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Nonclassical kinetics in three dimensions: Simulations of elementary $A+B$ and $A+A$ reactions

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Monte Carlo simulations are employed to study the rate laws of $A+A\rightarrow 0$ and $A+B\rightarrow 0$ diffusion-limited elementary reactions in three dimensions (3D). Using reflective instead of cyclic boundary conditions, we do observe the Zeldovich regime in 3D for the $A+B$ reaction. The time and density values for the crossover into the Zeldovich regime in 3D agree with the existing scaling laws and provide the hitherto missing scaling coefficient. We show that the behavior of the $A+A$ reaction rates and the early time behavior of the $A+B$ reaction rates in 1D, 2D, and 3D map the rate of distinct sites visited by a single random walker, giving nonclassical kinetics at early times in all cases. We also determine a simple scaling law for crossover to finite size effects, which depends only on the linear lattice length, except when the crossover to finite size effects and the crossover to the Zeldovich regime are concomitant.

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I. INTRODUCTION

Much work has been done on anomalous, nonclassical reaction kinetics, but the simulations, the experiments, and much of the theoretical work has been largely confined to low-dimensional systems [1–92]. The prevailing belief has been that classical kinetics [93–100] applies in three dimensions. For the pseudomonomolecular elementary reaction $A+C\rightarrow C+$ *products* and for the bimolecular elementary reactions of the form $A+A\rightarrow 0$ and $A+A\rightarrow A$ it is well known [4,14–17,22] that the critical dimension is two and therefore no anomalies should occur in dimensions higher than two. The same is true for $A+B\rightarrow 0$ reactions with a source term [47, 52]. For the elementary $A+B\rightarrow 0$ batch reactions there has been doubt whether the anomalous Zeldovich regime (with segregation of A and B) is obtainable in finite times for real systems in three dimensions (3D). Furthermore, for extremely long times, segregation may not occur in experimental systems because of various antisegregation factors such as minute convection currents [46] or back-reaction [30].

Theoretical and simulation work in lower dimensions have established the existence of [17, 23, 30] and crossover times for [101–103] the Zeldovich regime in $A+B$ reactions. Similarly, the depletion zone anomalies and their kinetic consequences for lower-dimensional $A+A$ and $A+C\rightarrow C$ reactions [50, 51, 53, 103] have been established by both theory and simulations. Challenging experiments have been carried out in low-dimensional systems — fractal and one-dimensional systems, bearing out the theoretical predictions [51, 91]. However, no such experiments are available for three-dimensional systems, except some old work on trapping and annihilation in crystals [104], where no deviations from classical, Smoluchowski kinetics have been reported for the $A+A$ and $A+C\rightarrow C$ cases (we exclude here the case of geminate recombination [97, 102, 105]). The aim of the present work is to encourage careful experiments in three dimensions by pointing out under what conditions anomalous kinetics should be observable for $A+B$ and even for $A+A$ reactions in three dimensions.

For the $A+B$ reaction in 3D, we map out the time and the density regimes for the Zeldovich segregation and its concomitant anomalous [92] rate law which describes the decay of the reactant density in time $t^{-3/4}$. Our simulations [92] are performed with reflective boundary conditions (typical for real systems) and with vessel (lattice) sizes larger than in most previous simulations. Previous simulations have mostly used cyclic boundary conditions, which act as effective convection currents, especially in three dimensions, and thus hinder the system's transition to the Zeldovich regime (unless other algorithmic changes are made [92]).

For the $A+A\rightarrow 0$ reactions we show that it takes much longer than usually assumed to reach the classical behavior. Furthermore, finite size effects can cut into the classical regime at longer times, especially for simulations with cyclic boundary conditions, thus giving the appearance of nonclassicality over the entire time regime of the simulation. We get better results using reflective boundary conditions as well as larger lattice sizes. We note that there is no rigorous theory available for the three-dimensional $A+A$ reaction and thus the Monte Carlo simulations are crucial to our conceptual framework.

The $A+B$ reaction rate is shown to match the anomalous early time behavior of the $A+A$ reaction rate until

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the crossover to the Zeldovich regime affects the $A + B$ rate. We claim that the anomalous behavior of the $A+A$ and $A+B$ reaction rates at early times are simply a reflection of the mapping of the $A + A$ reaction behavior onto that of the single random walker, specifically its rate of distinct sites visited [14, 15, 26]. As has been argued before [17, 30, 101], the $A+B$ reaction hugs the behavior of the $A+A$ reaction at early times. The result is that *both* $A + A$ and $A + B$ reactions relate to the single random walker's net visitation efficiency, a well known quantity [106–108]. We also note that the $A+C \to C$ reaction has been long shown [4, 11, 109] to follow this visitation efficiency under most circumstances. We thus demonstrate a unified, nonclassical early time behavior for all three elementary bimolecular reaction cases in three dimensions (as well as in one and two dimensions).

We stress the large role played by the boundary conditions in three dimensions. We demonstrate unequivocally the attainment of the Zeldovich regime and find the crossover time to this regime to follow the previously suggested universal formula. The crossover density ρ_s is also shown to follow the very simple relation given by a universal fraction of the original density, ρ_o, i.e., $\rho_s = f_d \rho_o$ where f_d is a constant depending only on dimensionality (but not on lattice size, ρ_s, etc.). We also find that the crossover time to finite size effects scales as L^2 regardless of reaction type or dimensionality.

