Two-species annihilation in three dimensions: a numerical study

1992 J. Phys. A: Math. Gen. 25 3205

(http://iopscience.iop.org/0305-4470/25/11/026)

J. Phys. A: Math. Gen. 25 (1992) 3205–3212. Printed in the UK

Two-species annihilation in three dimensions: a numerical study

F Leyvraz

Instituto de Física, UNAM, Laboratorio de Cuernavaca, Apdo. postal 20–364, Mexico

Received 25 June 1991, in final form 6 Feburary 1992

Abstract. Two-species diffusion-limited annihilation in less than four dimensions is well known to have a concentration decaying as $t^{-d/4}$, as opposed to the rate equation result of t^{-1}. This result had not, however, been demonstrated numerically in three dimensions, due to very strong transient effects. A variant of the model is proposed here, and is shown to reach the exactly known asymptotic behaviour in numerically accessible times. This also allows one to investigate open questions in this system with some certainty that the results are indeed asymptotic. In particular, it is shown that the distance between two particles of the same species scales identically to the distance between particles of different species. This is in contradistinction to recent (numerical and scaling) results in one and two dimensions. Some evidence is also presented that, contrary to previous suggestions, the domains formed in three-dimensional two-species annihilation are indeed regular objects with smooth interfaces.

1. Introduction

Diffusion-limited two-species annihilation has been studied in great detail in the last ten years. This is mainly due to the discovery [1] that for space dimension d less than four, this system can form a structure of A- and B-rich domains, due to the fact that diffusion is not strong enough to destroy the correlations induced by the reaction. A very simple scaling argument [1–2] was presented to show that, for the case of equal initial concentrations of A and B, the concentration $c(t)$ of either species behaves as

$$c(t) \propto \sqrt{c(0)}(Dt)^{-d/4} \tag{1.1}$$

where D is the diffusion constant. This differs from the rate-equation prediction for large times in three important respects. Firstly, the decay law at large times is different in the two cases. Secondly, the basic time scale is set by the diffusion constant and not by any reaction rate. Thirdly, the rate equations predict that there is no asymptotic dependence on the initial concentration $c(0)$, contrary to equation (1.1). All these predictions have been amply verified numerically in one and two dimensions as well as on fractals [2–5] and finally proved rigorously by Lebowitz and Bramson [6] for any d less than four.

The numerical situation in three dimensions is far from clear, however. In fact, there cannot be said to exist any compelling evidence for a decay as $t^{-3/4}$. In view of the rigorous results of Lebowitz and Bramson, this might seem to be a rather technical issue. Nevertheless, it is of some importance for practical reasons. To give but one

0305-4470/92/113205+08$04.50

example, it was recently realized [7] that the distance d_{AB} between two particles of different species could scale differently from the interparticle distance d_{AA} between particles of the same species. More specifically, it was shown by scaling arguments that in one dimension

$$d_{AB} \propto (Dt)^{3/8} \tag{1.2}$$

whereas d_{AA} varies as $(Dt)^{1/4}$. In two dimensions, the argument is somewhat more involved. Nevertheless, together with numerical evidence, a very good case can be made for the claim that d_{AB} grows as $t^{1/3}$. In three dimensions, however, the question remains entirely open. This is due to the fact that the scaling arguments require additional hypotheses concerning the domain interfaces which are, at the very least, questionable in three dimensions. Thus one requires some form of numerical simulation to determine the time dependence of d_{AA} and d_{BB}. But in order to be reliable, such a simulation should first be able to reproduce the exactly known results of the decay of concentrations, otherwise there must always be some doubt as to whether one is indeed in the asymptotic regime. This, however, is precisely what no simulation up to now has been able to do.

