Decay Kinetics in Ballistic Annihilation

E. Ben-Naim, S. Redner
Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215

F. Leyvraz
Instituto de Fisica, Laboratorio der Cuernavaca, UNAM, MEXICO

We study the kinetics of ballistic annihilation, $A+A\to 0$, 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. This non-universal behavior is confirmed numerically in one and two dimensions.

PACS. Numbers: 68.70+w, 03.20.+i, 05.20.Dd, 05.40.+j

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.

A number of interesting results have been recently reported for the kinetics of irreversible aggregation, $A_i + A_j \to A_{i+j}$, 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 processes such as the coalescence of fluid vortices [4] and planet formation by accretion [5]. For the ballistic aggregation model, a scaling argument suggests that the concentration of aggregates decays as $t^{-\alpha}$, with $\alpha=2d/(d+2)$, where d is the spatial dimension [2]. This dimension dependence for all d 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 predictions of the scaling argument [3].

Motivated in part by these intriguing features, we investigate the decay kinetics of the more elementary single-species annihilation process, $A+A\to 0$, for arbitrary continuous initial velocity distributions. We find that the decay of the density depends non-universally on the initial velocity distribution. A Boltzmann equation for the evolution of the velocity distribution accounts for the dependence of the decay exponent α on the form of the velocity distribution and on the spatial dimension. 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 one-dimensional single-species annihilation with a discrete bimodal initial velocity distribution, $P(v,t=0)\propto p\delta(v-1)+(1-p)\delta(v+1)$, the density decays as $t^{-1/2}$ for $p=1/2$, while the minority velocity species decays exponentially for $p\neq 1/2$ [6]. These results can be inferred by mapping the kinetics onto a first-passage process for a one-dimensional random walk. When the velocities are continuously distributed, this line of reasoning is inadequate to account for the wide range of possible kinetic behaviors.

At time $t=0$, the system consists of identical particles which are distributed in space with $P(v,t)i$ the initial concentration of particles of velocity v. Without loss of generality the average initial velocity can be chosen to be zero. 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, $\langle v^n\rangle^{1/n}=\big(\int dv\, v^n P(v,t)/c(t)\big)^{1/n}$.

A simple power counting argument relates the density decay exponent α 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 $t\sim 1/cv_{\rm rms}r^{d-1}$. If one assumes the following power law forms for the concentration and $v_{\rm rms}$,

$$c\sim t^{-\alpha}\qquad v_{\rm rms}\sim t^{-\beta}, \tag{1}$$

then the mean-free path argument indicates that 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 mean field prediction of $c\sim t^{-1}$ which arises from the naive rate equation $\dot c\propto -kc^2$.

A useful approach for determining the decay kinetics is to write a Boltzmann equation for the time evolution of the velocity distribution. For simplicity, consider the case of one dimension; 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 distribution 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 $v' < v$.

The sum of these two contributions leads to the Boltzmann equation for ballistic annihilation

$$P(x+v\Delta t, v, t+\Delta t) - P(x,v,t) = -kP(x,v,t)\Big[\int_v^\infty \int_{x-(v'-v)\Delta t}^{x} dx'\, P(x',v',t) + \int_{-\infty}^{v} dv' \int_x^{x+(v-v')\Delta t} dx'\, P(x',v',t)\Big], \quad (2)$$

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 the Boltzmann equation, we expand Eq. (1) to first order in Δt to arrive at

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

Since the initial velocity distribution is spatially homogeneous, and because of the homogeneity of the reaction process, we assume that the velocity distribution remains spatially homogeneous. Thus we write $P(v,t)$ to signify the time-dependent and spatially homogeneous concentration of particles with velocity v. This implies that the convective term $\partial P/\partial x$ in the Boltzmann equation may be set to zero, leading to

$$\frac{\partial P(v,t)}{\partial t} = -kP(v,t)\int_{-\infty}^{\infty} dv'\, |v-v'| P(v',t)\,. \quad (4)$$

Thus the $|v-v'|$ dependence of the integral kernel controls the reaction rate between two particles. Eq. (3) is also strongly 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 our analysis of the Boltzmann equation is to apply dimensional analysis, 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

$$P(v,t) = \frac{c_0}{v_0}\left(\frac{t}{t_0}\right)^{\beta-\alpha} f(z), \quad (5a)$$

where the scaling function $f(z)$ depends only on the dimensionless velocity

$$z = \frac{v}{v_0}\left(\frac{t}{t_0}\right)^{\beta}. \quad (5b)$$

Here $t_0 = 1/(kc_0v_0)$ is the initial characteristic time between reactions, with k the dimensionless reaction constant, c_0 the initial concentration, and v_0 the initial rms velocity. Upon substituting this scaling form into Eq. (3), we immediately confirm the exponent relation $\alpha+\beta=1$. Additionally, we obtain a rescaled Boltzmann equation for the scaling function

$$(2\beta-1)f(z) + \beta z f'(z) = -f(z)\int_{-\infty}^{\infty} dz'\, |z-z'|\, f(z'). \quad (6)$$