II. METHOD OF SIMULATION

Monte Carlo comuputer simulations are often used to model random processes such as diffusion [109, 110]. Our computer simulations for diffusion-limited chemical reactions are performed according to the following algorithm. A population of reactive particles is initially placed on a lattice by randomly choosing the coordinates for each particle. Particles diffuse on the lattice, which is modeled by independent random walks of the individual particles. The coordinates of all particles are monitored as a function of time. Steps are allowed to nearest-neighbor sites only. There is no interparticle interaction. A reaction occurs when two reactive particles collide, i.e., land at the same site. Every collision leads to a reaction with probability one. When two particles react in this fashion, they are removed from the system (they are annihilated). In the present study we treat the case where all reactants are generated only at time zero, before any reaction has occurred, and thus the particle density decreases as a function of time. For the $A + A$ type reaction, reaction occurs if two A particles collide. For the $A+B$ type reaction, reaction occurs when an A and a B particle collide. No reaction occurs if two A particles (or two B particles) collide. If an A (B) particle attempts to land on a site already occupied by another A (B) particle, the particle does not move in that time step (excluded volume condition).

For any space dimensionality, one-dimensional arrays are used to store the coordinates of the position of every particle. Another array, which has a dimensionality equal to the dimensionality of the lattice, is used to store the occupancy status of each site. A zero value for an array element specifies that the corresponding site is empty. For the $A + A$ reaction, a positive integer in an array element indicates that the corrsponding site is occupied by an A particle. The value of the integer is the tag number for the particle whose position is stored in the coordinate arrays. For example, in two dimensions, $M(17, 3) = 5$ shows that site (17,3) is occupied by the fifth particle.

For the $A + B$ reaction one additionally must distinguish between the two types of particles. A zero array element still specifies an empty site. Now we have positive and negative integer values in the site array. A negative integer specifies that a site is occupied by an A particle, while a positive integer specifies that the site is occupied by a B particle. The absolute values of the integers are now the tag numbers for particles. If here $M(17, 3) = -5$ this shows that site $(17, 3)$ is occupied by the fifth A particle.

The simulation proceeds by running through the particle list (coordinate arrays), moving one particle at a time in a random direction from (i, j) to (i', j'). Before a particle is moved, the product of the array elements $M(i, j)M(i', j')$ is formed. If this product is zero, this means that the new site is empty and the move is immediately performed. If this product is nonzero then, for the $A + A$ reaction, there is a reaction between the particles on the sites (i, j) and (i', j'), and both particles are removed from the system (annihilated). The site elements $M(i, j)$ and $M(i', j')$ are set equal to zero and the coordinate arrays are shrunk by two elements. The easiest way to make this change is to move the last two particles into the array positions with the tag numbers of the two annihilated particles. In the $A+B$ type reaction, if the $M(i, j)M(i', j')$ product is nonzero then this may or may not lead to reaction. If it is positive then the two colliding particles are of the same type, nothing happens, and the two particles remain in their positions. If the product is negative, this means that the two particles are of opposite type and they are annihilated. Again, the $M(i, j)$ and $M(i', j')$ elements are set equal to zero. The coordinate arrays are shrunk as in the previous case.

It may seem redundant to keep the same information in two separate arrays but it is a time saving practice. A simple alternative is to keep only the lattice array and to refer to this array when we need to know the occupancy of a given site. However, this method is not the most efficient. Consider the nature of the reaction process. If only the site array is kept, in each time step the entire array of sites must be scanned for unreacted particles. Using the present method, only the list of all remaining, unreacted particles is scanned once in each time step. It is straightforward after moving a particle to determine its new location. If this list were not kept in memory, then we would have to locate and move the reacting particles by sweeping through the entire lattice at each time step. This sweep is considerably more time consuming, especially when only a few particles are present.

III. RESULTS AND DISCUSSION

According to Argyrakis *et al.* [101] the $A + B \to 0$ batch reaction has three major time regimes: (1) the early time, "$A+A$ regime" (called so because of its similarity to the $A+A$ reaction behavior), (2) the Zeldovich regime, where segregation has occurred and the rate of reaction is much reduced, and (3) the finite size regime, where few particles are left and the reaction rate increases exponentially. The onset of this regime obviously depends on the lattice size. In the present work we explore all three regimes and are particularly interested in the two crossover behaviors. The crossover time from the $A+A$ to the Zeldovich regime is t_s and that to the finite size effect is t_l. If $t_l > t_s$, all three regimes exist; however, if $t_l < t_s$ the Zeldovich regime is "squeezed out." Obviously, for a genuine $A+A \to 0$ reaction there is no Zeldovich regime and there is only one crossover time, t_l, signaling the onset of the finite size effect.

For the $A+B$ reaction on a simple three-dimensional cube, Fig. 1 shows the standard presentation of the reaction progress, given by the reciprocal density: $\langle\rho^{-1}\rangle - \rho_0^{-1}$ vs time. Note that $\rho = \rho_A = \rho_B$ and $\rho_0 = \rho_A(t=0) = \rho_B(t=0)$. Figure 1 clearly demonstrates the asymptotic results of the Zeldovich theory, i.e., a $\rho^{-1} \sim t^{3/4}$ power law in the time interval of about $t = 10^3$ to 10^4. At later times the finite size effect regime is reached. Somewhat unexpectedly, only when reflective boundary conditions are employed is there a clear-cut crossover to the Zeldovich regime, followed by a t^{ϕ} power law where $\phi =$ 0.75, 0.75, and 0.75, respectively, for linear lattice lengths of $L =$ 200, 150, and 100. Upon employment of cyclic boundary conditions, finite size effects start earlier due to a faster decay, which results in a higher power law. For the same time intervals in which we found $\phi = 0.75$ using reflective boundary conditions, we now find $\phi =$ 1.00, 0.99, and 0.96, for $L =$ 200, 150, and 100, respectively, i.e., no Zeldovich regime. While past works [71, 27] have reported ϕ's of 0.85 or 0.89 as indicative that the Zeldovich regime is approached, we find that even for the $A+A$ regime, at early times, one gets an approximate value of $\phi = 0.85$ for all three 3D lattices, irrespective of the nature of the boundary conditions. This is because in this so-called $A+A$ regime the early slopes (power ϕ) mimic those of the $A+A$ reactions (Fig. 2) and these also show a ϕ of about 0.85, rather than 1, for reasons discussed below.