In the next section, I shall present a slight variation on the standard lattice model for two-species annihilation. This model is rather more strongly reactive than the usual one, so that deviations from the rate equations predictions are stronger and become noticeable more quickly. On the other hand, this model is subject to stronger finite-size effects than the usual one, so that especially large amounts of memory are required for these simulations. I shall show the results of a simulation on a cubic lattice with L equal to 200, which will be seen to be in excellent agreement with the theoretical predictions summarized above. In section 3, I shall show for the same simulations the results for the interparticle distances d_{AA} and d_{AB}. Both of these will be seen to grow in an identical way, and approximately as $t^{1/4}$, in contrast to the one- and two-dimensional cases. I also compute the number of nearest-neighbour AB pairs and show that their decay is consistent with a picture of compact domains with regular interfaces (i.e., the surface of these domains grows as the square of the radius). A scaling argument is given to argue that these findings are indeed consistent.

2. The model

The following is a very minor modification of the model originally described in [2]. I start with a lattice having an exactly equal number of A and B particles. The vast majority of runs were performed starting with a completely filled lattice, but runs with initial lattice fillings down to 0.1 were also performed. At each time step, one particle is chosen at random and its neighbours are checked. If there are any neighbours capable of reacting with the particle, one of them is chosen at random and the two are annihilated. If not, then a lattice direction is chosen at random and the particle attempts to move in this direction. If the new site does not contain any particles, the particle is moved to that site, otherwise nothing whatever happens. This last is to ensure that no site is ever occupied by more than one particle, a feature which simplifies the programming. This procedure introduces hard-sphere correlations between the particles. These are expected to become negligible in the relevant regime of small concentrations. The model originally used had all the same

characteristics, except that the rules for moving the particles were chosen slightly differently: a particle was first chosen at random, then moved in a random direction, and only if it then coincided with a particle of the opposite species did it react. If it coincided with a particle of the same species, the move was not performed. Thus, the difference between the two models is most aptly summarized as follows: if one thinks of the particles as having a given radius and reacting upon contact, then it may be said that the usual model uses particle of radius zero, whereas my variation consists of using a radius of half a lattice spacing.

The only significant difference to the original model is therefore that particles are more reactive. Thus the relative importance of the effects of diffusion are likely to be enhanced. This modification could be pursued further, for example, to include reactions to next-nearest neighbours. It is doubtful that this would improve matters, as finite-size effects would then become dominant. In the present model, they are already quite strong. The exact reason for this is not quite clear to the author.

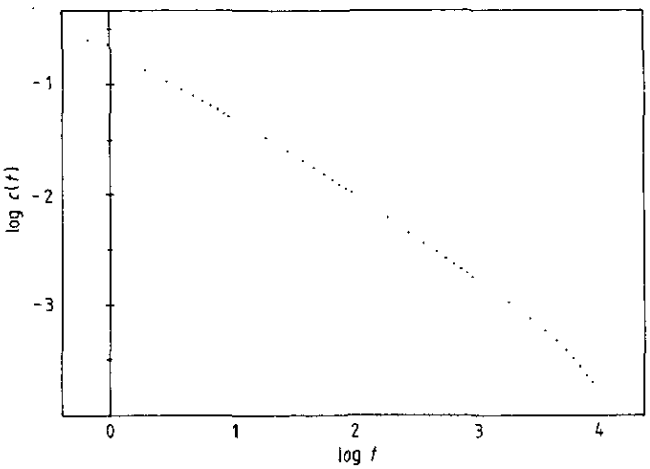

Figure 1. Plot of $\log c(t)$ versus $\log t$. The initial concentration is one (filled lattice). The slope is 0.75 within error.

The results for the $c(t)$ for a completely filled lattice are shown in figure 1 and figure 2. These correspond to ten runs on a lattice 200 on a side. The computations were performed on an Apollo 10000 and required typically of the order of ten hours of CPU time. (This performance could be considerably improved on any machine with sufficiently large memory. I was forced to resort to costly 'tricks' for the lattice to fit into memory.) In figure 1, one sees a fairly large power-law regime (extending approximately from $t = 30$ to $t = 1000$). The data show little scatter on this double logarithmic plot and therefore the fit to a decay of $t^{-3/4}$ is rather convincing. In figure 2, I have plotted $t^{\alpha}c(t)$ against $\log t$ for different values of α. This biased plot shows clearly the amplitude of the noise and indicates that the value of α equal to 0.75 yields a fairly horizontal line between $t = 30$ and $t = 1000$, whereas the values of α equal to 0.73 or 0.77 do not. It therefore seems that this model yields a $t^{-3/4}$ decay, as expected from the exact results of Bramson and Lebowitz. From these results, it is reasonable to conclude that the exponent for the decay of $c(t)$ is, to be conservative, equal to 0.75 ± 0.02, since the exponents limiting this range already show clear signs of not representing the asymptotic behaviour. An analysis of successive slopes confirms these confidence limits.