Notice that this equation is invariant 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 simple differential equation whose solution is

$$f(z) \sim |z|^{(1-2\beta)/\beta} \exp(-|z|/\beta) \qquad |z| \gg 1. \quad (7)$$

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

$$(2\beta-1) + \beta \lim_{z\to 0} z\,(\ln f(z))' = -2\int_0^\infty dz'\, |z'|\, f(z'). \quad (8)$$

Consider an initial velocity distribution with a power-law tail in the small velocity limit, $P(v,t=0) \propto |v|^{\mu}$. Our Monte Carlo simulations (discussed below) reveal that the scaled distribution retains the same power-law form, $f(z) \sim z^\mu$, in the small-z limit. Adopting this form in Eq. (5), then 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 $f(z)$. This moment, in turn, depends on the full details of the velocity distribution. For example, if we take as a trial function $f(z) \propto z^\mu e^{-z/\beta}$ in Eq. (6), *i.e.*, the product of the asymptotic behaviors, we obtain $\beta = \frac{1}{3+2\mu}$. Thus, by tuning β, $\alpha = 1-\beta$ can be set to any value between 0 and 1. This estimate for β manifests the strong dependence of the decay kinetics on the initial conditions. As the velocity distribution contains slower particles the concentration decays slower and conversely, the velocity decays faster. This estimated form qualitatively mirrors values for β obtained by numerical integration of Eq. (3) and on Monte Carlo simulations for various values of μ.

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

$$P(v,t) = \frac{c_0}{v_0}\left(\frac{t}{t_0}\right)^{\beta d-\alpha} f(\vec{z})\,, \quad \text{with} \quad \vec{z} = \frac{\vec{v}}{v_0}\left(\frac{t}{t_0}\right)^{\beta}, \tag{9}$$

where the exponent combination βd originates from an integration over d-dimensional velocity space. The corresponding rescaled equation for $f(\vec{z})$ becomes

$$\big((d+1)\beta - 1\big) f(\vec{z}) + \beta\vec{z}\cdot\nabla f(\vec{z}) = -f(\vec{z})\int_{-\infty}^{\infty} d\vec{z}'|\vec{z}-\vec{z}'|f(\vec{z}'). \tag{10}$$

To determine the relation between the exponents μ and β we again assume a small-z power law form $f(\vec{z}) \propto |\vec{z}|^\mu$, with $\mu > -d$, and a relatively sharp cutoff in $f(\vec{z})$ for large $|\vec{z}|$. When employed in the Boltzmann equation, 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 the case of one dimension, if we adopt $f(\vec{z}) \propto |\vec{z}|^\mu e^{-|\vec{z}|/\beta}$, then we find $\beta = \frac{1}{1+2d+2\mu}$. Conversely, as the spatial dimension increases, β decreases systematically, and the limit $\alpha = 1$ is approached but never reached. This behavior corresponds to the naive rate equation $\dot{c} = -kc^2$. Thus only in the $d = \infty$ limit are particle trajectories sufficiently transparent that the typical velocity does not decrease. This is in contrast to the situation of many diffusion-controlled reactions for which "transparent" behavior occurs for only $d >= d_c$ with d_c finite [1].

To test our approximate analysis, we have performed direct numerical integration of the Boltzmann equations, Eq. (3) and Eq. (5) (Table 1). 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. The integration was performed to 1000 time steps. To estimate the value of β, we computed the "test" scaling function $f(z;t)_{\rm test} \propto t^{1-2\beta_{\rm test}} P(v,t)$ at different times, and adjusted $\beta_{\rm test}$ to achieve the best data collapse between different data sets. We quantitatively made this determination by minimizing the rms deviation between pairs of data sets for which the time differed by a factor of 2. By this method, we obtained estimates for the exponent β with an uncertainty of less than 0.005.

We also performed Monte Carlo simulations for ballistic annihilation in one and two dimensions which are based on two independent approaches. One method simulates the ballistic motion as a biased random. In two dimensions, an particle at $\vec{r}_i$ 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 each occupied site $\vec{r}_i$ at random and the particle is moved by an amount $(\mathrm{sgn}(v_{ix}), 0)$ with probability $|v_{ix}|$ and by an amount $(0, \mathrm{sgn}(v_{iy}))$ with probability $|v_{iy}|$. If a particle lands on an occupied site, both particles are removed from the system. The time is then incremented by the inverse of the current number of particles in the system. The attraction of this stochastic method is that it is easily implemented in any spatial dimension. However, the stochastic nature of the individual particle moves introduces diffusion in addition to the primary ballistic motion. This may lead to a crossover associated with the transition between diffusion and drift in a biased random walk.

