Correlations in Ballistic Processes

E. Trizac*
Laboratoire de Physique Théorique (UMR 8627 du CNRS), Bâtiment 210, Université Paris-Sud, 91405 Orsay, France

P. L. Krapivsky†
Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA
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We investigate a class of reaction processes in which particles move ballistically and react upon colliding. We show that correlations between velocities of colliding particles play a crucial role in the long time behavior. In the reaction-controlled limit when particles undergo mostly elastic collisions and therefore are always near equilibrium, the correlations are accounted analytically. For ballistic aggregation, for instance, the density decays as $n \sim t^{-\xi}$ with $\xi = 2d/(d+3)$ in the reaction-controlled limit in d dimensions, in contrast with the well-known mean-field prediction $\xi = 2d/(d+2)$.

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Ballistic-controlled reaction processes [1–10] exhibit rich atypical behaviors, e.g., the persistent dependence of decay exponents on the spatial dimension d implying absence of the upper critical dimension; not surprisingly, ballistic-controlled processes proved very challenging to theoretical treatments. The key such process is ballistic aggregation [1] in which particles merge upon collisions so that mass and momentum are conserved (energy is necessarily lost). This model arises in various contents, e.g., it mimics the merging of coherent structures (such as vortices or thermal plumes) and accumulation of cosmic dust into planetesimals [11]. The one-dimensional (1D) version also has an interesting connection with dynamics of shocks representing solutions of the inviscid Burgers equation [12,13]. Ballistic aggregation was first investigated in a pioneering paper [1] by Carnevale, Pomeau, and Young, who argued that basic physical quantities behave algebraically in the long time limit; e.g., the density decays as

$$n(t) \sim t^{-\xi}, \qquad \xi = \frac{2d}{d+2}, \tag{1}$$

in d dimensions. To understand this result, one can use [5] a rate equation $dn/dt = -n/\tau$ for the density. The mean time τ between collisions related to the root mean squared (rms) velocity V, radius R, and density through $nV\tau R^{d-1} \sim 1$. Mass conservation implies that the average mass is $m \sim n^{-1}$. Therefore $R \sim n^{-1/d}$ and

$$\frac{dn}{dt} = -n^2 V R^{d-1} = -n^{1+1/d} V. \tag{2}$$

The particle of mass m is formed from m original particles (we measure mass in units of the initial mass and velocity in units of the initial rms velocity). Assuming velocities of those original particles are uncorrelated, we find that the average momentum p and velocity V scale as

$$p \sim m^{1/2}, \qquad V = p/m \sim n^{1/2}. \tag{3}$$

Plugging (3) into (2) and solving for $n(t)$ yields (1).

Surprisingly, the prediction $\xi = 2d/(d+2)$ for the decay exponent—perhaps the most known result in the field of ballistic-controlled processes—is erroneous. It turns out that the mean-field assumption that velocities of original particles contained within a typical aggregate particle are uncorrelated is incorrect in any finite dimension—only when $d \to \infty$ and velocities are orthogonal to each other with probability one are they indeed uncorrelated. The failure of the mean-field no-correlation assumption (3) has not been appreciated because the resulting formula $\xi_d = 2d/(d+2)$ is correct both for $d = 1$ and $d = \infty$. (No trivial explanation of the former assertion is known, yet the relation to the Burgers equation via the particles⟺shocks mapping [12,13] and the $t^{2/3}$ growth of the separations between adjacent shocks established by Burgers many years ago [12] proved that $\xi_1 = 2/3$.) Since ξ_d monotonously increases with d, it is not surprising that the actual values are not so different from the mean-field prediction (1). Therefore the observed disagreement in two dimensions [7] could be attributed to insufficient scale of the simulations. Interestingly, the beauty of ballistic aggregation in 1D, where the model admits an exact solution [4,8] and exhibits a deep connection to the Burgers equation, has supported the incorrect prediction (1) in higher dimensions.

