Unstirred Annihilation Reactions and Pair Correlations

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(Received 4 May 1992)

It has been claimed that the kinetics of reactions of the form $A+B\rightarrow 0$ can be well described using the Kirkwood superposition principle to decouple n-body correlations into products of pair correlations. The strength of this approximation is assessed through its predictions for the nearest available neighbor recombination scheme, for which analytic and Monte Carlo results are available. It is shown that it is much more successful than classical kinetics because of the inclusion of spatially nonuniform pair correlations, but fails asymptotically at large pair separations or long times because of the neglect of higher correlations.

PACS numbers: 82.20.−w, 05.40.+j, 72.80.Ng, 78.55.−m

The last decade has seen a rapid growth of interest in reactions of the form $A+B\rightarrow 0$ in situations where the motion of the reactants is not fast enough to keep their densities uniform everywhere—for a review see Ref [1]. For such reactions, classical kinetics fails and reaction rates become much slower than, for example, the bimolecular prediction for equal initial concentrations of A and B. Whatever the detailed recombination mechanism, such reactions have a common essential feature in the evolution of segregated clusters of like particles which originate in the initial spatial fluctuations of $[A]-[B]$. At long times the existence of these clusters dominates the recombination and produces a characteristic asymptotic behavior.

Three specific recombination mechanisms have been investigated, two of them approximately describing physical processes and the other an artificial model which emphasizes the statistics. Thus diffusion limited reactions (DL) [1], tunneling limited reactions (TL) [2], and nearest available neighbor (NAN) [3–7] reactions have all been discussed, usually, though not always, by either scaling arguments or Monte Carlo simulations. In the NAN scheme A-B pairs recombine in strict order of separation; the closest pair in an initially random distribution is removed first, then the next, and so on. Thus for NAN, the recombination distance R, i.e., the separation of the closest unlike pair at any stage of the recombination, replaces time as the ordering variable; time does not enter the NAN scheme. R is conveniently measured in units of the initial pair separation. At large R and in D dimensions, NAN scaling arguments [3] lead rapidly to the result that the pair population decreases asymptotically as $CR^{-D/2}$ for $R\rightarrow\infty$. With the possible exception of $D=1$ (cf. the discussion of Eggert's conjecture below), the only information on C comes from Monte Carlo simulations.

The asymptotic decay has this form for all three recombination mechanisms; in DL reactions the reactants move around by a random walk with distance mapping into time as $R\rightarrow t^{1/2}$, so that the pair density falls as $t^{-D/4}$. In TL the mapping is $R\rightarrow R_0\ln(\omega t)$, where ω is a hopping rate preexponential and R_0 a characteristic interaction range, and the pair density follows $[R_0\times\ln(\omega t)]^{-D/2}$. There may be some upper limit on D, for example, $D\leq 4$ for DL [1]. Since the asymptotic behavior is mechanism independent, NAN provides a unifying model.

At short time or small R the classical kinetics of the stirred reactor are maintained. Analytic methods capable of describing the approach to the asymptotic region, which must be recombination mechanism and D dependent are lacking. Limits exist, but the only analytic expression proposed is due to Eggert [5] for NAN in one dimension. His expression covers the whole range, including the asymptotic limit; it is supported by independent Monte Carlo simulations [6,7]. Eggert's conjecture came from an analysis of small A-B clusters and, though persuasive, remains to be proven. Thus any other method which assists analytic investigation is welcome.

Recently, Schnorer, Kuzovkov, and Blumen (SKB) [8] have suggested a method for TL recombination with equal initial concentrations. They derive an exact expression for the recombination rate in terms of an unlike pair correlation function, then use the Kirkwood superposition approximation to obtain this function. This procedure truncates the infinite hierarchy of rate equations involving increasingly large clusters by writing three particle correlation functions approximately in terms of like and unlike pair correlation functions. For brevity, this approach is referred to here as the SKB-K (for -Kirkwood) method.

SKB tested their model against a Monte Carlo simulation, calculating not only the decay [population $n(t)$ versus time] but also the time evolution of the two pair correlation functions. Generally the agreement was good and at short times was excellent. At long times, they claimed that the decay approached the asymptotic form $n(t)\sim[\ln(\omega t)]^{-1/2}$ expected for TL together with $D=1$. They noted, however, that at (very) long times the like pair correlation function calculated from the SKB-K method began to exceed that gotten from the Monte Carlo simulation at small separation r. The unlike pair function did better since it was zero out to about $r\sim R_0$

$\times \ln(\omega t)$ as expected.

It is clear that the SKB-K method gives a useful approximation to the TL decay problem; however, SKB claim "astonishingly accurate results" and recommend their approach as a powerful analytic method. This suggests that others should look for its limitations. One concern with the SKB-K method is that it appears to yield the correct asymptotic $n(t)$ but not the correct like pair correlation function. However, since in the time domain the recombination of close pairs persists to long times, errors in the number of more distant pairs may be largely hidden. That is, the number of surviving pairs at time t given by

$$n(t) = -\int_0^\infty \exp[-\omega t \exp(-R/R_0)] \frac{dn}{dR} dR \qquad (1)$$

is dominated by recombinations at small R. So long as the form of $n(R)$ is correct at small R, Eq. (1) will provide a good approximation to $n(t)$ to long times, though not asymptotically. Thus to examine the validity of the SKB-K method, which is essentially a spatial argument, one should compare the predictions with those of NAN which operates directly within the space domain.