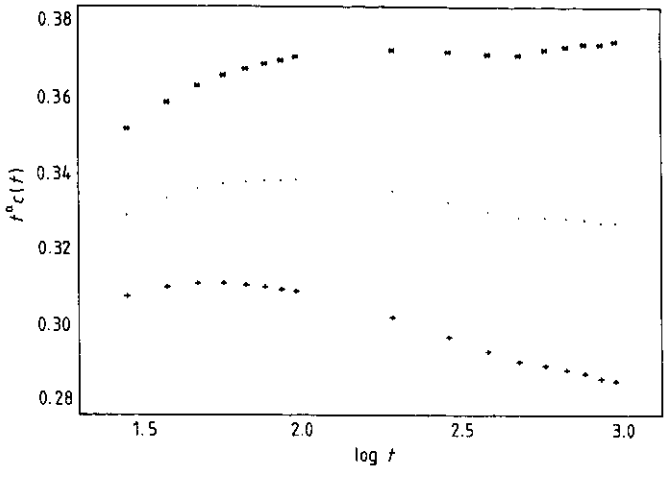

Figure 2. Same data as in figure 1, but replotted as $t^{\alpha}c(t)$ as a function of $\log t$ for the following values of α: points, $\alpha = 0.75$; crosses, $\alpha = 0.73$; and stars, $\alpha = 0.77$. It appears that the exponent $3/4$ gives the closest fit to a horizontal line.

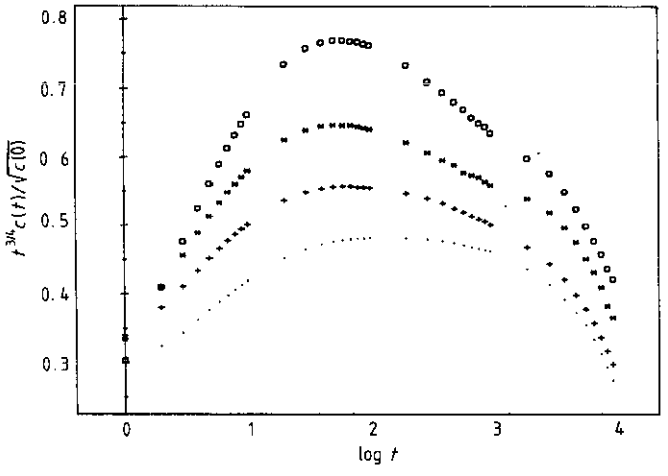

Figure 3. Plot of $t^{3/4}c(t)/\sqrt{c(0)}$ against $\log t$ for $c(0)$ equal to 1 (points), 0.2 (crosses), 0.1 (stars) and 0.05 (open circles). None of these except the first is truly asymptotic, but the convergence to a common value indicates that the $\sqrt{c(0)}$ is at least approximately valid.

