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# New Analytic Approach to Multivelocity Annihilation in the Kinetic Theory of Reactions

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A new, exact, analytic approach to multivelocity, one-species, ballistic annihilation in one dimension is proposed. For an arbitrary one-particle initial velocity distribution, the problem can be solved rigorously in terms of the two-particle conditional probability, which obeys a closed nonlinear integro-differential equation. We present a method for solving this equation for an arbitrary discrete velocity distribution. This method is applied to the three-velocity case. The outcome of numerical simulations compares well with our exact results.

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While equilibrium statistical mechanics has reached a rather mature phase, the foundations of nonequilibrium statistical mechanics are far less well understood. Accordingly, the study of simple nonequilibrium models is always very instructive.

Kinetics of diffusion-controlled or ballistically controlled reactions belong to this category. The diffusion-controlled case has received alot of attention during the past years [1–3]. Although very simple in appearance, the reacting systems can have complex and subtle behavior for both homogeneous initial conditions and inhomogeneous ones where reaction-diffusion fronts can be formed [4,5]. Below some upper critical dimension $d_u$, the fluctuations play a crucial role and mean-field-like theories cannot produce an adequate description [6,7]. Only a few analytical results have been obtained for such systems and many conclusions are based on numerical simulations.

A related, but different, class of problems is the one of ballistically controlled reaction. In this case, the reactants move freely and annihilate by pairs on contact. For a one-species problem (particles $A$) the reaction is $A + A \longrightarrow 0$. Such a process can model a recombination reaction in the gas phase or the fluorescence of laser excited gas atoms with quenching on contact; the one-dimensional aspect can be obtained by working in suitable porous media [8].

Let us consider the following situation. At time $t = 0$ the particles are randomly distributed in a $d$-dimensional space, with density $\sigma(0)$. Their velocities are independent random variables characterized by the same distribution $\phi(\vec{v}; t = 0)$. Among numerous questions that can be asked concerning the behavior of this system, two are natural. First, what is the time dependence of the density $\sigma(t)$, and, second, what is the time evolution of the velocity distribution $\phi(\vec{v}; t)$.

This ballistically controlled case has received much less attention than the diffusive one. The pioneering work has been done by Elskens and Frisch [9]. They considered a one-dimensional system, with a two-velocity initial distribution $\phi(v;0) = p\delta(v - c) + (1 - p)\delta(v + c)$. By combinatorial analysis they showed that for the symmetric case $p = 1/2$ the density decays as $\sigma(t) \sim t^{-1/2}$; the velocity distribution remains unchanged. For asymmetric initial distribution, the density relaxes exponentially towards its stationary value. However, this combinatorial approach is restricted to a dichotomic velocity distribution. A related problem has been investigated by Krug and Spohn in the framework of deposition model [10].

For more general velocity distributions (discrete with more than two velocities, or continuous) two types of approaches have been developed. In the first one, Leyvraz and Redner [11,12] have considered an approximation based on the associated Boltzmann equation. By scaling analysis, they showed that for a continuous distribution of the form $\phi(\vec{v};0) = |\vec{v}|^\gamma \theta(c - |\vec{v}|)$ ($\theta$ is the usual Heaviside function) one finds $\sigma(t) \sim t^{-\alpha}$, with $\alpha = (2d + 2\gamma)/(1 + 2d + 2\gamma)$. This result shows that the limit value $\alpha = 1$ obtained from a simple rate equation approach, neglecting the fluctuations, is realized in the limit $d \longrightarrow \infty$. This suggests that the upper critical dimension for this problem is $d_u = \infty$ and, thus, for all finite dimensions the fluctuations play an important role. The rigorous analytical results presented below show that the factorization of the two-particle distribution used in the Boltzmann approach is in contradiction with the annihilation dynamics. It is not surprising that for discrete velocity distributions the predictions of the Boltzmann approximation were found to disagree with the results of the numerical simulations.

The second approach is based on numerical simulations. They are mainly restricted to one-dimensional

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systems [11–13], although a few two-dimensional simulations have been performed. In one dimension, for the trimodal velocity distribution $\phi(\vec{v};0) = p_+\delta(v - c) + p_0\delta(v) + p_-\delta(v + c)$ with $p_+ = p_-$, one finds three different regimes depending upon $p_0$. If $p_0 < 1/4$, one finds that the density $\sigma(v;t)$ of particles with velocity $v = 0, +c, -c$ follows the long time behavior: $\sigma(0;t) \sim t^{-1}, \sigma(\pm c;t) \sim t^{-1/2}$. When $p_0 = 1/4$, $\sigma(0;t) \sim \sigma(\pm c;t) \sim t^{-2/3}$. Finally, for $p_0 > 1/4$, one finds that $\sigma(0;t)$ saturates to a finite stationary value, while $\sigma(\pm c;t)$ decays faster than a power law. Note that the true asymptotic behavior may be difficult to extract from numerical simulations due to the presence of important corrections to scaling.

