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Scaling Approach for the Kinetics of Recombination Processes

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A scaling theory is developed to describe the time evolution of the irreversible diffusive recombination process $A+B\rightarrow$ inert. Fluctuations are shown to alter radically the decay laws predicted from the rate-equation approach. For unequal initial densities, the minority species is predicted to decay as $t^{-\alpha}$ for short times, crossing over to an $\exp(-At^{\alpha})$ decay for long times, with $\alpha=d/4$ and $\alpha=(d+1)/4$ for unbiased and biased diffusion, respectively.

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Recently the kinetics of the recombination process $A+B\rightarrow$ inert has been intensively studied both theoretically[1-5] and experimentally.[6-10] In this reaction, the spatial distribution of the particles at time $t=0$ is random but globally homogeneous, and for $t>0$, one or both of the particle species move diffusively. There is no interaction between particles of the same type, but when an A and a B particle meet they instantly and irreversibly combine to form an inert species. The basic question is to calculate the number of particles remaining after time t.

A standard approximation to describe the kinetics of this reaction is the following rate equation[1]:

$$d\rho_A(t)/dt=-k\rho_A(t)\rho_B(t), \tag{1}$$

where $\rho_A(t)$ and $\rho_B(t)$ are the densities of species A and B at time t, and k is a rate constant. Such an equation should be valid when spatial fluctuations in the particle distributions are neglected. At long times, the solution to Eq. (1) is

$$\rho_A(t)\cong 1/kt \quad [\rho_A(0)=\rho_B(0)], \tag{2a}$$

$$\rho_A(t)\cong \exp\{-k[\rho_B(0)-\rho_A(0)]t\} \quad [\rho_A(0)<\rho_B(0)]. \tag{2b}$$

Equations (2) represent the mean-field prediction for the decay law, as spatial fluctuations are neglected in the rate equation.

However, both theoretical and experimental studies indicate slower decay laws, proportional to $t^{-\alpha}$, $0<\alpha<1$, when $\rho_A(0)=\rho_B(0)$, and proportional to $\exp(-kt^{\beta})$, $0<\beta<1$, when $\rho_A(0)<\rho_B(0)$. One of the primary theoretical approaches for this problem has been the continuous-time random-walk (CTRW) model.[1-4] Although the CTRW method predicts the observed anomalous decays, the exponents α and β depend on the assumed form of the waiting time distribution of the CTRW. It is not clear from the CTRW approach if the decay can be described in terms of universal scaling laws, and whether the spatial dimension d plays a fundamental role. Very recently, however, Toussaint and Wilszek[5] considered the recombination process in the framework of the discrete-time random-walk model. They found that spatial fluctuations in the particle densities play a basic role in determining the long-time decay. For equal initial densities of A and B particles both of which diffuse isotropically, they found that $\rho(t)$ decays as $t^{-d/4}$ for spatial dimensions $d<4$.

In this Letter, we develop a scaling approach to treat the more general situation of arbitrary initial densities of the two species, and also the case of a relative drift between the two species. We find a

power-law decay, $t^{-\alpha}$, for short times, crossing over to a quasi exponential decay, $\exp(-At^{\beta})$, for long times, with α conjectured to be equal to β. We derive the exponent α for both the case of isotropic diffusion and the case of a relative drift. We also elucidate the nature of the crossover in terms of simple arguments involving the spatial fluctuations of the particle density difference.

Consider a spatial region of linear dimension l and volume l^d. The initial number of A and B particles is

$$N_{A,B} \sim \rho_{A,B}(0) l^d \pm [\rho_{A,B}(0) l^d]^{1/2}, \tag{3}$$

where the second term indicates local fluctuations. If $\rho_A(0) < \rho_B(0)$, the particle number difference in this volume will be

$$N_A - N_B \sim [\rho_A(0) - \rho_B(0)] l^d \pm \{[\rho_A(0)]^{1/2} \pm [\rho_B(0)]^{1/2}\} l^{d/2}. \tag{4}$$

In the absence of fluctuations, $N_A - N_B$ is always less than zero for any size volume. However, fluctuations make it possible to have $N_A - N_B > 0$ within a sufficiently small region. The size of this region can be estimated by considering the maximum positive fluctuation in N_A and the maximum negative fluctuation in N_B in Eq. (4), and setting $N_A = N_B$. From this condition, we find a characteristic length scale

$$\xi \sim (2\{[\rho_B(0)]^{1/2} - [\rho_A(0)]^{1/2}\})^{-2/d}, \tag{5}$$

where a factor of 2 has been included for convenience. This length also determines a characteristic time scale, $t_\xi \sim \xi^2$, which is the time required for a particle to diffuse across a region of linear dimension ξ.

