Decay Kinetics of Ballistic Annihilation

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(Received 5 November 1992; revised manuscript received 22 January 1993)

We study the kinetics of ballistic annihilation, $A+A\rightarrow 0$, with continuous initial particle velocity distributions. The concentration and the rms velocity are found to decay as $c\sim t^{-\alpha}$ and $v_{\rm rms}\sim t^{-\beta}$, respectively, with the relation $\alpha+\beta=1$ holding in any spatial dimension. A "mean-field" Boltzmann equation for the evolution of the velocity distribution predicts that α and β depend strongly on the initial condition, a behavior which is confirmed numerically in one and two dimensions.

PACS numbers: 82.20.Pm, 02.50.−r, 03.20.+i, 05.20.Dd

For irreversible diffusion-controlled reactions, it is now widely appreciated that the density decays more slowly than the predictions of mean-field theory in sufficiently low spatial dimension. For two-species annihilation, this behavior is accompanied by the dynamic formation of large-scale spatial heterogeneities in an initially homogeneous system [1]. The contrasting situation where the reactants move ballistically has received much less attention, however, and relatively little is known.

Interesting results have been recently reported for the kinetics of irreversible aggregation, $A_i+A_j\rightarrow A_{i+j}$, with ballistic trajectories for the aggregates and with momentum conserving collisions [2,3]. Here the subscript refers to the (conserved) mass of the aggregates. This model has been invoked as an idealization of the coalescence of fluid vortices [4] and planet formation by accretion [5]. For ballistic aggregation, a scaling argument suggests that the concentration of aggregates decays with time as $t^{-\alpha}$, with $\alpha=2d/(d+2)$ and d the spatial dimension [2]. This dimension dependence is atypical of the behavior pattern exhibited by diffusion-controlled reactions. Furthermore, microscopic considerations show that the decay of the density of fixed-mass aggregates disagrees with the scaling predictions [3].

Motivated in part by these intriguing features, we investigate the decay kinetics of the more elementary single-species annihilation process, $A+A\rightarrow 0$, for arbitrary continuous initial velocity distributions. By analysis of the Boltzmann equation for the evolution of the velocity distribution, we can account for the decay of the density and the dependence of the exponent α on the initial velocity distribution and on d. Our predictions are verified in one and two dimensions by numerical integration of the Boltzmann equation and by Monte Carlo simulations. It is worth noting that for annihilation in one dimension with a discrete bimodal initial velocity distribution [6], $P(v,t=0)\propto p\delta(v-1)+(1-p)\delta(v+1)$, the density decays as $t^{-1/2}$ for $p=\frac{1}{2}$, while the minority velocity species decays exponentially for $p\neq\frac{1}{2}$. These results can be inferred by mapping the kinetics onto a first-passage process for a one-dimensional random walk. For continuously distributed velocities, this approach is inadequate to account for the wide range of possible kinetic behaviors.

At $t=0$, the system consists of identical particles whose velocities v are distributed according to an initial distribution $P(v,t=0)$ with zero mean. The decay kinetics appears to be independent of the initial spatial distribution of particles and for simplicity we focus on a random initial distribution. Particles move according to their initial velocity until a collision occurs, which results in the removal of both colliding particles. We are interested in determining the time dependence of the macroscopic concentration, $c(t)=\int dv\,P(v,t)$, and the moments of the velocity distribution, $\langle v^n\rangle^{1/n}=[\int dv\,v^nP(v,t)/c(t)]^{1/n}$.

A simple power counting argument relates the density decay exponent α in the decay of the concentration, $c(t)\sim t^{-\alpha}$, with the exponent β which characterizes the decay of the typical velocity, $v_{\rm rms}\sim t^{-\beta}$. Consider a system of identical particles of fixed radius r at concentration c which move with a velocity of the order of $v_{\rm rms}$. From an elementary mean-free-path argument, the time between collisions is $t\sim 1/cv_{\rm rms}r^{d-1}$ or $cv_{\rm rms}\propto t^{-1}$. Thus the relation $\alpha+\beta=1$ should hold for all spatial dimension d.