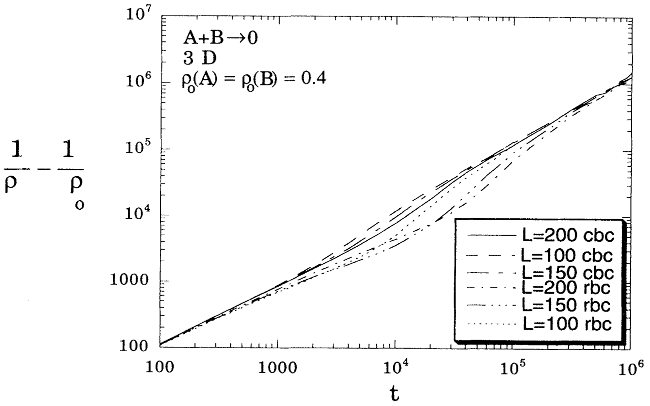

FIG. 1. $\langle\rho\rangle^{-1} - \rho_o^{-1}$ vs t for $A+B \to 0$ reaction on 3D lattices of linear size $L =$ 100, 150, and 200 with either cyclic or reflective boundary conditions. Cylic boundary conditions are designated by cbc, reflective only by rbc.

From Eq. (24) of Argyrakis *et al.* [101], the crossover time is given by

$$t_s \sim \frac{1}{8\pi D \rho_0^{2/d} f_d^{4/d}}\,, \tag{1}$$

where D is the diffusion constant ($1/2d$ in our simulation) and f_d a dimension (only) dependent constant. Obviously choosing a larger ρ_0 gives a shorter t_s. This not only saves computer time but helps to achieve $t_s < t_l$, where t_l is the finite size effect crossover time. The factor $\rho_0^{2/d}$ in the denominator of Eq. (1) makes it appear easier to reach t_s for $d = 3$, compared to lower dimensions for the same ρ_0. However, two factors oppose each other: (1) the $f_d^{4/d}$ factor is much smaller in $d = 3$, not only because of the power of 4/3 (note that $f_d < 1$), but also because of $f_3 \ll f_2 \ll f_1$ (see below) and (2) the finite size effects start "earlier" in cubic lattices simply because of the finite memory of the computer which limits the linear dimension of the simulated cube to be much smaller than that of a square, and even more so compared to a line (for the same total number of lattice sites). In order not to miss out on the Zeldovich regime we thus selected a high particle density, $\rho_0 = \rho_A(t=0) = \rho_B(t=0) = 0.4$. In addition, we simulated cubes that are larger, or at least as large, as in previous simulations [69, 70, 89].

As mentioned, even for our largest lattice, $L = 200$ (i.e., 8×10^6 sites), the cyclic boundary condition simulations do not show a Zeldovich regime. Our interpretation is that the cyclic boundary effects work against the segregation tendency by essentially circulating particles, like a convection current. The latter causes a continuous effective mixing at the boundary area and thus a breakup of the segregation zones, which are responsible for the Zeldovich regime.

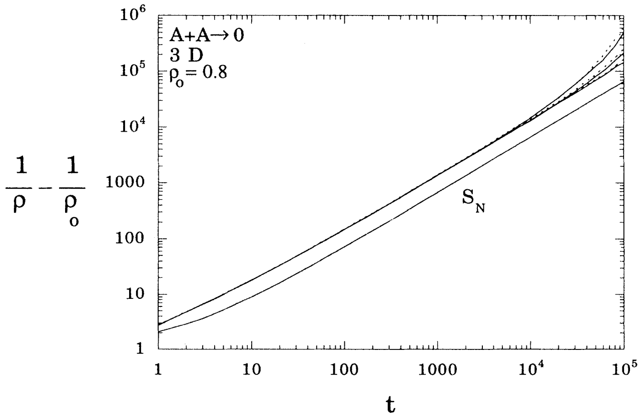

FIG. 2. $\langle\rho\rangle^{-1} - \rho_o^{-1}$ vs t for 3D lattices of linear size $L =$ 100, 150, 200 (top to bottom, respectively) for the $A+A \to 0$ reaction. Dashed lines indicate cyclic boundary conditions, solid lines indicate reflective boundary conditions. See text for discussion. Initial particle densities, in number per site, are 0.8. Also shown is the curve for S_N, the number of distinct sites visited by a single particle in N steps on a 3D lattice (lower single curve).

For comparison with the $A + B$ reaction we also simulated $A + A$ reactions. Figure 2 shows the behavior of the $A + A \to 0$ reaction on large cubes. Again the cyclic boundary conditions seem to hasten the finite size effects, although not as drastically as in the $A + B$ case. Due to the absence of segregation, the mixing effect is less crucial, though still affecting any nonclassical power (i.e., $\phi < 1$).

