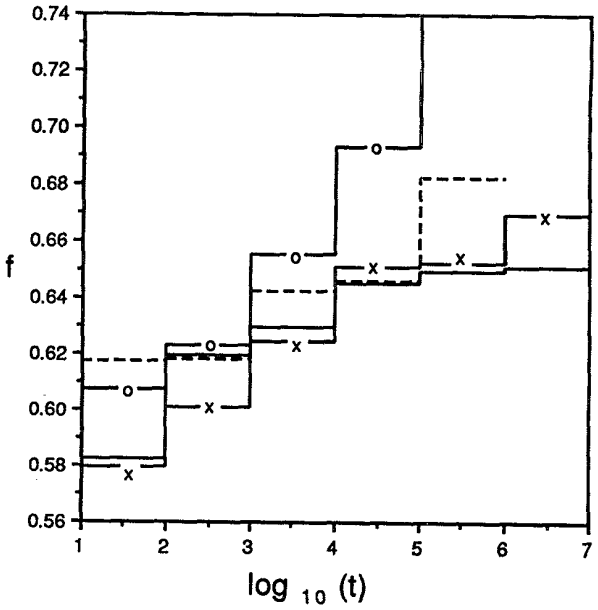

FIG. 3. The exponent f (equivalent to α) as a function of time (averaged for each decade) for the $A+A$ reaction on percolation clusters, and the number of sites visited, S_N. Solid line, S_N (two dimensions, 2000×2000, 1000 runs averaged). $\times$ line, S_N (three dimensions, $160\times160\times160$, 1000 runs averaged). Dashed line, $A+A$ reaction (two-dimensions, 2000×2000, 25 runs averaged, excluded volume). $\circ$ line, $A+A$ reaction (three dimensions, $160\times160\times160$, 25 runs averaged, excluded volume). All simulations performed with cyclic boundary conditions.

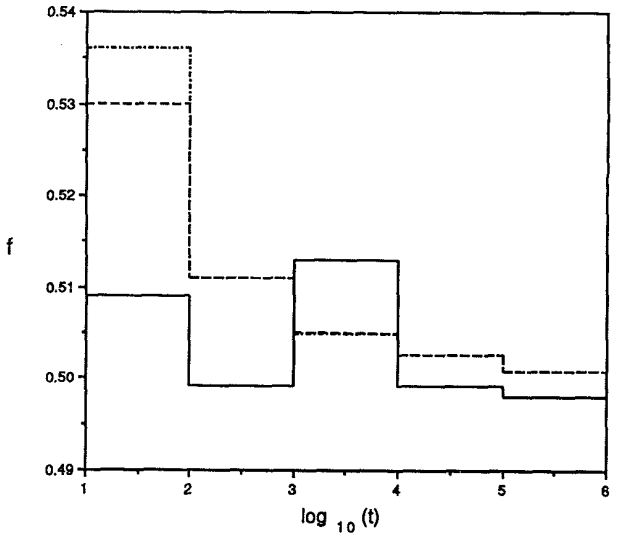

FIG. 4. The exponent f (equivalent to α), as a function of time (averaged for each decade) for one-dimensional lattices (lattice site $L=2\,000\,000$ sites). Solid lines, the number of sites visited, S_N (1000 runs averaged). Dashed line, $A+A$, reaction, $\rho_0=0.8$, 10 runs averaged. Dash-dotted line, $A+A$ reaction, with the timing performed as in the second case, described in the text. Note that the last two lines overlap beyond the first shown decade.