Since the lifetime of particles with velocity v is proportional to $1/v$, faster particles tend to annihilate more quickly, and the typical velocity should decay in time. By the relation between α and β, a value of α less than unity is therefore implied. We further argue that there is a strong dependence of the exponent α on the form of the initial velocity distribution. This behavior differs from the "transparent" limit of $c\sim t^{-1}$ which arises from the naive rate equation $\dot{c}\propto -kc^2$.

To determine the decay kinetics, we write a Boltzmann equation for the time evolution of the velocity distribution. For simplicity, consider the one-dimensional case; generalization to higher dimensions follows naturally. Let $P(x,v,t)$ be the density of particles with velocity v at position x and at time t. At time $t+\Delta t$, the velocity dis-

tribution changes both because of translation of particles and because of reactions. We treat the reaction term in a mean-field approximation by assuming that a particle at $x' < x$ and velocity $v' > v$ will necessarily react with the target particle at (x,v) when $x - x' < (v' - v)\Delta t$. There is a complementary contribution due to collisions between the target and a particle located at $x' > x$ with $v' < v$. These two contributions lead to the Boltzmann equation

$$P(x+v\Delta t,v,t+\Delta t) - P(x,v,t) = -kP(x,v,t)\left[\int_v^\infty dv' \int_{x-(v'-v)\Delta t}^{x} dx' P(x',v',t) + \int_{-\infty}^{v} dv' \int_{x}^{x+(v-v')\Delta t} dx' P(x',v',t)\right], \quad (1)$$

where k is a dimensionless reaction constant. Since a collision leads to particle annihilation, there is no collision-induced gain term in the equation. This approximate equation overcounts collisions, since the incident particle at x' may react with a third particle rather than with the target particle. We anticipate that such three-body interactions will have a relatively small effect on the kinetics.

To analyze this Boltzmann equation, we expand to first order in Δt to arrive at

$$\frac{\partial P(x,v,t)}{\partial t} = -v\frac{\partial P(x,v,t)}{\partial x} - kP(x,v,t)\int_{-\infty}^{\infty} dv' |v - v'| P(x,v',t). \quad (2)$$

Since the initial velocity distribution and the ensuing reaction process are spatially homogeneous, we assume that the velocity distribution remains spatially homogeneous. Thus we set the convective term $\partial P/\partial x$ to zero and write $P(v,t)$ to signify the time-dependent and spatially homogeneous concentration of particles with velocity v. This gives

$$\frac{\partial P(v,t)}{\partial t} = -kP(v,t)\int_{-\infty}^{\infty} dv' |v - v'| P(v',t), \quad (3)$$

where the $|v - v'|$ dependence of the integral kernel controls the reaction rate. Equation (3) is reminiscent of the Smoluchowski equation for ballistic aggregation [3]. Despite the uncontrolled nature of the approximations underlying Eq. (3), this formulation gives a useful quantitative description of the decay kinetics.

The first step in analyzing the Boltzmann equation is to apply dimensional arguments, together with the assumed asymptotic behaviors, $c \sim t^{-\alpha}$ and $v_{\rm rms} \sim t^{-\beta}$, to reduce Eq. (3) to a single variable equation. From these considerations, we expect that the velocity distribution will have the following scaled form:

$$P(v,t) = \frac{c_0}{v_0}\left(\frac{t}{t_0}\right)^{\beta-\alpha} f(z), \quad \text{with } z = \frac{v}{v_0}\left(\frac{t}{t_0}\right)^{\beta}. \quad (4)$$

Here z is the dimensionless velocity, $t_0 = 1/kc_0v_0$ the initial time between reactions, k the dimensionless reaction constant, c_0 the initial concentration, and v_0 the initial rms velocity.