According to the conventional scaling arguments [17, 30], for any elementary $A + A$ reaction with an initial random distribution of particles, the critical dimension is $d = 2$. Thus, for $d = 3$, the classical, mean field results apply, giving the textbook behavior, i.e., a linear ($\phi = 1$) dependence of the reaction progress on time:

$$\frac{1}{\rho} - \frac{1}{\rho_0} = kt \ , \tag{2}$$

where k is the traditional rate constant (in our simulations, $k = 1$, $1/2$, and $1/3$ in 1D, 2D, and 3D, respectively). However, our results (Fig. 2) show that at early times ϕ is in the range $0.8 - 0.9$, an apparent contradiction. An alternative scaling argument [14, 15, 80] starts from a model which depends on the single particle exploration volume, i.e., the number of distinct sites visited S_n, resulting in a linear dependence of the reaction progress on the exploration volume:

$$\frac{1}{\rho} - \frac{1}{\rho_0} \sim S_n \ . \tag{3}$$

While asymptotically in 3D [106] $S_n \sim t$, this is not the case at early time, where S_n is sublinear in time [106]. We have therefore added to Fig. 2 the relation of S_n vs t from an analytical solution of [106]. It is easily seen that the reaction progress ($\rho^{-1} - \rho_0^{-1}$) curve is effectively parallel to that of S_n vs time. This is seen even more clearly in Fig. 3. Here the $A + A$ reaction progress is essentially linear with S_n in all dimensionalities ($d = 1, 2, 3$) until finite size effects appear at long times. We also see in Fig. 3 that the corresponding $A+B$ reactions follow the $A+A$ curves at early times (only). In this figure, the crossover to the Zeldovich regime is more clear than in Fig. 1 and so Fig. 3 is actually used below to find crossover times t_s (and crossover densities ρ_s).

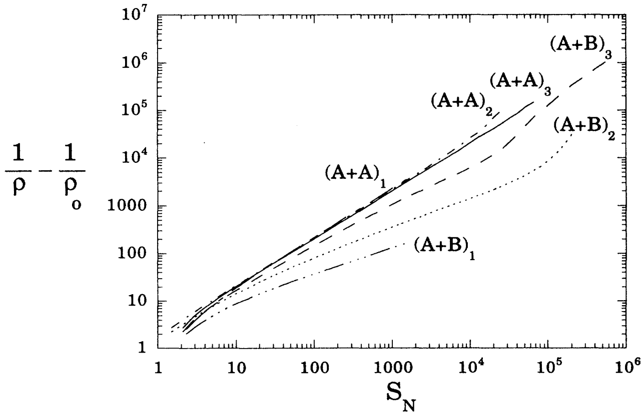

FIG. 3. $\langle\rho\rangle^{-1} - \rho_o^{-1}$ vs S_N for reactions on 1D, 2D, and 3D lattices. Boundary conditions are reflective. Initial particle densities in particle per site are 0.8 for $A + A \to 0$ and 0.4 per species for $A + B \to 0$. Subscripts correspond to the dimensionality of the lattice. Note that for the $A+A$ reactions the slope is effectively unity in the second, third and fourth decades.

Figure 4 is a scaling test based on Eq. (1). We find that for different initial densities (ρ_0) the crossover to segregation (Zeldovich) occurs approximately at the same $t\rho_0^{2/3}$ value. From this, one can derive the $\rho_s/\rho_0 = f_3$ values, which give approximately $f_3 = 0.007$. Comparing to the approximate f_2 and f_1 values derived before [101], $f_1 = 0.4$ and $f_2 = 0.03$, we find a rough but simple relation

$$f_3 < f_2 < f_1 \ , \tag{4}$$

which may be intuitively obvious.

Finite size effects after the Zeldovich regime: When $t_l > t_s$, finite size effects arise when the segregated aggregate size approaches the size of the lattice. Argyrakis *et al.* [101] give the expression

$$t_l \sim g_d^2 \frac{L^2}{\alpha_d^2 D} \ , \tag{5}$$

where g_d and α_d are constant for a given dimensionality d [92]. One way of testing this expression, and also deriving the crossover values t_l and ρ_l, is to plot the reaction progress $\rho^{-1} - \rho_0^{-1}$ vs t/L^2 for various lattice sizes L. Figure 5 demonstrates that this scaling idea works reasonably well for different lattice sizes L.

Finite size effects that appear before, and thereby nullify, the Zeldovich regime: When $t_l < t_s$ the $A + B$ reaction's finite size effect takes over directly from its "$A + A$ regime." Using Einstein's diffusion equation we write the scaling equation

$$t_l = \frac{1}{2dD} L^2 \ . \tag{6}$$

Obviously this case will arise for small lattices (small L), low initial densities ρ_0, or combinations thereof [Eqs.

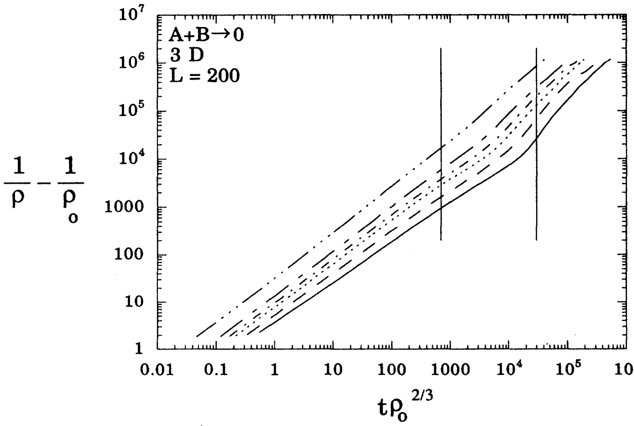

FIG. 4. $\langle\rho\rangle^{-1} - \rho_o^{-1}$ vs $t\rho_o^{2/3}$ for $A + B \to 0$ on a 200^3 lattice. Different curves arise from different initial densities: 0.01, 0.04, 0.07, 0.1, 0.2, and 0.4 (top to bottom, respectively) in particle per site per species. For all curves, crossover to the Zeldovich regime occurs between the two vertical lines.