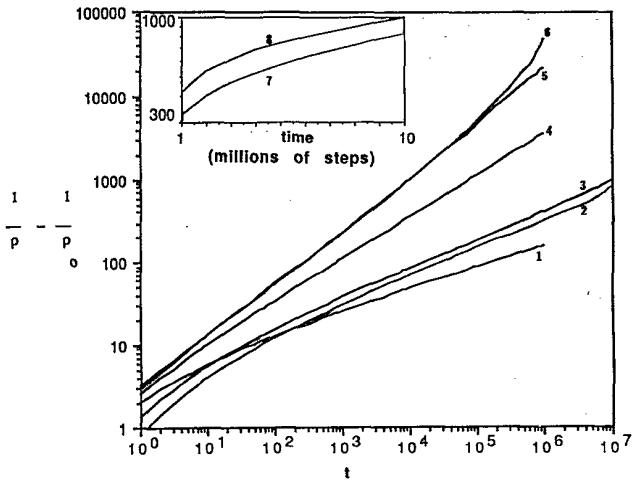

FIG. 5. Plot of $1/\rho-1/\rho_0$ as a function of time (log-log) for all the dimensionalities and types of reactions. Curve 1, one-dimensional $A+B$. Curve 2, two-dimensional $A+B$. Curve 3, three-dimensional $A+B$. Curve 4, one-dimensional $A+A$. Curve 5, two-dimensional $A+A$ Curve 6, three-dimensional $A+A$. Note that here $\rho=\langle\rho\rangle$; using $\langle 1/\rho-1/\rho_0\rangle$ or $\langle\log(1/\rho-1/\rho_0)\rangle$ gave essentially the same slopes. The insert gives a logarithmic-linear plot of $(1/\rho-1/\rho_0)$ vs time (for the last decade), demonstrating the finite-site effect (approach to exponential decay). Curve 7, three-dimensional $A+B$ reaction. Curve 8, two-dimensional $A+B$ reaction. Note that the Y axis is the same quantity as in the main figure.

differences at early times, but after $t=100$ steps, no differences exist. Also plotted is the S_N variation. For all these cases the expected value is $\alpha=f=0.5$, a value that is asymptotically approached.

Finally, in Fig. 5 we plot directly the $1/\rho-1/\rho_0$ behavior as a function of time. These lines were used to derive the exponents presented in the previous figures. The inset in this figure shows a logarithmic-linear plot of the two- and three-dimensional density behavior at long times. It gives an indication of the exponential behavior when the finite-size effects are manifested, which has been previously noted [20].

We further note that various other factors have been checked out and found not to matter, i.e., not affect our results within our uncertainties.

(1) The use of different random number generators (RAN and RAND, see above).

(2) Different ways (see Table I) of averaging the results, i.e., using $\log_{10}\langle\rho^{-1}-\rho_0^{-1}\rangle$ or $\langle\log_{10}(\rho^{-1}-\rho_0^{-1}\rangle$ versus $\log_{10}(\langle\rho\rangle^{-1}-\rho_0^{-1})$. Obviously, this is also an indicator for the quality of the results, i.e., our uncertainties.

(3) Minor changes in the critical percolation concentration, as mentioned above ($p_c=0.5931$ versus 0.5927 for the two-dimensional lattice).

DISCUSSION

We discuss our results here according to three major categories: (1) Comparisons among different models and algorithms; (2) finite-size effects; (3) the scaling laws, with emphasis on the $A+B$ reaction on fractals, where there has been some recent controversy.

(1) Effects of models and algorithms. The major points here are the comparisons between *analytic continuum models* and *lattice simulations.* First, there is the effect of excluded volume. Next, there are the possible effects of discretization. Furthermore, discretization forces us to be more explicit about questions such as vertical reactions. Finally, there have been different approaches to how percolation clusters are formed and how computer time steps are related to "real time."

Our results show that within the precision of the simulations, i.e., 1–2 % in scaling exponents, there appear to be no measurable effects due to any of the above-mentioned factors (see above). We emphasize that our simulations for the reactions started with high initial particle intensities (80% total), and covered six to seven decades in time. As mentioned, there were also no measurable effects due to the use of different random number generators (see above), including the presumably most sensitive case of the *single* random walker (with S_N as the variable). We thus conclude that previous literature discrepancies are most probably due to the use of small lattices, low particle densities, short times and/or insufficient numbers of runs. We note, parenthetically, that a number of previous simulations were strongly affected by short-time behavior, often compensated (or aggravated) by using the quantity ρ^{-1} rather than $\rho^{-1}-\rho_0^{-1}$ as the dependent parameter [4,7,9].

