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Annihilation kinetics in the one-dimensional ideal gas

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We consider the annihilation reaction $A+A\to 0$ on the real line with an initial equilibrium distribution of particles A (points or rods); the particles move freely before annihilating, with independent initial velocities. For the dichotomic distribution of velocities $P(v=c)=1-P(v=-c)=p$, we determine the fraction $S(t)$ of particles surviving at time t: (1) If $p=\frac{1}{2}$, $S(t)\sim t^{-1/2}$ by a central-limit effect; (2) if $p\neq\frac{1}{2}$, $S(t)\sim |2p-1|+At^{-3/2}\exp(-Bt)$ with known constants A and B. We also determine the asymptotic spatial distribution of surviving particles. From these results we derive some bounds on the decay of $S(t)$ for other velocity distributions, and we compare them to the decay of $S(t)$ for diffusive (Brownian) motion.

I. INTRODUCTION

The dependence of chemical kinetics on the motion of the reacting particles has recently attracted much attention, with the discussion of geometrical and dimensional effects on diffusion-limited reactions in various media.[1–4] As one assumes in these papers that particles move at random before they interact, it seems desirable to determine also how the laws of motion influence the space-time evolutions of the species concentrations. In this article we examine the case of free motion for point particles on the infinite line, with annihilation kinetics $A+A\to 0$; the diffusive analog of this model was solved analytically by Torney and McConnell.[3]

Starting from an initial equilibrium state, in which particles, uniformly distributed, have independent velocities with a common distribution $F(v)$, and assuming that particles immediately annihilate when they meet, what will be the fraction surviving at time t, $S(t)$, and what (nonequilibrium) measure will describe the gas at this time? We discuss these questions for the two-velocity case

$$F(v)=q\chi(v\geq -c)+p\chi(v\geq c),\quad q=1-p$$

with the characteristic function $\chi(A)=1$ if A is true and $\chi(A)=0$ otherwise.

The model is elaborated in Sec. II. In Sec. III we calculate the surviving fraction and the asymptotic spatial distribution of surviving particles for an initial Poissonian distribution in space. These results are generalized in Sec. IV to an arbitrary initial spatial distribution with the renewal property (see Sec. II) and to the case of rodlike particles. In Sec. V we use our results to derive (poor) inequalities for the case of general velocity distributions, but no exact estimate is obtained for the decay of $S(t)$. Conclusions are stated in the final section. We treat the mean-field analog of our model in Appendix A.

II. THE MODEL

At initial time, particles are distributed on the real line with positions x_k and velocities v_k, their label indicating their order. The positions have a Poissonian distribution with density σ and the velocities are independent. This initial distribution forms a *renewal process,* viz. the whole distribution to the right of particle k is independent of the whole distribution to its left, and this renewal process is translation invariant (thus homogeneous). As particles cannot cross each other's trajectories, this remains true during the annihilation process, and the distribution to the right of a surviving particle (k) is completely characterized by the distribution function

$$Q(x,v,t\mid v')=P(x_{R_k(t)}(t)-x_k(t)<x \text{ and } v_{R_k(t)}<v\mid v_k<v')$$

for the distance x and velocity v of the first neighbor (at time t) to the right of a particle moving at a smaller velocity than v'. Here $R_k(t)$ is the index of the first surviving particle to the right of particle k, and $x_k(t)=x_k+v_kt$. Of course Q vanishes if $x\leq 0$.

At initial time

$$Q(x,v,0\mid v')=G_0(x)F(v)\ ,$$

where $G_0(x)=P(x_{k+1}-x_k<x)$ and $F(v)=P(v_k<v)$. At later times, other functions of interest (derived from Q) are the *survival probability* $S(t;v)$ for particles with given velocity v, and its average $S(t)=\int_{-\infty}^{\infty}S(t;v)dF(v)$. In our case, $S(t)$ completely determines $S(t;\pm c)$ by the sum rules

$$pS(t;c)+qS(t;-c)=S(t)\ ,$$

$$pS(t;c)-qS(t;-c)=p-q\ .$$

N.B., by symmetry, we need only to consider the cases $p \geq \frac{1}{2}$ through the computations.