TABLE I. Parameters describing crossover to finite size effects.

	$A+A$	$A+A$	$A+A$	$A+B$	$A+B$	$A+B$	$A+B$
Dimension	1	2	3	1	2	$3(L<50)$	$3(L>50)$
ϕ_{calc}	0.5	0.85 − 0.9[a]	0.8 − 1	0.25	0.5	0.8 − 1[b]	0.75
a_{calc}	2	0.6	0.3–0.4	2	0.5	0.2	c
λ_{calc}	1	1.7	1.6 − 2	0.5	1	1.6 − 2	1.5
λ_{obs}	1.1 ± 0.1	1.7 ± 0.2	2.3 ± 0.4	0.6 ± 0.3	1.0 ± 0.2	1.7 ± 0.4	1.4 ± 0.4

[a] Range due to logarithmic correction.

[b] Range due to time dependent behavior of S_N.

[c] The factor $(q_3/\alpha_3)^2$ in Eq. (5) is not known [101].

(1) and (6)]. Basically we expect this case to be equivalent to the finite size effects of the $A+A$ reaction. Some approaches have assumed that the condition for the crossover density ρ_l is given by comparing the average interparticle distance to the lattice size:

$$\left(\frac{1}{\rho_l}\right)^{1/d} \sim L \tag{7}$$

or, equivalently,

$$\frac{1}{\rho_l} \sim L^d \; . \tag{8}$$

We show below that this relation is not borne out by the simulations — see Fig. 6 and Table I.

A different approach is based on the time it takes a particle to reach the wall, given by the Einstein analog to Eq. (6). Equation (6) again relates to L^2 [compare Eq. (5)]. Thus the primary relation is based on the time t_l, rather than the density ρ_l. Using the asymptotic power law [14] relating ρ to t, gives

$$\frac{1}{\rho_l} \sim \frac{k}{\phi} t_l^{\phi} \; , \tag{9}$$

where k is the rate constant. Obviously here $\rho_0^{-1} \ll \rho_l^{-1}$. We assume that ϕ can be taken from the regime immediately preceding the crossover time t_l. As pointed out earlier, the power ϕ depends on the dimensionality d, the kind of reaction ($A+A$ or $A+B$), and the particular regime (Zeldovich or pre-Zeldovich).

Combining Eqs. (6) and (9):

$$\frac{1}{\rho_l} = aL^{\lambda} \; , \tag{10}$$

where a is constant, $a = (k/\phi)(D/2d)^{\phi}$ and $\lambda = 2\phi$. Figure 6 appears to bear out this relation for the various sizes, dimensionalities, reaction kinds, and regimes, as can be seen in the last row of Table I.

From this last discussion, it is apparent that for all crossovers to finite size effects the primary quantity is t_l rather than ρ_l, with the simple universal scaling relation

$$t_l \sim L^2 \; . \tag{11}$$

The validity of this relation can be seen in Fig. 7. On the other hand, for the crossover to the d-dimensional segregated Zeldovich regime, the primary quantity is ρ_s rather than t_s, with the simple universal scaling relation (Eq. 23 of [101])

$$\rho_s = f_d \rho_0 \; . \tag{12}$$

This is easy to understand; the origin of this effect is the

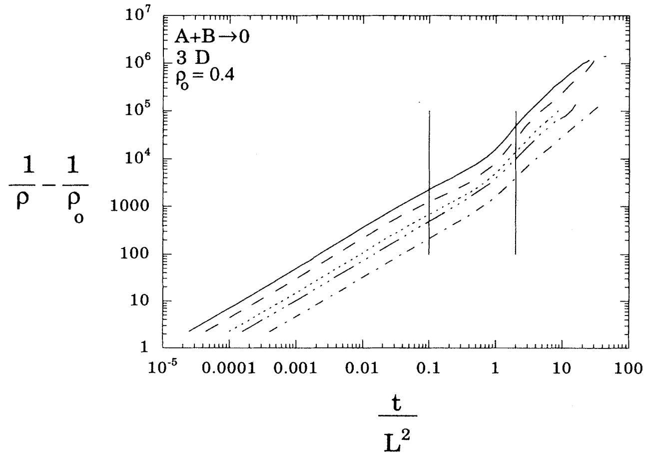

FIG. 5. $\langle\rho\rangle^{-1} - \rho_o^{-1}$ vs t/L^2 for $A+B \rightarrow 0$ in three dimensions for $L = 50, 80, 100, 150, 200$. Initial particle density in particles per site is 0.4 per species. For all curves, the crossover to the Zeldovich regime occurs between the two vertical lines.

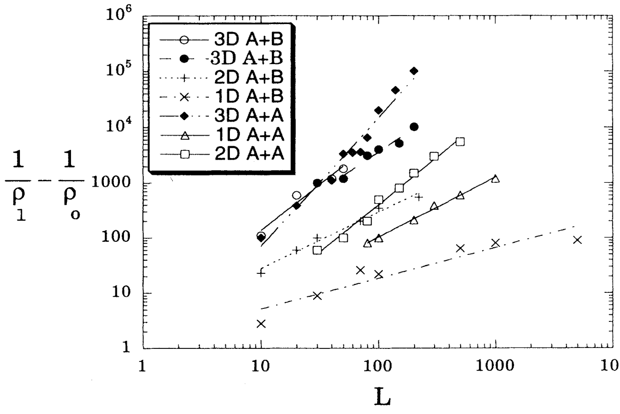

FIG. 6. $\langle\rho_l\rangle^{-1} - \rho_o^{-1}$ vs L for $A+A \rightarrow 0$ and $A+B \rightarrow 0$ in 1D, 2D, and 3D. For the 3D $A+B$ case, open circles depict linear lattice sizes with $L<50$ and filled circles depict linear lattice sizes with $L>50$. The $L>50$ points are the only data in the Zeldovich regime.

initial time density fluctuation. When both crossover regimes overlap, the situation is more complex.