It does not appear likely that it would be possible to test that the time scale is indeed set by the diffusion constant D, since it was already necessary to make this model as reactive as possible in order to reach the asymptotic behaviour for the concentration. On the other hand, there is no reason to expect any difficulty in testing the dependence on $c(0)$, which is another of the characteristics predicted by the scaling theory, but not borne out convincingly by numerical experiment. Figure 3 shows a plot of $t^{3/4}c(t)$ for various initial concentrations $c(0)$, scaled by $c(0)^{-1/2}$. These should all fall upon one flat line. As seen in figure 3, this is far from being the case. Thus one concludes that for initial concentrations of less than one (in particular for such small initial concentrations as 0.05) the asymptotic regime is not reached in numerically accessible time. At first sight, this might be attributed to the fact that

particles with a low initial concentration take a fairly long time to encounter each other, namely of the order of $c(0)^{-2/d}$. This cannot explain the large discrepancies found at times between $t = 100$ and $t = 1000$, though, since in the worst case ($c(0) = 0.1$) the time necessary for encounters is of the order of 10. Thus one is forced to the conclusion that strong deviations from asymptotic behaviour persist over the entire range of numerically accessible times when the initial concentration is low. However, it should be noted that the discrepancies between the various curves diminish as t increases, at least as long as finite-size effects do not arise. This can be explained if one supposes (naturally enough) that apart from the leading behaviour one has a mean-field type correction such as

$$c(t) \simeq \sqrt{c(0)}t^{-3/4} + \text{constant} \times t^{-1}. \tag{2.1}$$

Rescaling by $c(0)^{-1/2}$ would emphasize the second term for small $c(0)$, thus explaining the upward trend. Nevertheless, this fit must be viewed as rather qualitative confirmation that one is in the asymptotic regime rather than anything else. Summarizing, it can be said that this modified model can indeed reproduce the known theoretical predictions between $t = 30$ and $t = 1000$ for a lattice 200 on a side.

3. Interparticle distances

Let me first recall the arguments given earlier [7], to compute exponents for interparticle distances. If one defines c_{AB} to be the concentration of nearest-neighbour AB pairs and d_{AB} as the average interparticle distance for AB pairs, a relation between the two is obtained as follows: in a time of the order of d_{AB}^2, a significant portion of the nearest-neighbour AB pairs will have annihilated if the random walk is compact, that is, for $d \leqslant 2$. Calling Δc the change in concentration occurring in the time interval $\Delta t = d_{AB}^2$, one then obtains

$$\frac{\Delta c}{\Delta t} \propto -\frac{k c_{AB}}{d_{AB}^2}. \tag{3.1}$$

Thus, since it is known that $c(t)$ varies as $t^{-d/4}$, any information concerning c_{AB} gives information on d_{AB} and vice versa. In one dimension, it is obvious that c_{AB} varies as $t^{-1/2}$, since one has exactly two AB pairs in each domain. To obtain a similar result in higher dimensions requires two sets of assumptions. Firstly, one needs to know how the interface of the domains scale with time. This can be obtained if one assumes compact domains with smooth boundaries. This leads to the length of the interface growing as $t^{(d-1)/2}$. Secondly, one needs to know how the interface particles are distributed along it. In particular, this requires knowing the average distance between interface particles. Two possibilities suggest themselves: either the particles, being of the same species, are separated by a distance d_{AA} growing as $t^{1/4}$, or else, as they belong to the interface, they are separated by a distance of order d_{AB}. In two dimensions, the latter hypothesis leads to d_{AB} growing as $t^{1/3}$, which has been clearly confirmed numerically. The corresponding behaviour of c_{AB}, decaying as $t^{-5/6}$ has also been confirmed.

In three dimensions, an additional difficulty occurs equation (3.1) is no longer correct, since it is no longer true that nearest-neighbour particles of different species

are overwhelmingly likely to react in a time of the order of their distance squared. While it is not quite clear how to take this into account, the following modification of equation (3.1) might be appropiate for d greater than two

$$\frac{dc}{dt} \propto -\frac{kc_{AB}}{d_{AB}^d} \tag{3.2}$$

since the probability of encounter of two particles starting at a distance R decays as $R^{-(d-2)}$. This, together with the two hypotheses mentioned above (compact domains with smooth boundaries and interface particles separated by a distance of d_{AB} irrespective of species) leads to the final result

$$d_{AB} \propto t^{1/4} \tag{3.3}$$

so that the entire effect should disappear and d_{AB} is expected to scale as d_{AA}. At this stage, however, it is absolutely imperative to check that this is indeed true, as the hypotheses I have been making are too numerous for comfort. Furthermore the hypothesis of domains with smooth boundaries has been questioned precisely in the case of interest to us, namely three dimensions. In fact, due to the ability of walkers to bypass one another in three dimensions, one would expect a rather diffuse interface.