Making the comparison turns out to be rather straightforward, since the replacement of the quantum mechanical exponential by the delta function of NAN simplifies the calculation of the SKB-K model considerably. As an example, consider SKB's Eq. (4) which gives the pair population $n(t)$ at time t in terms of the time-dependent unlike pair correlation function $Y(r,t)$:

$$\frac{dn(t)}{dt} = -n(t)^2 \int_0^\infty w(r') Y(r',t) dr' ,$$

where $w(r)$ is the reaction rate at distance r. For NAN we have instead

$$\frac{dn(R)}{dR} = -n(R)^2 \int_0^\infty \delta|r'-R| Y(r',R) dr' = -2n^2(R) Y(R,R) . \qquad (2)$$

R, the distance to which pairs have recombined, replaces t in NAN and the delta function ensures that recombination only occurs at $r = \pm R$. The equations which SKB get for the pair correlation functions via the kinetic equations and the Kirkwood approximation [their equations (6) and (7)] simplify in a similar way to give

$$\partial[\ln X(r,R)]/\partial R = -2n(R) Y(R,R)[Y(|r-R|,R) + Y(r+R,R) - 2] \qquad (3)$$

and

$$\partial[\ln Y(r,R)]/\partial R = -\delta|r-R| - 2n(R) Y(R,R)[X(|r-R|,R) + X(r+R,R) - 2] . \qquad (4)$$

$X(r,R)$ is the like pair correlation function. Equations (2)–(4) can then be integrated numerically to find $n(R)$.

Figure 1 shows the comparison of $n(R)$ calculated in this way with the asymptotic limit

$$n(R) \to \tfrac{1}{2} \exp(-\gamma/2) R^{-1/2} \approx 0.3746 R^{-1/2} \qquad (5)$$

of Eggert's expression [5]

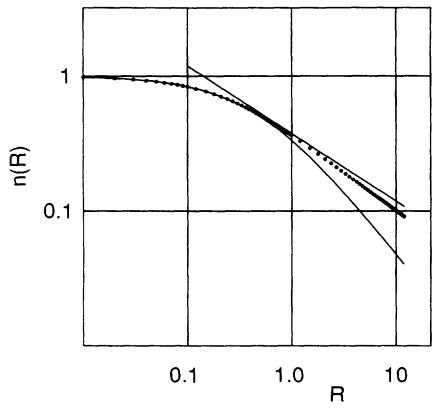

FIG. 1. The pair population $n(R)$ remaining after recombination to distance R. The straight line shows the asymptotic limit from Eq. (5) and Monte Carlo simulations. The points are from Eqs. (2)–(4) derived from the SKB-K approximation, and the curve from the classical kinetics of Eq. (7).

$$d[\log n(R)]/d(\log R) = [\exp(-4R) - 1]/2 , \qquad (6)$$

where γ is Euler's constant. Equation (6) is known to be analytically correct at small R, to give the right asymptotic slope, and to be in close agreement with the Monte Carlo simulations. The SKB-K $n(R)$ approaches the asymptote accurately, follows it briefly, but then drops away faster than it should. The difference between these two curves shows the limits of the SKB approximation. At $R = 5$ the discrepancy is about 10%.

Figure 2 compares the logarithmic slopes $d[\log n(R)]/d[\log(R)]$ from Eqs. (2)–(4) and from Eq. (6). The latter shows the expected power law with slope $-\frac{1}{2}$ at large R; interestingly, the SKB-K approximation also produces an apparent power-law asymptote, with a slope in our most accurate integration of $q = -0.56$. In the time domain, the SKB-K approximation therefore leads to $n(t) \sim [\ln(\omega t)]^q$, with $q < \frac{1}{2}$ falling faster than the true asymptote. SKB results show just such an underestimate (their Fig. 2).

These results are readily compared with those of classical, stirred kinetics where the distributions remain uncorrelated, i.e., $Y(r,R) = X(r,R) = 1$ at all r and R. Equation (2) immediately yields

$$n(R) = 1/(1+2R) . \qquad (7)$$

This system acts as a lower limit to $n(R)$ in the NAN

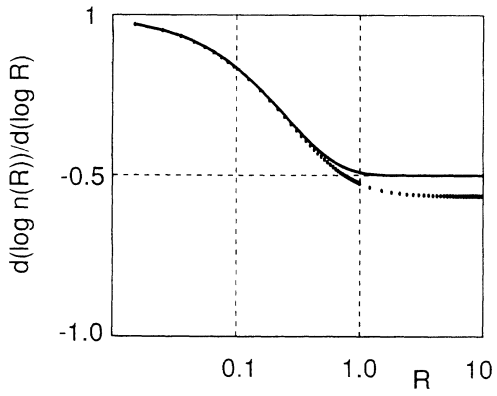

FIG. 2. The logarithmic slopes of $n(R)$ from the SKB-K approximation (points) and Eggert's Eq. (6) (line).