III. THE POISSONIAN CASE

A. Annihilation dynamics

With the dichotomic velocity distribution, a particle can annihilate only a particle moving with the opposite velocity. Thus, if particle $k=0$ has velocity $v_0=c$, it annihilates with a particle k' coming from its right; and all particles between them must already have disappeared. We decompose the evaluation of the survival probability $S(t;c)$ into two operations.

If particle $k=0$ has velocity c, denote by a_k the probability that it finally annihilates with particle $k\,(>0)$. As $a_k=0$ if k is even, let $a_{2n+1}=qb_n$: b_n is the probability that all particles $(1 \leq k \leq 2n)$ annihilate each other, with $b_0=1$. But the particle $k=1$ annihilates the particle $k=2m$ with probability pqb_{m-1}. Summing over all possibilities ($m=1$ to n) gives a recursive relation for b_n, $n \geq 1$,

$$b_n = \sum_{m=0}^{n-1} p(qb_m)b_{n-m-1} \,.$$

Introducing the generating function

$$B(s) = \sum_{n=0}^{\infty} b_n s^n$$

yields

$$B(s) = \frac{1-\sqrt{1-4pqs}}{2pqs}, \quad b_n = (pq)^n \frac{(2n)!}{n!(n+1)!} \,.$$

The final survival probability for a particle with velocity c and the average surviving fraction are thus

$$S(\infty;c) = 1 - \sum_{n=0}^{\infty} qb_n = \begin{cases} 0 & \text{if } p \leq \frac{1}{2} \\ (p-q)/p & \text{if } p \geq \frac{1}{2} \end{cases}$$

$$S(\infty) = |p-q| \,.$$

Annihilation for two particles separated by an initial distance x occurs at $t=x/2c$. The survival probability $S(t;c)$ at time t is thus

$$S(t;c) = \sum_{n=0}^{\infty} a_{2n+1} P(x_{2n+1} - x_0 \geq 2ct)$$

and for the initial Poisson distribution

$$P(x_{2n+1} \geq x) = \int_x^{\infty} \frac{e^{-\sigma y}}{(2n)!} (\sigma y)^{2n} \sigma dy \,.$$

Hence

$$S(t;c) = 1 - \sqrt{q/p} \int_0^{2ct} e^{-\sigma y} I_1(2\sqrt{pq}\,\sigma y) \frac{dy}{y} \,,$$

with I_1 the modified Bessel function. The total surviving fraction is

$$S(t) = 1 - 2\sqrt{pq} \int_0^{2ct} e^{-\sigma y} I_1(2\sqrt{pq}\,\sigma y) \frac{dy}{y} \,.$$

For short times, $S(t) \simeq 1 - 2pq\sigma ct + \cdots$, while for long times it decays to $|p-q|$.

If $p=\frac{1}{2}$, the integral is calculated analytically and shown in Fig. 1:

$$S(t) = S(t;\pm c) = e^{-2\sigma ct}[I_0(2\sigma ct) + I_1(2\sigma ct)] \,.$$

The asymptotic empty state is attained at an algebraic rate:

$$S(t) \simeq (\pi\sigma ct)^{-1/2} + \cdots$$

which can be motivated by a central-limit argument: $S(t)$ is grossly determined by the imbalance between particles of the two "velocity species" in an interval of size $2ct$; as the initial distribution is independent, with density σ, this imbalance is of order $(2\sigma ct)^{1/2}$ for a population of order $2\sigma ct$.

If $p > \frac{1}{2}$, the density of majoritarian particles does not decay to zero, so that particles with $v=-c$ more easily find their annihilation companion (Fig. 2):

$$S(t) - S(\infty) \simeq (pq)^{1/4} \frac{e^{-2r\sigma ct}}{\sqrt{8\pi r}} (\sigma ct)^{-3/2} \,,$$

with $r = 1 - 2\sqrt{pq}$. Note that, with the long-time behavior of the annihilation rate $-dS/dt$ being nonuniform with respect to p, this asymptotic form of $S(t)$ does not converge to the inverse-square expression as $r \to 0$ (i.e., $p \to \frac{1}{2}$).

These asymptotic decays do not depend on the Poissonian nature of the initial spatial distribution (see Sec. IV): they arise from the purely combinatorial problem of determining the annihilation companion's index k—its actual initial position having expectation $k\sigma^{-1}$ and variance $k\sigma^{-2}$.