IV. CONCLUSIONS AND SUMMARY

Our simulations for the $A + B$ reaction have demonstrated the existence of the Zeldovich segregation regime in three dimensions and the validity of its peculiar power law, $\rho^{-1} \sim t^{3/4}$. This was achieved using simulations that employed large enough cubic lattices, reflective boundary conditions, and large initial densities. We have also validated, for cubic lattices, the scaling law for the crossover density ρ_s and crossover time t_s pertaining to the onset of the segregated Zeldovich regime and established the empirical f_3 value for the simple scaling relation $\rho_s = f_d \rho_0$. The crossover time to the Zeldovich regime depends on density only, implicating the source of the Zeldovich type behavior — initial spatial fluctuations in reactant density.

We show as well that even for the $A + A$ reaction and the $A + A$ regime of the $A + B$ reaction, the early time regime does not give the classical kinetics result $\rho^{-1} - \rho_0^{-1} = kt$ but rather $\rho^{-1} - \rho_0 \sim S_n \sim t^{\phi}$, where ϕ is a power smaller than unity over a significant time regime. This regime for $A + B$ may cross over directly into the Zeldovich regime where $\phi = 3/4$. In such a case the reaction may never reach the classical behavior of $\phi = 1$. Concomitantly, the particle distribution cannot be random if $\phi < 1$, because then the reaction rate is not second order in the density [103]. We note that for a random particle distribution the binary collision probability is always second order in the density, i.e., proportional to ρ^2.

We have also validated in three dimensions the scaling of the finite size effect crossover time t_l for $t_l \gg t_s$, i.e., for the Zeldovich regime of the $A + B$ reaction, namely, $t_l \sim L^2$, where L is the linear size of the reaction domain. Furthermore, we have also shown that also for $t_l \ll t_s$, i.e., the non-Zeldovich regime finite size crossover, the basic relation is $t_l \sim L^2$. These simple scaling relations apply universally to both $A + A$ and $A + B$ reactions, for both reaction regimes of $A + B$, at all dimensionalities ($d = 1, 2, 3$) and for all initial densities ρ_0 and lattice sizes L (see Fig. 7). The fact that the crossover time to finite size effects depends only on the linear lattice size emphasizes the fact that the reactant particles obey the Einstein diffusion equation and that it is the particles' mean free paths that determine when finite size effects set in, i.e., when the mean free path length is on the order of the linear lattice size. When $t_l \cong t_s$, the situation is more complex. Finally we have shown some unexpected boundary condition effects. These are relevant not only for simulations but also for mesoscopic (small, finite) experimental systems.

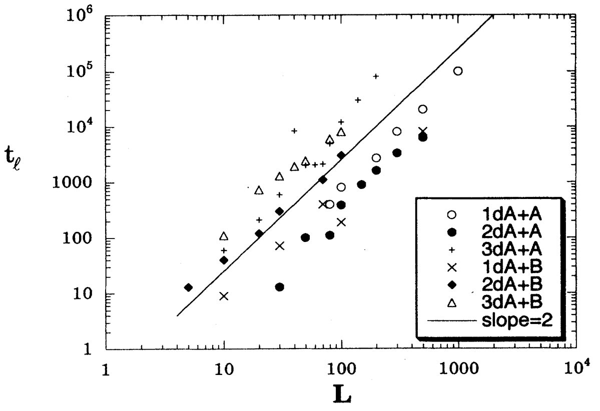

FIG. 7. t_l vs L for $A + A \to 0$ and $A + B \to 0$ in 1D, 2D, and 3D. The straight line has a slope of 2.00. Note: $A + B$ results do not include the Zeldovich regime.

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[1] A. A. Ovchinnikov and Y. G. Zeldovich, Chem. Phys. B **28**, 215 (1978).

[2] M. Bramson and D. Z. Griffeath, Wahrscheinlichskeitstheorie Gebiete **53**, 183 (1980).

[3] M. Bramson and D. Z. Griffeath, Ann. Prob. **8**, 183 (1980).

[4] R. Kopelman and P. Argyrakis, J. Chem. Phys. **72**, 3053 (1980).

[5] P. W. Klymko and R. Kopelman, J. Lumin. **24/25**, 457 (1981).

[6] P. W. Klymko and R. Kopelman, J. Phys. Chem. **86**, 3686 (1982).

[7] N. G. van Kampen, Int. J. Quantum Chem. **16**, 101 (1982).

[8] P. G. de Gennes, J. Chem. Phys. **76**, 3316 (1982).

[9] J. Keizer, J. Phys. Chem. **86**, 5052 (1982).

[10] J. Keizer, J. Chem. Phys. **79**, 4877 (1983).

[11] A. Blumen, J. Klafter, and G. Zumofen, Phys. Rev. B **27**, 3429 (1983).

[12] D. C. Torney and H. M. McConnel, J. Phys. Chem. **87**, 1441 (1983).

[13] D. C. Torney and H. M. McConnel, Proc. R. Soc. London Ser. A **387**, 147 (1983).