In the above arguments, I have been using the term 'nearest neighbour' in a rather vague fashion. In one dimension, the neighbours of a particle are uniquely defined, but in any higher dimensions this ceases to be the case and an arbitrary definition must be resorted to. In the simulations to be presented below, I took the following definition: for every particle I looked at the ten nearest other particles. The number of AA nearest neighbours, for example, was then calculated to be the total number of such pairs encountered with both particles being A. The quantities such as the number of AB pairs were symmetrized so that there should be no distinction between the number of AB pairs and that of BA pairs. This remark is necessary, because it is possible for one particle to be among the ten nearest neighbours of another, but not vice versa. A simple example of this is given by four particles on a line at the positions 1, 2, 4 and 8 respectively. It is clear that particle 2 is the nearest neighbour of particle 3, but not vice versa: the nearest neighbour of particle 2 is particle 1. The number ten was chosen because it appeared to be sufficiently large to ensure that the nearest neighbours would be found in all directions, not only in the direction pointing inside the domain to which the particle belongs. As a clear example of the distortions brought about by having too small a number, consider what would happen in one dimension if one were only to look for *the* nearest neighbour and if all A particles were separated from their nearest neighbours by a distance of the order of $t^{1/4}$ (this is not in fact the case): it is immediately obvious that for long periods there would be virtually *no* AB nearest-neighbour pairs. Of course, this would eventually occur no matter how many nearest neighbours were taken, as long as it were not specified that both directions had to be considered. However, ten nearest neighbours would have been sufficient, in this hypothetical case, up to times of the order of 10^8, so that this same definition should not cause undue concern in the case of three dimensions, where it is not practical to determine neighbours along specific directions.

The results of the simulation are shown in figure 4, where d_{AA} and d_{AB} are plotted against time on a double-logarithmic scale. One sees that the distance between A

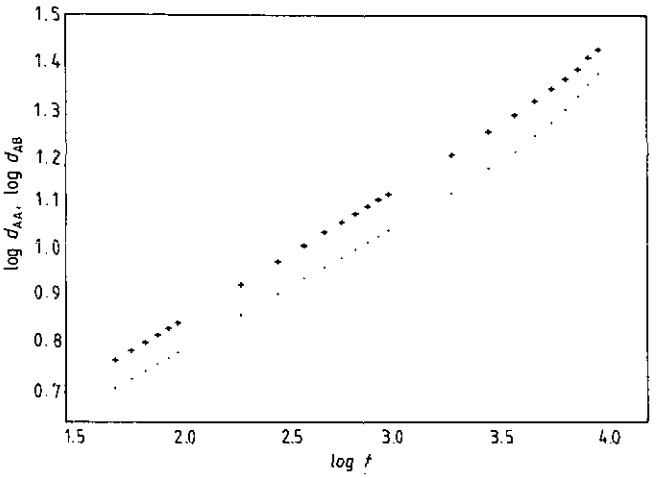

Figure 4. Logarithm of the interparticle distances for like species (points) as well as unlike species (crosses) plotted against $\log t$. The two lines are quite convincingly parallel, but their amplitude remains clearly different.