B. The spatial distribution of surviving particles

The distribution of particles at any time t forms a renewal process in space, characterized by the functions

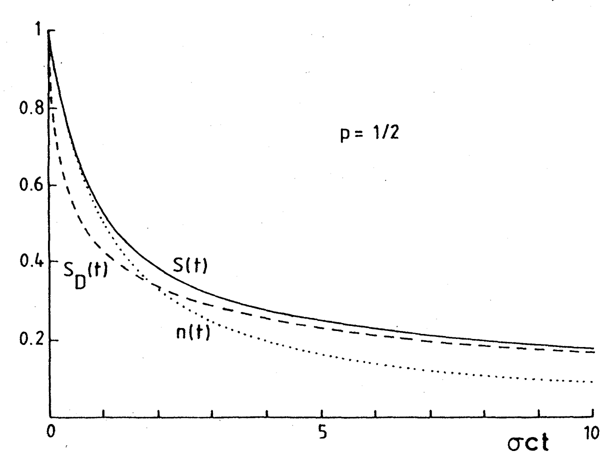

FIG. 1. Surviving fraction as a function of time in the balanced case ($p=\frac{1}{2}$). The dotted line corresponds to the mean-field model; the broken line to the Brownian motion of Torney and McConnell (Ref. 3) with coefficient $D=c/\sigma$.

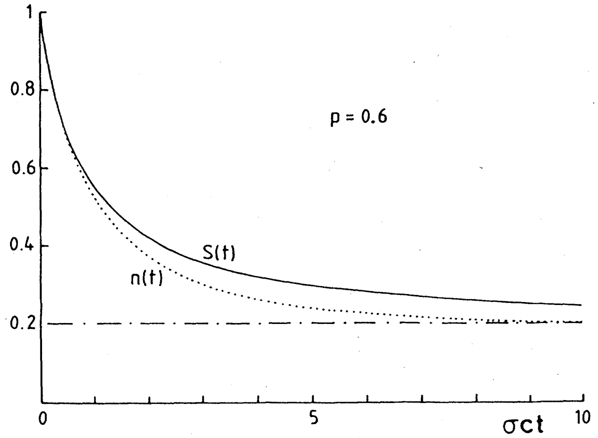

FIG. 2. Surviving fraction as a function of time in the unbalanced case ($p \neq \frac{1}{2}$). The dotted line is the mean-field solution; the broken-dotted line is the asymptote. This function also determines the asymptotic spatial distribution (Secs. III B and V).

$Q(x,v,t \mid v')$. With the dichotomic distribution $F(v)$ we prefer the densities

$$g(x,v,t;v') = \frac{d}{dx} P(x_{R_k(t)}(t) - x_k(t) \leq x \text{ and } v_{R_k(t)} = v \mid v_k = v')$$

for the two velocities $v' = \pm c$. Of course, $g=0$ if $x<0$.

The initial spatial distribution has no correlations:

$$g(x,c,0;v_0) = p\sigma e^{-\sigma x} ,$$

$$g(x,-c,0;v_0) = q\sigma e^{-\sigma x} ,$$

for both values of v_0. If the spatial distribution remained Poissonian, $g(x,v,t;v')$ would exhibit the same form with density $\sigma S(t)$ and probabilities $pS(t;c)/S(t)$ and $qS(t;c)/S(t)$. This in turn would justify the mean-field picture, which we show in Appendix A to be wrong.

The functions $g(x,c,t;v_0)$ can be determined by arguments similar to those for $S(t;c)$; here we shall only give the asymptotic functions $g(x,v,\infty;v')$. Then $g(x,v,\infty;v_0)=0$ for any x,v,v_0 if $p=\frac{1}{2}$.

For $p > \frac{1}{2}$, $g(x,v,\infty;-c)$ is irrelevant and $g(x,-c,\infty;c)=0$: the first right neighbor of particle 0 (with $v_0=c$) at $t=\infty$ also moves at c. Now, particle k becomes the first right neighbor of particle 0 at $t=\infty$ if and only if it survives and all intermediate particles annihilate:

$$P(R_0(\infty)=k) = \frac{S(\infty;c)}{S(\infty;c)} \frac{p}{q} a_k ,$$

where we divided by the survival probability of particle 0 which conditions the statement. Moreover, the distance between the particles moving at c is constant and equals $2c$ times the time it would have taken them to annihilate if they had had opposite velocities:

$$g(x,c,\infty;c) = -\frac{1}{4qc}\frac{dS}{dt}(t) = \left[\frac{p}{q}\right]^{1/2} \frac{e^{-\sigma x}}{x} I_1(2\sqrt{pq}\,\sigma x) .$$