Substituting this scaling form into Eq. (3), we immediately confirm the exponent relation $\alpha + \beta = 1$. Additionally, we obtain an equation for the scaling function,

$$(2\beta - 1)f(z) + \beta z f'(z) = -f(z)\int_{-\infty}^{\infty} dz' |z - z'| f(z'). \quad (5)$$

Notice the invariance under the transformation $f(z) \to a^2 f(az)$, so that a unit normalization of $f(z)$ can be achieved by a scale change in z. To find the large-z tail of the scaled velocity distribution, we approximate $|z - z'| \sim |z|$ in the integral and use the fact that $f(z)$ vanishes as $z \to \infty$. These steps reduce Eq. (5) to a differential equation whose large-z solution is

$$f(z) \sim |z|^{(1-2\beta)/\beta} \exp(-|z|/\beta), \quad |z| \gg 1. \quad (6)$$

Near the origin, Eq. (5) admits different forms for $f(z)$, and, correspondingly, the exponent β depends on the form of the initial velocity distribution. To treat the small-z limit, we divide Eq. (5) by $f(z)$ to yield

$$(2\beta - 1) + \beta \lim_{z\to 0} z[\ln f(z)]' = -2\int_0^\infty dz' |z'| f(z'). \quad (7)$$

Consider an initial velocity distribution with a power-law dependence near the origin and a cutoff at v_0, $P(v,t=0) \propto |v|^\mu \theta(v_0 - |v|)$. Our Monte Carlo simulations (discussed below) reveal that the scaled distribution retains the same power-law form in the small-z limit, $f(z) \propto |z|^\mu$. Adopting this form in Eq. (7), the second term is simply equal to $\beta\mu$. The resulting equation then predicts that β is a monotonically decreasing function of μ (for $\mu > -1$) whose precise form depends on the first moment of $f(z)$ which, in turn, depends on the full details of the velocity distribution. For example, for the trial function $f(z) \propto |z|^\mu e^{-|z|/\beta}$ in Eq. (7), i.e., the product of the asymptotic behaviors, we obtain $\beta = 1/(3+2\mu)$. Thus by tuning μ, the exponents α and β can take on any value between 0 and 1, subject to the condition $\alpha + \beta = 1$. Notice that α is less than unity, in general, showing that the reaction does not conform to bimolecular reaction kinetics. Paradoxically, when the concentration decays relatively quickly, $\alpha \cong 1$, the typical velocity decays slowly, and *vice versa*. This exponent variation occurs for any physically reasonable trial form for $f(z)$, and is corroborated by numerical simulations.

The generalization of the scaling approach for the Boltzmann equation to higher spatial dimensions is straightforward. The scaled velocity distribution function

now takes the form

$$P(v,t)=\frac{c_0}{v_0}\left(\frac{t}{t_0}\right)^{\beta d-\alpha} f(\mathbf{z}) \text{ with } \mathbf{z}=\frac{\mathbf{v}}{v_0}\left(\frac{t}{t_0}\right)^{\beta}, \quad (8)$$

where the exponent combination βd originates from an integration over d-dimensional velocity space. To relate the exponents μ and β in the d-dimensional version of the Boltzmann equation, we again assume a small-z power-law form $f(\mathbf{z}) \propto |\mathbf{z}|^{\mu}$, with $\mu > -d$, and a relatively sharp cutoff in $f(\mathbf{z})$ for large $|\mathbf{z}|$. These assumptions again lead to a qualitatively correct μ dependence of β. Namely, β monotonically decreases with μ, and has the limits $\beta \to 1$ for $\mu \to -d$, and $\beta \to 0$ for $\mu \to \infty$. As in one dimension, if we adopt $f(\mathbf{z}) \propto |\mathbf{z}|^{\mu} e^{-|\mathbf{z}|/\beta}$, then we find $\beta = 1/(1+2d+2\mu)$. Conversely, as the spatial dimension increases, the limiting value $\alpha = 1$, corresponding to the transparent limit, $\dot{c} = -kc^2$, is approached but never reached. Thus only in the $d = \infty$ limit are particle trajectories sufficiently independent that the typical velocity does not decrease. This is in contrast to many diffusion-controlled reactions for which transparent behavior occurs when $d \geq d_c$ with d_c finite [1].