[14] P. W. Klymko and R. Kopelman, J. Phys. Chem. **87**, 4565 (1983).

[15] P. G. de Gennes, Compt. R. Acad. Sci. Paris **296**, 881 (1983).

[16] P. Evesque, J. Phys. (Paris) **44**, 1217 (1983).

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

[18] D. C. Torney, J. Chem. Phys. **79**, 3606 (1983).

[19] R. Kopelman, J. Hoshen, J. S. Newhouse, and P. Argyrakis, J. Stat. Phys. **30**, 335 (1983).

[20] P. Evesque and J. Duran, J. Chem. Phys. **80**, 3016 (1984).

[21] L. W. Anacker and R. Kopelman, J. Chem. Phys. **81**, 6402 (1984).

[22] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984).

[23] K. Kang, P. Meakin, J. H. Oh, and S. Redner, J. Phys. A **17**, L665 (1984).
[24] L. W. Anacker, R. P. Parson, and R. Kopelman, J. Phys. Chem. **89**, 4758 (1985).
[25] P. V. Elyutin, J. Phys. C **17**, 1867 (1984).
[26] R. Kopelman, P. W. Klymko, J. S. Newhouse, and L. Anacker, Phys. Rev. B **29**, 3747 (1984).
[27] P. Meakin and H. E. Stanley, J. Phys. A **173**, L17 (1984).
[28] L. W. Anacker, R. Kopelman, and J. S. Newhouse, J. Stat. Phys. **36**, 591 (1984).
[29] J. S. Newhouse, P. Argyrakis, and R. Kopelman, Chem. Phys. Lett. **107**, 48 (1984).
[30] K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985).
[31] L. W. Anacker, R. P. Parson, and R. Kopelman, J. Phys. Chem. **89**, 4785 (1985).
[32] J. S. Newhouse and R. Kopelman, Phys. Rev. B **31**, 1677 (1985).
[33] Z. Racz, Phys. Rev. Lett. **55**, 1707 (1985).
[34] G. Zumofen, A. Blumen, and J. Klafter, J. Chem. Phys. **82**, 3198 (1985).
[35] D. ben-Avraham and S. Redner, Phys. Rev. A **34**, 501 (1986).
[36] J. S. Newhouse and R. Kopelman, J. Chem. Phys. **85**, 6804 (1986).
[37] R. Kopelman, S. Parus, and J. Prasad, Phys. Rev. Lett. **56**, 1742 (1986).
[38] R. Kopelman, J. Stat. Phys. **42**, 185 (1986).
[39] L. Peliti, J. Phys. A **19**, L365 (1986).
[40] D. ben-Avraham, J. Stat. Phys. **48**, 315 (1987).
[41] A. A. Lushnikov, Phys. Lett. A **120**, 135 (1987).
[42] S. Redner, D. ben-Avraham, and B. Kahng, J. Phys. A **20**, 1231 (1987).
[43] R. Kopelman, Philos. Mag. B **56**, 717 (1987).
[44] J. Prasad and R. Kopelman, J. Phys. Chem. **91**, 265 (1987).
[45] J. Prasad and R. Kopelman, Phys. Rev. Lett. **59**, 2103 (1987).
[46] P. Argyrakis and R. Kopelman, J. Phys. Chem. **91**, 2699 (1987).
[47] L. W. Anacker and R. Kopelman, Phys. Rev. Lett. **58**, 289 (1987).
[48] C. R. Doering and D. ben-Avraham, Phys. Rev. A **38**, 3035 (1988).
[49] A. Blumen, G. Zumofen, and J. Klafter, in *Fractals, Quasicrystals, Chaos, Knots and Algebraic Quantum Mechanics*, edited by A. Amann *et al.* (Kluwer, New York, 1989), p. 21.
[50] R. Kopelman, Science **41**, 1620 (1988).
[51] R. Kopelman, S. J. Parus, and J. Prasad, in *Excited State Relaxation and Transport Phenomena in Solids*, edited by J. L. Skinner and M. D. Fayer, special issue of Chem. Phys. **128**, 209 (1988).
[52] K. Lindenberg, B. J. West, and R. Kopelman, Phys. Rev. Lett. **60**, 1777 (1988).
[53] E. Peacock-López and J. Keizer, J. Chem. Phys. **88**, 1997 (1988).
[54] V. Kuzovkov and E. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).
[55] S. Kanno, Prog. Theor. Phys. **79**, 1330 (1988).
[56] J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988); **60**, 1885 (1988).
[57] S. J. Parus and R. Kopelman, Mol. Cryst. Liq. Cryst. **175**, 119 (1989).
[58] E. Clement, L. M. Sander, and R. Kopelman, Phys. Rev. A **39**, 6472 (1989).
[59] J. Prasad and R. Kopelman, Chem. Phys. Lett. **157**, 535 (1989).
[60] E. Clément, L. M. Sander, and R. Kopelman, Phys. Rev. A **39**, 6455 (1989); **39**, 6466 (1989).
[61] K. Lindenberg, B. J. West, and R. Kopelman, in *Noise and Chaos in Nonlinear Dynamical Systems*, edited by S. Capelin and F. Moss (Cambridge University Press, Cambridge, England, 1989), and references therein.
[62] Z. Cheng, S. Redner, and F. Leyvraz, Phys. Rev. Lett. **62**, 2321 (1989).
[63] C. R. Doering and D. ben-Avraham, Phys. Rev. Lett. **62**, 2563 (1989).
[64] R. Kopelman, S. J. Parus, and Z-Y. Shi, in *Dynamical Processes in Condensed Molecular Systems*, edited by J. Klafter, J. Jortner, and A. Blumen (World Scientific, Singapore, 1989), p. 231.
[65] S. J. Parus and R. Kopelman, Phys. Rev. B **39**, 889 (1989).
[66] P. Argyrakis and R. Kopelman, J. Phys. Chem. **93**, 225 (1989).
[67] R. Kopelman, in *Dynamical Processes in Condensed Molecular Systems*, edited by A. Blumen, J. Klafter, and D. Haarer (World Scientific, Singapore, 1990), p. 173.
[68] L. A. Harmon and R. Kopelman, J. Phys. Chem. **94**, 3454 (1990).
[69] P. Argyrakis and R. Kopelman, Phys. Rev. A **41**, 2114 (1990).
[70] P. Argyrakis and R. Kopelman, Phys. Rev. A **41**, 2121 (1990).
[71] Z. Jiang and C. Ebner, Phys. Rev. **41**, 5333 (1990).
[72] P. Argyrakis and R. Kopelman, in *Dynamics in Small Confining Systems*, edited by J. M. Drake, J. Klafter, and R. Kopelman (Materials Research Society, Pittsburgh, 1990), p. 195.
[73] J-C. Lin, C. R. Doering, and D. ben-Avraham, Chem. Phys. **146**, 355 (1990).
[74] K. Lindenberg, B. J. West, and R. Kopelman, Phys. Rev. A **42**, 890 (1990).
[75] J. Prasad and R. Kopelman, J. Lumin. **45**, 258 (1990).
[76] R. Kopelman, C. S. Li, and Z-Y. Shi, J. Lumin. **45**, 40 (1990).
[77] R. Kopelman, L. W. Anacker, E. Clement, L. Li, and L. Sander, J. Lumin. **45**, 323 (1990).
[78] S. J. Parus and R. Kopelman, J. Lumin. **45**, 43 (1990).
[79] Z-Y. Shi and R. Kopelman, J. Lumin. **45**, 275 (1990).
[80] R. Kopelman and Y-E. Koo, Isr. J. Chem. **31**, 147 (1991).
[81] T. Ohtsuki, Phys. Rev. A **43**, 6917 (1991).
[82] M. Bramson and J. L. Lebowitz, J. Stat. Phys. **62**, 297 (1991).
[83] F. Leyvraz and S. Redner, Phys. Rev. Lett. **66**, 2168 (1991).
[84] R. Schoonover, D. ben-Avraham, S. Havlin, R. Kopelman, and G. H. Weiss, Physica A **171**, 232 (1991), and references therein.
[85] A. Blumen, S. Luding, and I. M. Sokolov, J. Stat. Phys. **65**, 849 (1991).
[86] V. Privman, J. Stat. Phys. **69**, 629 (1992).
[87] L. Li and R. Kopelman, J. Phys. Chem. **96**, 8079 (1992).
[88] Z-Y. Shi and R. Kopelman, Chem. Phys. **167**, 149 (1992).