For this spatial distribution:

$$\sigma\langle x\rangle = (p-q)^{-1} ,$$

$$\sigma^2\langle \delta x^2\rangle = (p-q)^{-3} .$$

The average interparticle distance at $t=\infty$ must be the inverse surviving density. The variance $\langle \delta x^2\rangle$ indicates a departure from the Poissonian distribution inversely proportional to the imbalance $p-q$. Indeed the chances for a particle to survive are enhanced if it is preceded by particles with the same velocity: this larger variance denotes the presence of clusters and holes in the asymptotic distribution of comoving (surviving) particles.

IV. OTHER INITIAL CONDITIONS

Our combinatorial arguments apply equally well to any distribution of the initial interparticle distances, provided the spatial distribution remains a renewal process:

$$g(x,c,0;v_0) = h(x)p ,$$

$$g(x,-c,0;v_0) = h(x)q ,$$

for $v_0 = \pm c$. Actually $h(x)$ and g may even be singular as long as $h(x)dx$ defines a probability measure on $[0,\infty]$, with a finite expectation $\bar{x} = \sigma^{-1}$. We denote by $H(w)$ the Laplace transform of h:

$$H(w) = \int_0^\infty e^{-wx} h(x)dx .$$

The surviving fraction is then

$$S(t) = 1 - \int_0^{2ct} \tilde{h}(x)dx$$

and the asymptotic spatial distribution is

$$g(x,c,\infty;c) = \frac{\tilde{h}(x)}{2q} ,$$

where $\tilde{h}$ has the generating function

$$\tilde{H}(w) = \sum_{n=0}^{\infty} 2pq b_n H^{2n+1}(w) = \frac{1-(1-4pqH^2)^{1/2}}{H} .$$

The moments of $\tilde{h}(x)$ and its behavior for large x are deduced from this expression in Appendix B. In particular, the asymptotic decay of $S(t)$ assumes the same form for any initial distribution $h(x)$:

if $p=\frac{1}{2}$: $S(t) \simeq (\pi\sigma c t)^{-1/2} + \cdots$

if $p>\frac{1}{2}$: $S(t) \simeq |p-q| + \left[\frac{pq\alpha}{4\pi r^2 c^3 t^3}\right]^{1/2} e^{-2r\sigma c t} + \cdots$

with h-dependent constants σ, α, and r. This was expected since the asymptotic decay of $S(t)$ mainly depends on the combinatorial properties of the initial distribution of left- and right-moving particles.

Extending our results to hard rods is formally trivial. Let d be the diameter of the rods and $g(x,v,t;v_0)$ be the center-to-center spatial function. Then $g(x,v,t;v_0)$ and the initial function $h(x)$ vanish if $x<d$. On the other hand, annihilation is assumed to occur immediately on contact:

$$S(t)=1-\int_0^{2ct+d}\tilde{h}(x)dx ,$$

where $\tilde{h}$ is the same function as for $d=0$. For an initial Poissonian distribution (with the excluded volume effect $\bar{x}=\sigma^{-1}+d$):

$$h(x)=\sigma e^{-(x-d)\sigma}\chi(x>d) ,$$

$$H(w)=\frac{e^{-wd}}{1+w/\sigma} ,$$

$$H(w)=\left[1+\frac{w}{\sigma}\right]e^{wd}-\left[\left[1+\frac{w}{\sigma}\right]^2 e^{2wd}-4pq\right]^{1/2} .$$

For any renewal initial distribution with finite expectation, the decay of $S(t)$ is clearly the same as for the point particles—up to a shift of t by $d/2c$.