To test our approximate analysis, we have performed direct numerical integration of the general-d Boltzmann equation (Table I). In one dimension, a typical integration was based on dividing the velocity range $[-1,1]$ into 200 bins with a time step of $\Delta t = 0.15$. A finer level of resolution gives essentially identical results. To estimate the value of β, we computed the "test" scaling function $f(z;t)_{\text{test}} \propto t^{1-2\beta_{\text{test}}} P(v,t)$ at different times, and adjusted β_{test} to achieve the best data collapse by minimizing the rms deviation between different data sets. Up to 1000 time steps, we obtained estimates for β with an uncertainty of less than 0.005.

We also performed Monte Carlo simulations for ballistic annihilation based on two independent approaches (see Fig. 1). One method models the ballistic motion as a biased random walk. In two dimensions, a particle at $\mathbf{r}_i$ is assigned a velocity (v_{ix}, v_{ix}), with $|v_{ix}|, |v_{iy}| < 1$, according to an initial velocity distribution with support in $[-1,1]$ [2]. A move attempt consists of picking an occupied site $\mathbf{r}_i$ at random and moving the particle by $(\text{sgn}(v_{ix}),0)$ with probability $|v_{ix}|$ and by $(0,\text{sgn}(v_{iy}))$ with probability $|v_{iy}|$. If a particle lands on an occupied site, both particles are removed. After each move, the time is incremented by the inverse of the current number of particles. The advantage of this stochastic method is that it is easily implemented in any spatial dimension, but at the expense of introducing diffusion in addition to the primary ballistic motion.

A second method is an exact synchronous time evolution, an approach which is practical only in one spatial dimension. Particle velocities and positions are initialized on a periodic one-dimensional chain. The collision time for each nearest-neighbor pair is computed and the minimum such time $\tau_{\min}$ is retained. The particles then move ballistically over a time $\tau_{\min}$, so that the particle pair whose collision time equals $\tau_{\min}$ is removed, and the time is incremented by $\tau_{\min}$. The determination of $\tau_{\min}$ and subsequent update of particle positions by this minimum time interval is then iterated.

Our two simulation methods give essentially identical results for continuous velocity distributions and we quote exponent estimates based on the biased random walk algorithm, since it can be applied in both one and two dimensions (Table I). Typically there is a substantial temporal range for which the effective exponent, i.e., the slopes of successive pairs of data points on a double logarithmic scale, is stable, and we adopt the average value of the slope in this range as the exponent estimate. The ac-

TABLE I. Numerical values for the decay exponents α and β based on numerical integration of the Boltzmann equation, Eq. (4), and on Monte Carlo (MC) simulations. Results are given for several representative initial velocity distributions.

Dimension	$P(v,t=0)/c_0$	MC β	MC α	Numerical integration α
1	Uniform	0.22	0.76	0.77
1	$\lvert v\rvert^{-1/2}/4$	0.42	0.56	0.60
1	$\lvert v\rvert^{-4/5}/10$	0.66	0.32	0.37
2	Uniform	0.10	0.89	0.91

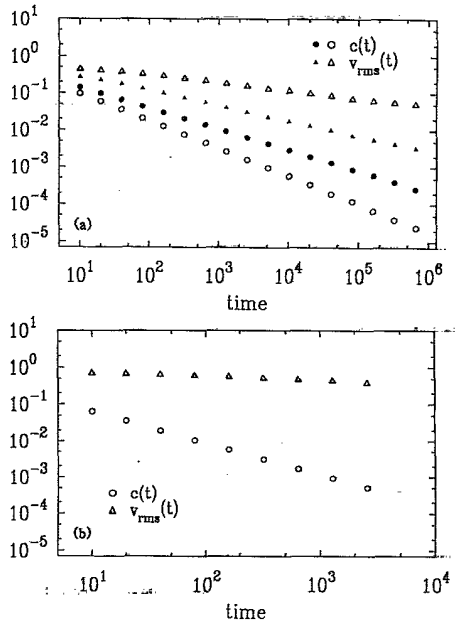

FIG. 1. Representative Monte Carlo simulation results for the concentration and the rms velocity vs time. (a) 50 realizations on a 100000 site ring at initial concentration $c_0 = 0.5$ with a uniform initial velocity distribution (○ and △), and $P(v,t=0) = c_0|v|^{-1/2}/4$ (● and ▲). (b) 100 realizations on a 100 × 100 periodic square lattice with $c_0 = 0.5$ and a uniform initial velocity distribution.