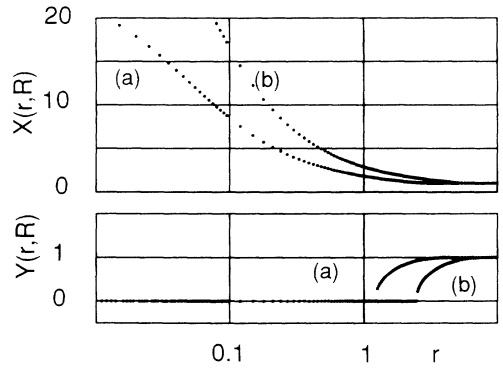

FIG. 3. Like and unlike pair correlation functions as a function of separation. Recombination has proceeded to (a) $R=1.25$, (b) $R=2.5$.

scheme because the effect of correlations is always to slow the reaction by separating unlike pairs. For NAN, the approximation fails from the beginning, since $Y(r,R)$ must be zero for $r<R$. There is for NAN no distinguishable equivalent of the SKB's "raw" approximation, with unlike particle correlations only because this makes $Y(r,R)$ a unit step function at $r=R$ which via Eq. (2) again yields Eq. (7).

Equation (7) is thus also the result of the approximation used by Dunstan [9] and critically discussed by Eggert [10], though derived in a rather different way here. Figure 1 shows that for $R\lesssim 0.4$ all approaches agree well because little segregation has occurred. Unlike the SKB-K result, $n(R)$ from Eq. (7) never approaches the asymptotic slope; it is in this region that the SKB-K approximation is most successful.

Figure 1 shows that the SKB-K approach breaks down seriously, i.e., $n(R)$ is 10% below the true asymptotic value, when $R\sim 5$. Since SKB used an unscaled interaction length $R_0=5$ and an initial interparticle separation of 10, we use $R=0.5\ln(\omega t)$ to map to time. Then breakdown occurs roughly when $\omega t\approx 2\times 10^4$, though this estimate ignores the important contribution at this time from earlier decays [cf. Eq. (1) above]. Nonetheless, by these times SKB's integration of the SKB-K approximation (their Fig. 2) is significantly below and outside the scatter of their TL simulation, as expected. Even with a tunneling preexponential slower than a typical dipole allowed transition, e.g., $\omega=10^6\ \mathrm{s}^{-1}$, this failure will occur at 20 ms. A real steady-state experiment will certainly reach into much longer times.

Another and perhaps more important measure of the limits of the SKB approach is $1-n(R)$, i.e., the remaining population when the approximation fails. Using the 10% discrepancy discussed above as a criterion, the SKB method fails when some 15% of the carriers still remain. Their approach therefore cannot hope to describe the slow recombination of the rest of the population as monitored, for example, by a LESR [light (induced) electron spin resonance] experiment.

The SKB-K approximation also produces the like and unlike pair correlation functions $X(r,R)$ and $Y(r,R)$ which are shown in Fig. 3. $X(r,R)$ and $Y(r,R)$ must continue to be unity at large r where the initially random distribution remains undisturbed. For NAN, $Y(r,R)$ is of course zero for $r<R$. The increasing importance of the clumps of like particles is seen in the increase in $X(r,R)$ for $r<R$.

It is the development of clusters of like charges which slows these reactions and produces an asymptotic power law for $n(R)$ with slope $-\frac{1}{2}$ from an initially random distribution. The Kirkwood approximation used by SKB makes a start in describing the clusters, but its restriction to two-particle correlations leads to the faster recombination rate with logarithmic slope $q\approx -0.53$ as $R\rightarrow\infty$ because of the neglect of higher-order correlations. It nonetheless provides a much better description of the approach to the asymptote. To a degree this is fortuitous, since Fig. 2 shows the true slope of $-\frac{1}{2}$ is reached early by SKB-K. At greater R there is a gradual divergence because of the difference $q-\frac{1}{2}$. Any truncation method, it seems, will fail asymptotically. Nonetheless, pair correlations together with the Kirkwood approximation can account clearly for much of the change of exponent from -1 in the unstirred reactor to $-\frac{1}{2}$ in the unstirred system. It is interesting that in a study of reactions of the form $A+A\rightarrow A$, i.e., particles of one kind only, Lin, Doering, and ben-Avraham [11] found that the superposition approximation was successful to the point of yielding the correct asymptotic slope. The crucial difference between their system and the present one is the development of clusters of unlike particles which can only happen when two species (or more) participate in the reaction.

It is possible that an extension of the SKB-K method might lead to convergence on to the scaling result, but it remains to be seen whether this will be easier to achieve than an extension of Eggert's cluster calculation. At

present our best understanding of these unstirred reactions, particularly in $D > 1$, comes from Monte Carlo calculations. It may be possible to apply SKB-K to $D > 1$, but a more profitable line of inquiry may be an exploration of the kinetics of initially correlated electron-hole distributions, resulting, e.g., from excitonic effects.

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