V. NONDICHOTOMIC VELOCITY DISTRIBUTIONS

For a general velocity distribution, the annihilation companion cannot be determined by our combinatorial arguments. But we can use them to derive estimates of the annihilation rate: if the velocity distribution function $F(v)$ is such that $P(v_0c<v<v_0+c)=0$ for some $v_0\in\mathbb{R}$, $c>0$, let

$$p=P(v\geq v_0+c),\quad q=P(v\leq v_0-c) .$$

The annihilation proceeds more slowly for the dichotomic distribution F_2 with parameters c and $p=1-q$ than for the actual distribution F. Therefore

$$\int_{-\infty}^{v_0-c} S_F(t;v)dF(v)\leq qS_{F_2}(t;-c) ,$$

$$\int_{v_0+c}^{\infty} S_F(t;v)dF(v)\leq pS_{F_2}(t;c) ,$$

$$S_F(t)\leq S_{F_2}(t) .$$

The case of continuous distributions is, however, not covered by these considerations.

VI. CONCLUSIONS

For the dichotomic distribution with $p=\frac{1}{2}$, the surviving fraction decays asymptotically like $t^{-1/2}$ as it does when the particles have a Brownian motion.[3] But here the decay results from a central limit effect, while in the diffusive case it would rather be related to the scaling connection of lengths with time. Furthermore, the asymptotic decay proved very sensitive to the actual velocity distribution, exhibiting an exponential behavior for $p\neq\frac{1}{2}$. A further study of nondichotomic (especially continuous) velocity distributions is very desirable to complete our understanding of these one-dimensional reaction dynamics.

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APPENDIX A: THE MEAN-FIELD EQUATIONS

The macroscopic analog of our model is a two-species annihilation kinetics described by two densities n_+, n_-, with the rate equations

$$\dot{n}_+(t)=\dot{n}_-(t)=-cn_+n_-$$

and the rate constant c. These densities play a role similar to $\sigma pS(t;c)$ and $\sigma qS(t;-c)$ and may be considered as a mean-field description of our model.

With the initial conditions $n_+(0)=\sigma p$ and $n_-(0)=\sigma q$, one finds if $p\neq\frac{1}{2}$,

$$n_\pm=\frac{n_\pm(p-q)\sigma}{2} ,$$

$$n(t)=\sigma(p-q)\frac{pe^{2\sigma ct(p-q)}+q}{pe^{2\sigma ct(p-q)}-q} ,$$

and if $p=\frac{1}{2}$,

$$n_+=n_-=\frac{\sigma}{\sigma ct+2} .$$

These expressions have the same asymptotic values as $\sigma pS(t;c)$ and $\sigma qS(t;-c)$, to conform with the sum rules, but they decay at faster rates because no retardating effect (such as cluster formation) is admitted in the mean-field picture. In a mean-field system, the spatial distribution would always be Poissonian, with decaying densities $n_\pm(t)$.

APPENDIX B: ASYMPTOTIC BEHAVIORS

The asymptotic evolution of the surviving fraction $S(t)$ and the density $\tilde{h}(x)$ are determined by the small-w behavior of the Laplace transform $\tilde{H}(w)$. Since $\bar{x}=\int_0^\infty xh(x)dx<\infty$, one has

$$H(w)=1-\bar{x}w+o(w) .$$

If $p=\frac{1}{2}$, elementary algebra yields

$$\tilde{H}(w)=1-(\bar{x}w)^{1/2}+o(w)^{1/2}$$

with $\sigma=\bar{x}^{-1}$.

For $p>\frac{1}{2}$, the asymptotic behavior of $S(t)$ depends on the branch-point singularity of H located at $w=r$:

$$\tilde{H}(w)=\sqrt{2pq}-(8pq\alpha)^{1/2}(w-r)^{1/2}+o(w-r)^{1/2}$$

where r and α are such that

$$H(r)=\frac{1}{2\sqrt{pq}} ,$$

$$2\sqrt{pq}\,H(w)=1-\alpha(w-r)+o(w-r) .$$

The moments of the asymptotic spatial distribution $g(x,c,\infty;c)$, i.e., the derivatives $\langle x^n\rangle=\tilde{H}^{(n)}(0)/2q$, are easily expressed in terms of $\overline{x^n}=H^{(n)}(0)=\int_0^\infty x^n h(x)dx$:

$$\langle x\rangle=\frac{\overline{x}}{p-q} ,$$

$$\langle x^2\rangle-\langle x\rangle^2=\frac{\overline{x^2}-\overline{x}^2}{p-q}+\frac{4pq}{(p-q)^3}\overline{x}^2 .$$

The relation between H and $\tilde{H}$ makes clear that the asymptotic moment $\langle x^n\rangle$ exists only if the initial moment $\overline{x^n}$ does.

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