curacy of the simulation can be inferred from the deviation of the numerical estimate for $\alpha+\beta$ from its expected value of unity. The basic conclusion from our numerics is that the decay exponents α and β do indeed depend on the nature of the initial velocity distribution. Notice that the numerical integration of the Boltzmann equation is an excellent approximation for the simulation results. One reason for the success of this latter approach is that there is essentially no velocity correlations beyond nearest-neighbor particles.

The nonuniversality displayed by ballistic single-species annihilation with continuous velocity distributions suggests several interesting avenues for further investigation. One such situation is ballistic annihilation with a trimodal initial velocity distribution, $P(v,t=0) \propto p_+\delta(v-1) + p_0\delta(v) + p_-\delta(v+1)$, with $p_+ + p_0 + p_- = 1$. This system exhibits considerably richer kinetics than that of ballistic annihilation with a bimodal velocity distribution [6,7]. For the symmetric situation of $p_+ = p_- \equiv p = (1-p_0)/2$, numerical simulations reveal a decay which depends nonuniversally on p_0. For $p_0 \to 0$, the density of stationary particles decays as $c^{(0)} \sim t^{-\alpha_0}$, with $\alpha_0 \cong 1$, while the density of mobile particles decays as $c^{(\pm)} \sim t^{-\alpha_\pm}$, with $\alpha_\pm \cong \frac{1}{2}$, as might be expected. However, when the value of p_0 is increased, there is a systematic decrease in α_0 and a corresponding increase in $\alpha_\pm$. When p_0 reaches 0.25, we find $\alpha_0 \cong \alpha_\pm \cong \frac{2}{3}$. For larger values of p_0, $c^{(0)}$ saturates to a finite limiting value while $c^{\pm}$ decays faster than a power law.

Another interesting variation is an initial bimodal velocity distribution with superimposed diffusion (which arises if the bimodal velocity system is simulated by biased random walks). At long times, same-velocity particles can annihilate because of the diffusion. By dimensional analysis, the time-dependent concentration $c(t)$ must be a geometric combination of c_0, $(v_0 t)^{-1}$, and $Dt^{-1/2}$, only. By requiring that $c(t)$ matches with the known limiting behaviors at the appropriate crossover times to the case of no drift [8] and no diffusion [6], we determine that $c(t) \sim t^{-3/4}$. This has been confirmed in MC simulations.

Finally, diffusive single species annihilation with a continuously distributed distribution of diffusion coefficients for each reactant may prove interesting. Rapidly diffusing particles will explore a larger area and should decay more quickly in time. Hence, it is reasonable to assume that the average diffusion coefficient of the surviving particles will decay as $\langle D \rangle \sim t^{-\beta}$. When used in an estimate of the mean collision time between particles, this gives the exponent relation $2\alpha/d + \beta = 1$. Based on the corresponding behavior observed in ballistic reactions, we anticipate that variable exponents α and β may also occur for reactions where the particles possess continuously distributed diffusion coefficients.

In summary, ballistic annihilation with general particle velocity distributions exhibits a rich variety of decay kinetics. Numerical and analytical approaches indicate nonuniversality in the exponents that describe the time dependence of the concentration and the typical velocity. An approximate theory, based on a mean-field Boltzmann equation, successfully accounts for the dependence of these exponents on the initial velocity distribution. It is intriguing that an initial velocity distribution with a large component of slower particles gives a weak decay of the concentration and relatively faster decay of the typical velocity. As the spatial dimension is increased, the "transparent" limit $\alpha = 1$ is approached but apparently never reached.

We gratefully acknowledge the ARO, NSF, and CONACYT for partial support of this research.

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