The purpose of this article is twofold. First, we clarify the role of velocity correlations in the general case, where they lead to significant deviations from mean-field predictions. Second, we propose a procedure that allows an analytical treatment of correlations for virtually any ballistic-reaction process in the reaction-controlled limit; in particular, this method gives exact decay exponents.

The no-correlation assumption is generally wrong for all ballistic-controlled processes, so we first demonstrate this assertion for one particularly simple process. We choose a toy ballistic aggregation model in which all particles are identical, and when two particles moving with velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ collide they form an aggregate

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particle moving with velocity $\mathbf{v} = \mathbf{v}_1 + \mathbf{v}_2$. Compared to the original ballistic aggregation model, the toy model has a number of advantageous properties. First, the volume fraction decays indefinitely, thereby driving the system into the dilute limit and justifying ignoring multiple collisions. Second, the mean-free path n^{-1} grows faster than the interparticle distance $n^{-1/d}$ for $d > 1$. These two features indicate that for $d > 1$ the Boltzmann equation approach is exact at large times.

For the toy model, (2) becomes $dn/dt = -n^2 V$ and the supposed absence of correlations gives $V \sim n^{-1/2}$. Thus, the mean-field argument implies $n \sim t^{-\xi}$ with $\xi = 2$ independently on dimension d. Numerically, we find that this universality does not hold: ξ increases with dimension and approaches the mean-field prediction only when $d \to \infty$. For instance, we find (with an accuracy better than 1%)

$$\xi \approx \begin{cases} 1.33 & \text{when } d = 1, \\ 1.55 & \text{when } d = 2, \\ 1.65 & \text{when } d = 3. \end{cases} \tag{4}$$

These results were obtained by solving the Boltzmann equation describing the toy model

$$\frac{\partial P(\mathbf{v}, t)}{\partial t} = \int d\mathbf{u}\, d\mathbf{w}\, P(\mathbf{u}, t) P(\mathbf{w}, t) |\mathbf{u} - \mathbf{w}|\, \delta(\mathbf{u} + \mathbf{w} - \mathbf{v}) - 2P(\mathbf{v}, t) \int d\mathbf{w}\, P(\mathbf{w}, t) |\mathbf{v} - \mathbf{w}|. \tag{5}$$

We have solved this equation numerically implementing a direct Monte Carlo (DMC) simulation scheme (see, e.g., [14] for the general method, and [9] for an application to a ballistic-controlled reaction process). The idea is to rephrase Eq. (5) as a stochastic process. In each step two particles, for example, with velocities $\mathbf{u}$ and $\mathbf{w}$, are selected at random among a population of N particles, and the reaction happens with a probability proportional to $|\mathbf{u} - \mathbf{w}|$. If the reaction has been accepted, a new particle of velocity $\mathbf{u} + \mathbf{w}$ replaces two original particles, so the number of particles changes to $N - 1$. The time is incremented by $(N^2|\mathbf{u} - \mathbf{w}|)^{-1}$, and the process is iterated again. This numerical scheme allows us to treat systems with an initial number of particles of the order of 10^7. The master equation associated to this Markov chain is precisely (5) so that we obtain the numerically exact solution of our problem. The exponent values (4) significantly differ from the mean-field prediction $\xi = 2$, and leave no doubt that the no-correlation assumption is wrong.

In the Boltzmann Eq. (5), the relative velocity $|\mathbf{v} - \mathbf{w}|$ gives the rate of collisions, and its nonlinear character makes analytical progress hardly possible. An old trick to overcome this difficulty is to replace the actual relative velocity by the rms velocity [15]. This results in the Maxwell model that played an important role in the development of kinetic theory [16,17]. For the toy model, we have (hereafter the dependence on time is suppressed for ease of notation)

$$\frac{1}{V}\frac{\partial P(\mathbf{v})}{\partial t} = \int d\mathbf{u}\, P(\mathbf{u}) P(\mathbf{v} - \mathbf{u}) - 2nP(\mathbf{v}). \tag{6}$$