The aim of this Letter is to present a new exact analytic approach to the multivelocity one-dimensional problem. We would like to stress that it is extremely rare to find an exact solution to a nonequilibrium problem. It is shown that for an initial state with no correlations between the velocities and random spatial distribution, the dynamics of the system is rigorously determined by the conditional probability density $\mu(x_{21}, v_2|0, v_1;t)$: that if, at time $t$, there is a particle at point $x_1$ moving with velocity $v_1$, one finds its right nearest neighbor at distance $x_{21} = x_2 - x_1 > 0$, with velocity $v_2$. This two-particle conditional probability obeys a closed nonlinear evolution equation.

Then, a matrix formalism is introduced, allowing one in principle to solve the equation for an arbitrary initial discrete velocity distribution. This formalism is used to solve explicitly the trimodal symmetric case. The long time limits for the particle density and the velocity distribution are computed. These analytic results confirm the outcomes of numerical simulations. However, our approach gives not only the leading exponents, but also the amplitudes and corrections to scaling. For some particular values of $p_0$, strong corrections to scaling are predicted.

We summarize here the main results showing that, for a large class of initial conditions, the two-particle conditional probability $\mu(x_2, v_2|x_1, v_1;t)$ governs all the dynamics and presents its evolution equation. The density $\mu$ satisfies the normalization condition $\int d2\, \mu(2|1;t) = 1$, where a convenient shorthand notation $j \equiv (x_j, v_j), dj \equiv dx_j dv_j, j = 1, 2, \ldots$, has been used. At the initial moment the particles are supposed to be uniformly distributed in space with no correlations between their velocities. The initial state of the fluid is thus translationally invariant, and each particle has at $t = 0$ the same probability density $\phi(v;0)$ to move with velocity $v$.

The important characteristic of the annihilation dynamics is that only those particles which suffered no collisions are present in the system. Let us denote by $S(v;t)$ the probability that a free trajectory corresponding to velocity $v$ remains unperturbed during the time interval $[0, t]$. This event can occur only if the particle following the trajectory suffered no collision either from the left or from the right. The assumed absence of correlations between the velocities in the initial state implies the product structure

$$S(v;t) = S^L(v;t)S^R(v;t), \tag{1}$$

where $S^L(v;t)$ and $S^R(v;t)$ are the probabilities for the absence of collisions with the left and right neighbors, respectively. The translational invariance makes them independent of the position variable.

A detailed study of the evolution of the probability $S^R(v;t)$ leads to

$$S^R(v_1;t) = \exp\left\{-\int_0^t d\tau \int dv_2\, v_{12}\theta(v_{12})\mu(0^+, v_2|0, v_1;\tau)\right\}. \tag{2}$$

Moreover, for a symmetric initial velocity distribution $\phi(v;0) = \phi(-v;0)$, one finds that

$$S^L(v_1;t) = S^R(-v_1;t) \tag{3}$$

holds. The next step is to find the equation of motion for $\mu(2|1;\tau)$.

In principle, the evolution couples an infinite set of conditional distributions $\mu_s(2, 3, \ldots, s|1;t)$, $s = 2, 3, \ldots$, with $\mu_2(2|1;t) \equiv \mu(2|1;t)$. $\mu_s(2, 3, \ldots, s|1;t)$ represents the probability density for finding at time $t$ the $s - 1$ consecutive right nearest neighbors of particle 1 moving with velocities $v_2, v_3, \ldots, v_s$, respectively, at distances $0 < x_{21} < x_{31} < \cdots < x_{s1}$. At the initial time $t = 0$, the particles are supposed to be uniformly distributed in space with no correlations between their velocities. Thus

$$\mu_s(2, 3, \ldots, s|1;t = 0) = \prod_{j=2}^{s} \mu(j|j - 1;t = 0), \quad s = 3, 4, \ldots. \tag{4}$$