Our second method is an exact time evolution by synchronous dynamics, an approach which is restricted to 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 pair collision time $\tau_{\rm min}$ is retained. The particles then move ballistically over a time $\tau_{\rm min}$, so that the particle pair whose collision time equals $\tau_{\rm min}$ is removed, and the time is incremented by $\tau_{\rm min}$. The determination of $\tau_{\rm min}$ and subsequent update of particle positions by this minimum time interval is then iterated.

dimension	$P(v,t=0)/c_0$	MC β	MC α	NI α
1	uniform	0.20	0.77	0.77
1	$\|v\|^{-1/2}/4$	0.42	0.56	0.60
1	$\|v\|^{-4/5}/10$	0.66	0.32	0.37
2	uniform	0.10	0.89	0.91

Table 1 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.

Our two simulation methods give essentially identical results and we quote exponent estimates based on the biased random walk algorithm, since it can be applied in both one and two dimensions (Table 1). The exponents are determined by measuring the slopes of successive pairs of data points when time-dependent quantities are plotted on a double logarithmic scale. Typically there is a non-negligible temporal range for which the value of the slope is most stable, and we adopt the average value of the slope in this range as the exponent estimate. The accuracy 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 are indeed non-universal and depend on the nature of the initial velocity distribution. The numerical integration of the Boltzmann equation also provides an excellent approximation for the simulation results.

The non-universality 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 non-universally 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 $\alpha_\pm \cong 1/2$, 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 $\alpha_0 \cong \alpha_\pm \cong 2/3$. For larger values of p_0, $c^{(0)}$ saturates at a finite limiting value while $c^\pm$ decays faster than a power law.

Another interesting variation is ballistic fusion, $A + A \to A$, in which the collision product takes on the velocity of one of the incident particles according to a specified rule (such as retaining the smaller, or the larger of the two incident velocities). Numerical simulations of this process give results which are distinct from those of the stoichiometrically identical momentum conserving aggregation process.

Finally, it may prove interesting to study single species annihilation for which the diffusion coefficient of each reactant is drawn from a continuous distribution. Particles with a larger diffusion coefficient will explore a larger area and thus may be expected to decay more rapidly in time. Hence, it is reasonable to assume that the average diffusion coefficient of the surviving particles will decay according to the power law $\langle D\rangle \sim t^{-\beta}$. When this is used in an estimate of the mean collision time between particles, one finds the relation $2\alpha/d + \beta = 1$ between the diffusion coefficient decay exponent and the concentration decay exponent. Based on the behavior observed in ballistic reactions, we anticipate that non-universality in α and β may also occur for reactions in which the particles possess continuously distributed diffusion coefficients.

In summary, the kinetics of ballistic annihilation with general distributions of particle velocities exhibits a rich variety of decay kinetics. Both numerical and analytical approaches indicate that there is non-universality 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 Army Research Office and CONACYT for partial support of this research.

[1] See *e. g.*, Ya. B. Zeldovich and A. A. Ovchinnikov, *Chem. Phys.* **28**, 215 (1978);D. Toussaint and F. Wilczek, J. Chem. Phys. **78** 2642 (1983); K. Kang and S. Redner, *Phys. Rev. A* **32**, 435 (1985); G. Zumofen, A. Blumen, and J. Klafter, *J. Chem. Phys.* **82**, 3198 (1985); R. Kopelman, *Science* **241** 1620 (1988); M. Bramson and J. L. Lebowitz, J. Stat. Phys. **65**, 941 (1991); F. Leyvraz and S. Redner, *Phys. Rev. A* **46**, 3132 (1992).

[2] G. F. Carnevale, Y. Pomeau and W. R. Young, *Phys. Rev. Lett.* **64**, 2913 (1990).

[3] Y. Jiang and F. Leyvraz, (to be published).

[4] J. C. McWilliams, *J. Fluid Mech.* **146**, 21 (1984).

[5] G. Wetherill, in *The Formation and Evolution of Planetary Systems* (Cambridge Univ. Press, 1988).

[6] Y. Elskens and H. L. Frisch, *Phys. Rev. A* **31**, 3812 (1985).

[7] However a restricted trimodal aggregation-annihilation process gives essentially the same results as bimodal annihilation (Ref. 2). See, W. S. Sheu, C. Van den Broeck, and K. Lindenberg, *Phys. Rev. A* **43**, 4401 (1991).

FIGURE CAPTIONS

Fig 1 Representative Monte Carlo simulation results for the concentration and the rms velocity vs./ time. (a) An average over 5000 realizations for an initial velocity distribution $P(v,t=0) = c_0|v|^{-1/2}/4$ on a 1000-site lattice at initial concentration $c_0 = 0.3$. (b) An average over 500 realizations for a uniform distribution of velocities on a 100×100 lattice at initial concentration $c_0 = 0.3$.