Integrating (6), we find that the density $n = \int d\mathbf{w}\, P(\mathbf{w})$ satisfies $dn/dt = -n^2 V$, while $nV^2 = \int d\mathbf{w}\, w^2 P(\mathbf{w})$ remains constant. Hence, $V = n^{-1/2}$ and $\xi = 2$ showing that the mean-field no-correlation approach is essentially the Maxwell model in context of ballistic processes [18]. The Maxwell model is an uncontrolled approximation to the Boltzmann equation for the hard-sphere gas and, not surprisingly, the exponents found within this approach are generally erroneous (see [19] for an alternative simplification, the so-called very hard particle approach). Of course, one could anticipate that the exponent $\xi = 2$ characterizes the Maxwell model without computations—the essence of the Maxwell model, that is the fact that collisions are completely random, assures that the no-correlation condition does hold.

We now present an argument that emphasizes the role and importance of correlations between velocities of colliding particles and applies to all ballistic-controlled reaction processes. The key point is to supplement an evolution equation for the mass density by an evolution equation for the density of kinetic energy. For an arbitrary ballistic-controlled reaction process, we denote $P(m, \mathbf{v}, t)$ the joint mass-velocity distribution function, and $e = mv^2$ the kinetic energy of a given particle (for the toy model, we set $m = 1$). The evolution equations for the density n and kinetic energy density $nE = \int mv^2 P(m, \mathbf{v}, t)\, dm\, d\mathbf{v} = n\langle mv^2 \rangle$ read

$$\frac{dn}{dt} = -\frac{n}{\tau}, \qquad \frac{d(nE)}{dt} = -\frac{n\langle \Delta e \rangle_{\mathrm{coll}}}{\tau}. \tag{7}$$

The first equation is just the definition of the time dependent collision frequency; $1/\tau$, the second additionally contains the kinetic energy $\langle \Delta e \rangle_{\mathrm{coll}}$ lost on average in a binary collision. In the scaling regime, the quantities $\langle \Delta e \rangle_{\mathrm{coll}}$ and $E = \langle mv^2 \rangle$ exhibit the same time dependence, so the dissipation parameter $\alpha = \langle \Delta e \rangle_{\mathrm{coll}}/E$ is asymptotically time independent. From Eqs. (7), we get $d\ln(nE)/d\ln n = \alpha$, or $V^2 = nE \sim n^{\alpha}$. The mean-free path argument $\tau^{-1} \sim nVR^{d-1} \sim t^{-1}$ gives $n^{1/d}V \sim t^{-1}$ for ballistic aggregation. Combining these two relations and the definition of ξ, we obtain $\xi = (1/d + \alpha/2)^{-1}$. Similarly for the toy model $nV^2 \sim n^{\alpha}$ and $nV \sim t^{-1}$ leading to $\xi = 2/(1 + \alpha)$.

To use this formalism, we must precisely define the collisional average involved in (7). An average change of a quantity $\mathcal{A}(1, 2)$ in a binary collision is [20]

$$\langle \Delta \mathcal{A} \rangle_{\mathrm{coll}} = \frac{\int d1\, d2 |\mathbf{v}_1 - \mathbf{v}_2|^{\nu} [\Delta \mathcal{A}(1, 2)] P(1) P(2)}{\int d1\, d2 |\mathbf{v}_1 - \mathbf{v}_2|^{\nu} P(1) P(2)}, \tag{8}$$

where we have used shorthand notations $i = (m_i, \mathbf{v}_i)$ and

$di = dm_i d\mathbf{v}_i$ ($i = 1, 2$). In the key case of hard spheres, we have $\nu = 1$, whereas the cases $\nu = 0$ and $\nu = 2$ correspond to Maxwell and very hard particle models [19], respectively. We now illustrate the formalism for the toy model. The kinetic energy lost in a collision is $\Delta e = \mathbf{v}_1^2 + \mathbf{v}_2^2 - (\mathbf{v}_1 + \mathbf{v}_2)^2 = -2\mathbf{v}_1 \cdot \mathbf{v}_2$. Hence,

$$\langle \Delta e \rangle_{\rm coll} = -2 \frac{\int d\mathbf{v}_1\, d\mathbf{v}_2 |\mathbf{v}_1 - \mathbf{v}_2|^\nu (\mathbf{v}_1 \cdot \mathbf{v}_2) P(\mathbf{v}_1) P(\mathbf{v}_2)}{\int d\mathbf{v}_1\, d\mathbf{v}_2 |\mathbf{v}_1 - \mathbf{v}_2|^\nu P(\mathbf{v}_1) P(\mathbf{v}_2)}.$$