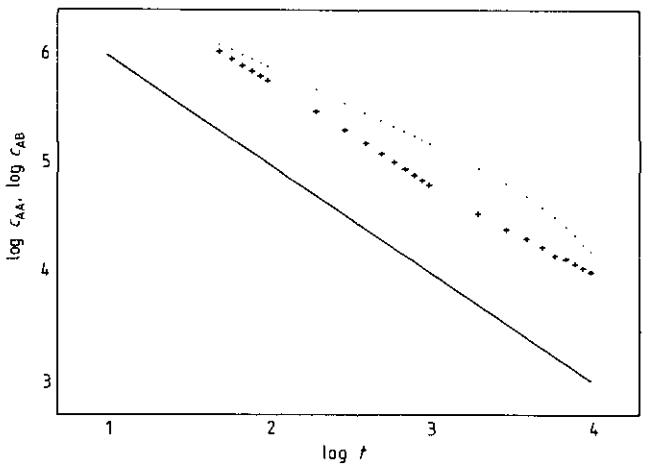

Figure 5. Logarithm of the concentration of nearest-neighbour pairs of like species (points) and unlike species (crosses) plotted against $\log t$. The full line shows slope -1, and is presumably parallel to the power-law for the concentration of nearest-neighbour pairs of unlike species.

particles and the distance between A particles and B particles are very convincingly parallel on this doubly logarithmic plot, if one disregards the finite-size effects that take place for $t > 1000$. However, the exponent found is roughly equal to 0.26 ± 0.02, slightly higher than 0.25, though probably not significantly so. There is no doubt, on the other hand, that it is really less than one third (which is what one observes in the transient regime). Figure 5 shows the simulation results for the time dependence of the concentration of nearest-neighbour pairs. This decreases with a power law of 0.97 ± 0.02, in close agreement with the theoretical prediction of t^{-1}. Thus one is led to the conclusion that the domains in three dimensions may well be compact objects with a reasonably smooth interface. As to the concentration of AA pairs, one expects to find it decaying as $t^{-3/4}$, similarly to the concentration. An

analysis of the data by successive slopes gives an exponent of 0.70 ± 0.02, however. As things stand, this is a rather minor discrepancy, which I believe may be attributed to insufficient accuracy of the data.

4. Conclusions

Summarizing, I have defined a variation upon the usual model of AB annihilation. This model has the advantage of reaching the (known) asymptotic behaviour for the decay of the concentration in numerically accesible times. Apart from the academic interest of verifying the result of Bramson and Lebowitz numerically, this also enables one to verify conjectures about three-dimensional behaviour of AB annihilation.

In particular, I have investigated the behaviour of the interparticle distances. This was motivated by the finding [7] that, in one and two dimensions, the AB interparticle distances scale differently from the AA interparticle distances. A scaling argument in the spirit of those given previously was attempted, and indicated that this difference in scaling should disappear in three dimensions. However, as this argument is based on a rather large number of questionable assumptions, it is obviously desirable to verify it numerically. Such a verification is possible in the above model, as the asymptotic regime can be reached. This is confirmed by the fact that the AA and AB interparticle distances scale (approximately) as $t^{1/4}$, whereas they scale as $t^{1/3}$ during the transient regime when the concentration behaves approximately as t^{-1}.

The conclusion of the scaling argument, namely that the difference in the scaling behaviour of d_{AA} and d_{AB} disappears in three dimensions, is confirmed by the numerical simulation. This is therefore an indication that the assumptions made in the scaling argument are indeed valid. The most questionable of these is certainly the one assuming that the interface can be described by a reasonably sharp surface. It would be interesting to pursue these questions further, using the above model to attain the asymptotic regime.

Acknowledgment

The financial support of CONACyT is gratefully acknowledged.

References

[1] Zeldovich Ya B and Ovchinnikov A A 1978 *Chem. Phys.* **28** 215
Toussaint D and Wilczek F 1983 *Chem. Phys.* **78** 2642
[2] Kang K and Redner S 1984 *Phys. Rev. Lett.* **52** 955
[3] Meakin P and Stanley H E 1984 *J. Phys. A: Math. Gen.* **17** L173
[4] Zumofen G *et al* 1985 *J. Chem. Phys.* **82** 3198
[5] Argyrakis P and Kopelman R 1985 *Phys. Rev.* B **31** 6008
[6] Bramson M and Lebowitz J L 1988 *Phys. Rev. Lett.* **61** 2097
[7] Leyvraz F and Redner S 1991 *Phys. Rev. Lett.* **66** 2168
Argyrakis P and Kopelman R *Phys. Rev.* A **41** 2121