A remarkable property of the dynamical hierarchy resulting from the annihilation process is its compatibility with the factorization of distributions $\mu_s$ for $s > 2$ into products of the basic densities $\mu(j|j - 1;t)$ for all times. This is not an approximation but a rigorous result, as shown in [14]. The infinite hierarchy then becomes equivalent to a single equation for $\mu(2|1;t)$. Using the Laplace transform,

$$\tilde{\mu}(z, v_2|v_1;t) = \int_{0^+}^{\infty} dx\, \exp(-xz)\mu(x, v_2|0, v_1;t), \tag{5}$$

one finds [14]

$$\left\{\frac{\partial}{\partial t} + zv_{21} + \frac{\dot{S}^R(v_1;t)}{S^R(v_1;t)} - \frac{\dot{S}^R(v_2;t)}{S^R(v_2;t)}\right\}\tilde{\mu}(z, v_2|v_1;t) - v_{21}\mu(0^+, v_2|0, v_1;t) = \int dv_3 \int dv_4\, \tilde{\mu}(z, v_3|v_1;t)\tilde{\mu}(z, v_2|v_4;t)v_{34}\theta(v_{34})\mu(0^+, v_4|0, v_3;t), \tag{6}$$

where the dot denotes the time derivative.

Now, we aim at computing the time dependent density $\sigma(t)$ and the distribution $\phi(v,t)$ for a discrete multivelocity distribution. Our method can be generalized to all discrete velocity cases. However, for the sake of simplicity we consider first the case of a three-velocity distribution. We shall sketch below the main steps of the method. A detailed discussion will be given elsewhere [13]. The initial velocity distribution $\phi(v,t=0)$ is given by

$$\phi(v;0) = p_+\delta(v-c) + p_0\delta(v) + p_-\delta(v+c), \quad (7)$$

and we restrict ourselves to the symmetric case $p_+ = p_-$.

The density of particles with velocity $v$ at time $t$, $\sigma(v;t)$, can be written in terms of the survival probability $S(v,t)$ as

$$\sigma(v;t) = \sigma S(v;t)\phi(v;t=0). \quad (8)$$

The survival probability $S(v;t)$ obeys

$$S(+c;t) = S(-c;t) = S^R(+c;t), \quad (9)$$

$$S(0;t) = [S^R(0;t)]^2, \quad (10)$$

with the initial condition $S^R(+c;0) = S^R(0;0) = 1$. These probabilities of absence of collision can then be written in terms of the two-particle conditional probabilities as

$$S^R(+c;t) = \exp\left\{-\int_0^t d\tau[c\,\mu(0^+,0|0,+c;\tau) + 2c\,\mu(0^+,-c|0,+c;\tau)]\right\}, \quad (11)$$

$$S^R(0;t) = \exp\left\{-\int_0^t d\tau c\,\mu(0^+,-c|0,0;\tau)\right\}. \quad (12)$$

There are two key points in our approach. First, the equation of motion for the Laplace transform of the nine possible two-particle conditional probabilities can be put in a matrix form. Let us introduce two matrices $\mathcal{N}$ and $C$ whose matrix elements are given by

$$N_{ij}(z;t) = M_{ij}(z;t) \times \exp\left[-zv_{ij}t + \int_0^t d\tau \sum_{k=1}^{3}[B_{ik}(\tau) - B_{jk}(\tau)]\right], \quad (13)$$

$$C_{ij}(z;t) = B_{ij}(t) \times \exp\left[-zv_{ij}t + \int_0^t d\tau \sum_{k=1}^{3}[B_{ik}(\tau) - B_{jk}(\tau)]\right], \quad (14)$$

where $(i,j = 1,2,3)$

$$M_{ij}(z;t) = \tilde{\mu}(z,v_j|v_i;t), \quad (15)$$

$$B_{ij}(t) = v_{ij}\,\theta(v_{ij})\,\mu(0^+,v_j|0,v_i;t), \quad (16)$$

with $v_1 = +c$, $v_2 = 0$, $v_3 = -c$. The equation of motion (6) can be shown to take the form

$$\frac{\partial}{\partial t}\mathcal{N}(z;t) + C(z;t) = \mathcal{N}(z;t)C(z;t)\mathcal{N}(z;t). \quad (17)$$

The second point is the observation that the matrix $C$ has a specific structure. Only its elements above the diagonal are nonzero. It is this property that allows one to determine the matrix elements of $\mathcal{N}(z;t)$ recursively. The explicit expressions for the matrix elements $M_{ij}(z,t)$ are too cumbersome to be given here [13]. An important point at this stage is that the solution is only implicit: the $\tilde{\mu}(z,v_j|v_i;t)$ are expressed in terms of the densities at contact $\mu(0^+,v_j|0,v_i;t)$. One has still to solve the consistency equations:

$$\mu(0^+,v_j|0,v_i;t) = \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{2i\pi}\,\tilde{\mu}(z,v_j|v_i;t). \quad (18)$$