For the Maxwell model ($\nu = 0$), the isotropy of $P(\mathbf{v}, t)$ shows that $\langle \Delta e \rangle_{\rm coll} = 0$, so $\alpha = 0$ and $\xi = 2/(1 + \alpha) = 2$ in agreement with our previous calculation. Similarly for very hard particles ($\nu = 2$, see [19]), we use isotropy to simplify α and arrive at

$$\alpha = 2 \frac{\int d\mathbf{v}_1\, d\mathbf{v}_2 (\mathbf{v}_1 \cdot \mathbf{v}_2)^2 P(\mathbf{v}_1) P(\mathbf{v}_2)}{[\int d\mathbf{v}\, \mathbf{v}^2 P(\mathbf{v})]^2}.$$

The isotropy allows one to compute the ratio of the integrals to yield $\alpha = 2/d$ leading to $\xi = 2d/(d + 2)$. For other values of ν, including the case of interest $\nu = 1$, the dissipation parameter α depends on details of the velocity distribution, and isotropy alone is not sufficient to determine α. The reason for the failure of the mean-field argument—which amounts to the complete neglect of collisional correlations ($\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle_{\rm coll} = 0$)—is now clear: In general, a collision involving a pair $(\mathbf{v}_1, \mathbf{v}_2)$ with a negative product $\mathbf{v}_1 \cdot \mathbf{v}_2 < 0$ has a higher probability than a collision with $\mathbf{v}_1 \cdot \mathbf{v}_2 > 0$. The dissipation parameter α is therefore positive so that $\xi = 2/(1 + \alpha) < 2$. Thus, the mean-field prediction $\xi = 2$ is an upper bound for ξ.

The above framework applies to any irreversible process with ballistic transport. For ballistic aggregation, the omission of collisional correlations amounts to setting $\alpha = 1$, i.e., that the typical energy dissipated in a collision is the mean kinetic energy per particle. However, particles with larger velocities undergo more frequent collisions so that the mean energy dissipated exceeds the energy of a typical particle. Hence, $\alpha = \langle \Delta e \rangle_{\rm coll}/E > 1$ so that ξ is smaller than the mean-field prediction $2d/(d + 2)$. Previous molecular dynamics (MD) simulations have shown that $\xi \simeq 0.85 \pm 0.04$ in 2D for low volume fractions, with scaling laws extending over two decades in time [7]. The DMC technique allows one to reach much larger time scales. Figure 1 shows that, after an initial transient, the density exhibits a clear power law behavior over five decades in time. We estimate $\xi \simeq 0.86 \pm 0.005$, in agreement with MD simulations. The inset displays the behavior of $E = \langle mv^2 \rangle$, the quantity that is (asymptotically) time independent according to the mean-field prediction (3); we find $E \sim t^{-0.28}$ [21]. We have also performed DMC and MD simulations in 3D giving $\xi \simeq 1.06 \pm 0.01$. As expected, the actual values of ξ are smaller than the mean-field prediction $\xi = 2d/(d + 2)$ [22].