[89] P. Argyrakis and R. Kopelman, Phys. Rev. A **45**, 5814 (1992).

[90] G. Zumofen, J. Klafter, and A. Blumen, Phys. Rev. A **45**, 8977 (1992).

[91] Z-Y. Shi and R. Kopelman, in *Dynamics in Small Confining Systems*, edited by J. M. Drake, J. Klafter, R. Kopelman, and D. D. Awshalom, MRS Symposia Proceedings No. 290 (Materials Research Society, Pittsburgh, 1993), p. 279.

[92] F. Leyvraz and S. Redner, Phys. Rev. A **46**, 3132 (1992).

[93] M. von Smoluchowski, Z. Phys. Chem. **92**, 129 (1917).

[94] B. Sveshnikoff, Acta Physicochim. URSS **3**, 257 (1935).

[95] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[96] F. C. Collins and G. E. Kimball, J. Colloid Sci. **4**, 425 (1949).

[97] T. R. Waite, Phys. Rev. **107**, 463 (1957); **107**, 471 (1957).

[98] L. Monchik, J. K. Magee, and A. H. Samuel, J. Chem. Phys. **26**, 935 (1957).

[99] R. M. Noyes, in *Progress in Reaction Kinetics*, edited by G. Porter (Pergamon, London, 1961), Vol. 1.

[100] G. Wilemski and M. Fixman, J. Chem. Phys. **58**, 4009 (1973); **64**, 4559 (1976).

[101] P. Argyrakis, R. Kopelman, and K. Lindenberg, Chem. Phys. **177**, 693 (1993).

[102] K. Lindenberg, P. Argyrakis, and R. Kopelman, in *Chaos and Order: The New Synthesis*, edited by M. Millonas (Springer, New York, in press).

[103] K. Lindenberg, P. Argyrakis, and R. Kopelman, J. Phys. Chem. **99**, 7542 (1995).

[104] V. M. Agranovich and M. D. Galanin, in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1982), Vol. 3, pp. 1–371.

[105] K. Lindenberg, P. Argyrakis, and R. Kopelman, J. Phys. Chem. **98**, 3389 (1994).

[106] E. W. Montroll and G. H. Weiss, J. Math. Phys. **6**, 167 (1965).

[107] S. Havlin and D. ben-Avraham, Adv. Phys. **36**, 695 (1987).

[108] F. S. Henyey and V. Seshadri, J. Chem. Phys. **76**, 5530 (1982).

[109] D. ben-Avraham, J. Chem. Phys. **88**, 941 (1988).

[110] P. Argyrakis, Comput. Phys. **6**, 525 (1992).