It is convenient to rewrite the conditions (18) in terms of the survival probabilities. A subtle analysis leads eventually to the condition

$$p_0T^4(z) - (2p_0+1)T^2(z) - 2\left(\frac{z}{c\sigma}+1\right)T(z) + p_0 - 1 = 0, \quad (19)$$

where $T(z) \equiv \int_0^\infty e^{-zt}\dot{S}^R(0;t)\,dt$. The asymptotic regime of the survival probability $\dot{S}^R(0;t)$ can be obtained by considering $T(z)$ in the neighborhood of $z=0$. At $z=0$,

$$T(0) = \int_0^\infty dt\,\dot{S}^R(0;t) = S^R(0,\infty) - 1, \quad (20)$$

and by definition $S^R(0,\infty) \in [0,1]$.

For $p_0 > 0$, three cases have to be distinguished (the formulas correspond to the asymptotic regime $t \longrightarrow \infty$).

(i) $0 < p_0 < \frac{1}{4}$: One finds for the densities

$$\sigma(0;t) = \frac{2p_0}{1-4p_0}\left(\frac{1}{c\pi t}\right)\{1 + \mathcal{O}([1-4p_0]^{-3}t^{-1})\}, \quad (21)$$

$$\sigma(+c;t) = \sqrt{\left(\frac{1}{4}-p_0\right)\frac{\sigma}{c\pi t}}\{1 + \mathcal{O}([1-4p_0]^{-3/2}t^{-1/2})\}. \quad (22)$$

Thus the corrections to scaling become particularly important when $p_0 \longrightarrow \frac{1}{4}$.

(ii) $p_0 = \frac{1}{4}$: One finds for the densities

$$\sigma(0;t) = \frac{\sigma}{4\Gamma^2(2/3)}\left(\frac{2}{c\sigma t}\right)^{2/3} + \mathcal{O}(t^{-1}), \quad (23)$$

$$\sigma(+c;t) = \frac{3\sigma}{8}\left[\frac{1}{3}\left(\frac{2^{1/3}}{\Gamma(2/3)}\right)^2 + \frac{1}{\Gamma(1/3)}\right]\left(\frac{1}{c\sigma t}\right)^{2/3} + \mathcal{O}(t^{-1}). \quad (24)$$

In addition,

$$\lim_{t\longrightarrow\infty}\frac{\sigma(+c;t)}{\sigma(0;t)} = \frac{1}{2} + \frac{3}{2}\frac{\Gamma^2(2/3)}{2^{2/3}\Gamma(1/3)} \simeq 1.15. \quad (25)$$

(iii) $\frac{1}{4} < p_0 \le 1$: One finds for the densities

$$\sigma(0;\infty) \simeq \sigma(2\sqrt{p_0}-1)^2, \quad (26)$$

$$2\sigma(+c;t) \simeq \sigma(0;t) - \sigma(0;\infty) \simeq 2\sigma A e^{-c\sigma ut}(c\sigma t)^{-3/2}, \quad (27)$$

where $A$ and $u$ are known constants [13]. The results of the numerical simulations [12] are in good agreement with our exact results.

Annihilation dynamics creates strong correlations between the velocities of colliding particles, which excludes a Boltzmann-like approximation. Our results show that pairs of nearest neighbor particles have the tendency to align their velocities and propagate in the same direction. This is clearly seen on $\bar{w}(v;t)$, the mean velocity of the nearest neighbor of a particle moving with velocity $v$. Indeed, in the limit $t \longrightarrow \infty$, one finds for $p_0 < \frac{1}{4}$

$$\bar{w}(v;\infty) = \begin{cases} \pm c & \text{if } v = \pm c, \\ (\sqrt{2} - 1)c \, \frac{1-4p_0}{1-2p_0} & \text{if } v = 0, \end{cases}$$

and for $p_0 \geq \frac{1}{4}$

$$\bar{w}(v;\infty) = v(p_0^{-1/2} - 1)\,.$$

In the case of a more general discrete velocity distribution the method for solving the problem is similar to the one of the trimodal case. The problem can again be written in a matrix form and solved recursively [13]. However, the algebra becomes very tedious already for four velocities. The case of a continuous velocity distribution, for which qualitatively different behavior may be expected, is under investigation.

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