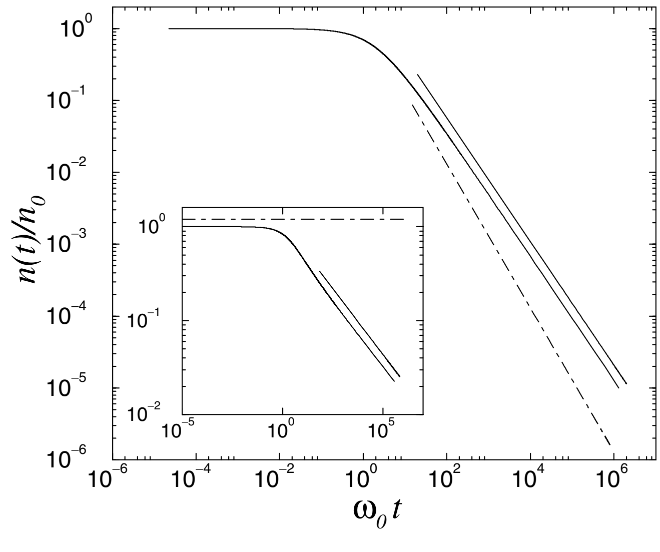

FIG. 1. Density versus time in the 2D aggregation model. The continuous straight line has slope -0.86. The inset shows that the average energy $\langle mv^2 \rangle$ decays as $t^{-0.28}$. Mean-field predictions are shown by the dashed lines (slope -1 in the main graph and 0 in the inset). The nonlinear Boltzmann equation describing ballistic aggregation has been solved by DMC for a system of $N = 4 \times 10^7$ particles. The initial density is n_0, and ω_0 denotes the initial collision frequency of the equilibrium hard sphere fluid.

Ballistic-controlled processes are generally intractable analytically. Following the fruitful line of attack on difficult problems—generalize them—let us consider a process in which colliding particles react with probability ϵ and scatter elastically with complementary probability $1 - \epsilon$. The mean-field no-correlation argument is so general that it applies to these processes; in particular, according to the mean-field the exponent ξ is independent on ϵ. Remarkably, we can now compute the exponent ξ for one special value of ϵ, viz. for $\epsilon \to 0^+$. In this reaction-controlled limit, particles undergo mostly elastic collisions. Therefore, the particles are always at equilibrium, i.e., the velocity distribution is Maxwellian. This key feature makes the problem tractable. Consider, for instance, the toy model. One can compute

$$\langle \Delta e \rangle_{\rm coll} = -2 \frac{\int d\mathbf{v}_1\, d\mathbf{v}_2 |\mathbf{v}_1 - \mathbf{v}_2|^\nu (\mathbf{v}_1 \cdot \mathbf{v}_2) P(\mathbf{v}_1) P(\mathbf{v}_2)}{\int d\mathbf{v}_1\, d\mathbf{v}_2 |\mathbf{v}_1 - \mathbf{v}_2|^\nu P(\mathbf{v}_1) P(\mathbf{v}_2)},$$

for arbitrary ν when $P(\mathbf{v})$ is Maxwellian [23]. In particular, for the important case $\nu = 1$, we obtain $\alpha = 1/d$, so that $\xi = 2d/(d + 1)$. This exact result provides a useful check of numerical scheme (our DMC simulations in two and three dimensions are indeed in excellent agreement with the theoretical prediction). In contrast, the mean-field no-correlation argument predicts $\xi = 2$ irrespective of the value of ϵ. We see again that this is correct only in the $d \to \infty$ limit. Note also that $\xi = 2d/(d + 1)$, which is exact for the reaction-controlled ($\epsilon \to 0^+$) version of the toy model, provides a better "guess" for ξ in the original ($\epsilon = 1$) model than the mean-field approach [compare $\xi = 1$, 4/3 and 3/2 in 1D, 2D, and 3D to the numerical values (4)].

Remarkably, the exponent ξ in the reaction-controlled limit of ballistic aggregation can be computed even though the mass distribution $\Pi(m) = n^{-1} \int d\mathbf{v}\, P(m, \mathbf{v})$ is unknown. The important point is that, when $\epsilon \to 0^+$, the joint mass/kinetic energy distribution function factorizes. Then one finds $\alpha = 1 + 1/d$, or, equivalently, $\xi = 2d/(d+3)$ independently on $\Pi(m)$ [24]. This exact result of course agrees with DMC simulations. Interestingly, it also provides a reasonable approximation of ξ for the original ($\epsilon = 1$) aggregation model: $\xi = 0.8$ in 2D and 1 in 3D, to be compared to 0.86 and 1.06, respectively.