(2) Finite-size effects. These effects are expected to be most visible at long times, when the particles are more likely to "hit" the boundaries (cyclic in our case). This well-known situation is especially crucial when the interaggregate gap [23,24] approaches the lattice size. Here, while for infinite lattices the gap continues to grow in time monotonically, this can no longer be true for a

TABLE I. Representative α values for $A+B\rightarrow 0$ in two- and three-dimensional critical percolation clusters, respectively (top part is two dimensional, bottom is three dimensional).

Time Range ($\log_{10}$)	$\log_{10}(\langle\rho\rangle^{-1}-\rho_0^{-1})$	From $\log_{10}\langle\rho^{-1}-\rho_0^{-1}\rangle$	$\langle\log_{10}(\rho^{-1}-\rho_0^{-1})\rangle$
3–6	0.344±0.001	0.345	0.344
4–6	0.344±0.002	0.346	0.345
5–6	0.356±0.002	0.361	0.358
6–7	0.373±0.007	0.389	0.381
3–6	0.336	0.339	0.338
4–5	0.341	0.341	0.341
5–6	0.318	0.329	0.324
6–7	0.411±0.02	0.495	0.452

finite lattice, irrespective of boundary conditions. Our simulations have been cut off about one time decade beyond this "critical" (or crossover) time, t_c. Obviously, this also correlates with a relatively small surviving particle population. Our comparison with theoretical expectations [20] shows good qualitative agreement with the expected exponential time decay (see Fig. 5).

(3) The scaling laws. Our simulations of single random walkers and $A+A$ reactions in *one dimension* and on two- and three-dimensional critical percolation clusters were done in order to investigate the above-mentioned points and to be used as a *reference* (or "blank") with respect to the $A+B$ simulations on critical percolation clusters. The same is true for the $A+B$ reaction in one dimension. As stated, irrespective of the effects of excluded volume, discretization, finite size, etc., there is an excellent agreement with the asymptotic scaling laws, within the simulation uncertainties (about 1–2 %). These observations allow us to zero in on the controversial scaling laws for $A+B$ reactions on fractals. It appears that over a couple of time decades (from about 10^4 to 10^6 steps) the agreement with the Kang and Redner [8] scaling laws is as good as the agreement of the $A+A$ reactions with the de Gennes, Kang and Redner, and Klymko and Kopelman [6,8] scaling laws for fractals. Furthermore, the agreement of the $A+B$ reaction simulation in one dimension with the Ovchinnikov-Zeldovich [3] scaling theory is not any better. We note that this scaling law in one dimension is supported unanimously by all workers [4,7,9,14]. Finally, no better agreement is shown for the $A+A$ reaction in one dimension or for the single random-walk simulations, the case for which there are rigorous formulations [25,26].

Similar recent simulations on Sierpinski lattices have led to the same conclusion [16]. However, one could argue there [17] that these are simply connected, as well as ordered fractals (in contrast to the disordered, multiply connected percolation clusters). Furthermore, these simulations may be argued to be less clear-cut due to hierarchical effects [16] or even finite-size effects [20]. It is thus interesting to find that the same scaling laws, going back to the simple Kang and Redner law [8], appear to work for the percolation clusters in both two and three dimensions.

What can we say about the more subtle scaling law of Sheu and co-workers [15,17]? We note that these laws give only upper and lower bounds, and it has been shown [19] that the Kang and Redner law falls between these bounds. There are thus three possibilities: (1) The "real" behavior is close enough to the Kang and Redner law to be within the simulation uncertainties (about 2%). (2) There is a *time crossover* from the Kang and Redner law to a different truly asymptotic behavior, which we cannot see due to our finite-time (finite-size) effects. (3) The Kang and Redner law is indeed the "truly asymptotic law." Possibilities (1) and (2) above obviously call for even more refined simulations. However, if possibility (3) is the "true behavior" then this calls for further theoretical work that might explain why the Kang and Redner law works, in spite of the fact that only the spectral dimension is included and all the other types of fractal dimensions are irrelevant. Intuitively, it appears (to us) that the segregated A (and B) aggregates can hardly be described completely just by the spectral dimension. A more detailed formulation, taking into account the shape of the peripheries of these aggregated and/or those of the *interaggregate domains* ("gaps"), may shed light on this intriguing problem.

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