Many other ballistic-reaction processes are solvable in the reaction-controlled limit. For instance, for ballistic annihilation [3], there is no exact solution in any dimension, yet, in the reaction-controlled limit, the exact value of the density decay exponent is given by $\xi = 4d/(4d+1)$. This result is in surprisingly good agreement with numerical values for $\epsilon = 1$: $\xi = 4/5$ vs 0.804 [25] in 1D; $\xi = 8/9 \simeq 0.89$ vs 0.87 [9] in 2D; $\xi = 12/13 \simeq 0.92$ against 0.91 [9] in 3D. We have studied several other ballistic-reaction processes [26]; e.g., a simplified ballistic aggregation model in which mass and momentum are conserved yet the radius does not grow. For this model, the mean-field prediction is $\xi = 2/3$ independently on dimension d, whereas in the reaction-controlled limit, we get the exact result $\xi = 2d/(3d+1)$ (i.e., 0.571 in 2D and 0.6 in 3D). It is again instructive to compare these values with numerical results for $\epsilon = 1$: $\xi \simeq 0.60$ in 2D, and $\xi \simeq 0.62$ in 3D.

We have shown that correlations between velocities of colliding particles govern the behavior of all reacting processes with ballistic transport. We illustrated the importance of correlations on several models and demonstrated that ignoring correlations is equivalent to using the Maxwell model, which is an uncontrolled approximation of the hard-sphere gas. We also devised a procedure that clarifies the role of correlations in the general case and allows an exact computation of decay exponents in the reaction-controlled limit, when particles undergo mostly elastic collisions and therefore are always near equilibrium. The failure of mean-field theory to describe this limit emphasizes the inevitable presence of correlations in all reacting processes with ballistic transport.

*Electronic address: Emmanuel.Trizac@th.u-psud.fr
†Electronic address: paulk@bu.edu

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[19] A way to simplify the kernel $|\mathbf{v} - \mathbf{w}|$ in (5) is to replace it by $(\mathbf{v} - \mathbf{w})^2/V$ [17]. The corresponding particles are called very hard since the collision rate grows faster than for hard spheres. In this case, $dn/dt = -2n^2 V$ and $d(nV^2)/dt = -4n^2V^3/d$ from which $\xi = 2d/(d+2)$. Interestingly, the Maxwell and very hard particle routes, respectively, provide upper and lower bounds for the exact exponent ξ given in (4).
[20] If particles have different radii R_i (in ballistic aggregation, $R \sim m^{1/d}$), the collision kernel in Eq. (7) becomes $(R_1 + R_2)^{d-1}|\mathbf{v}_1 - \mathbf{v}_2|$ for $\nu = 1$, instead of $|\mathbf{v}_1 - \mathbf{v}_2|$ that is valid only when all particles have the same size.
[21] This exponent together with the value $\xi = 0.86$ perfectly fulfills the scaling constraint derived from $\tau \propto t$.
[22] We also estimated ξ directly from α that was computed by measuring the kinetic energy dissipated in successive collisions. Such a route gives accurate values of α from which we deduced the error bars mentioned above for $\xi = (1/d + \alpha/2)^{-1}$. We also mention that the asymptotic regime does not depend on the initial conditions chosen.
[23] The transformation $\{\mathbf{v}_1, \mathbf{v}_2\} \to \{\mathbf{v}_1 + \mathbf{v}_2, \mathbf{v}_1 - \mathbf{v}_2\}$ simplifies the integrals. In the general case, $\alpha = \nu/d$.
[24] To simplify the integrals, we now use the transformation $\{\mathbf{v}_1, \mathbf{v}_2\} \to \{(m_1\mathbf{v}_1 + m_2\mathbf{v}_2)/(m_1 + m_2), \mathbf{v}_1 - \mathbf{v}_2\}$. In the general case, $\alpha = 1 + \nu/d$ implying $\xi = 2d/(d + 2 + \nu)$.
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