For short times, $t < t_\xi$, local fluctuations in the density difference will determine the decay rate. In this time regime, we expect to have a power-law decay of the particle density.[5] For $\rho_A(0) \to \rho_B(0)$, ξ diverges, and the power-law decay should hold for all times. For $\rho_A(0) \neq \rho_B(0)$, we expect a new type of decay at long times which is governed by the spatial fluctuations of the majority species, rather than density-difference fluctuations. This crossover can be expressed in terms of the following scaling *Ansatz*:

$$\rho_{A,B}(t) \sim C_{A,B} t^{-\alpha} f_{A,B}(t/t_\xi), \tag{6}$$

where $f_A(x)$ and $f_B(x)$ are scaling functions of the dimensionless variable $x \equiv t/t_\xi$, and C_A and C_B are constants which depend on $\rho_A(0)$ and $\rho_B(0)$. These unknown quantities can be fixed by use of scaling and the conservation of the particle density difference,

$$\delta\rho \equiv \rho_B(t) - \rho_A(t) = \rho_B(0) - \rho_A(0).$$

From Eq. (6), we have

$$\delta\rho = [C_B f_B(x) - C_A f_A(x)] t^{-\alpha}. \tag{7}$$

On the other hand, from Eq. (5), $\delta\rho$ can be written as

$$\xi^{-d/2}\{[\rho_B(0)]^{1/2} + [\rho_A(0)]^{1/2}\}/2.$$

Substituting this in Eq. (7) yields

$$C_B f_B(t/t_\xi) = \tfrac{1}{2}\{[\rho_B(0)]^{1/2} + [\rho_A(0)]^{1/2}\} t_\xi^{-d/4} t^{\alpha} + C_A f_A(t/t_\xi). \tag{8}$$

Finally, from the fact that f_B is a function *only* of the scaling variable t/t_ξ, and the condition $C_A = C_B$ when $\rho_A(0) = \rho_B(0)$, we find

$$\alpha = d/4,$$

$$C_A = C_B = \{[\rho_A(0)]^{1/2} + [\rho_B(0)]^{1/2}\}/2. \tag{9}$$

Our result for α thus yields the $t^{-d/4}$ decay first predicted by Toussaint and Wilczek,[5] and we also recover their $[\rho_A(0)]^{1/2}$ amplitude for equal initial particle densities. This decay law should hold below four dimensions where fluctuation phenomena should dominate at large times.

The arguments given above can be extended to the situation where there is a relative drift between the A and B particles in addition to the diffusive motion. In this case, there are two different length scales which characterize the spatial volume explored by each particle. This may be relevant for understanding recombination of charged particles in an external electric field. Along the drift, the particle will move a distance $l_\parallel \sim t$, while in the $d-1$ perpendicular directions, the particle will move a distance $l_\perp \sim t^{1/2}$. Thus the volume explored by a drifting, diffusing particle will be proportional to $l_\parallel l_\perp^{d-1}$, and this volume grows with time as $t^{(d+1)/2}$. Within such a volume, the local number of particles will be

$$N_{A,B} \sim \rho_{A,B}(0) l_\parallel l_\perp^{d-1} \pm [\rho_{A,B}(0) l_\parallel l_\perp^{d-1}]^{1/2}. \tag{10}$$

Following the arguments that led to Eq. (5), we find a characteristic parallel length along the drift direction, $\xi_\parallel$, which varies as

$$\xi_\parallel \sim (2\{[\rho_B(0)]^{1/2} - [\rho_A(0)]^{1/2}\})^{-4/(d+1)}, \tag{11}$$

and a perpendicular length, $\xi_\perp \sim \xi_\parallel^{1/2}$. On the basis of scaling, the time dependence of the particle den-

sity should now have the form

$$\rho_{A,B}(t) \sim C_{A,B} t^{-\alpha} f_{A,B}(t/t_{\xi_\parallel}), \tag{12}$$

where $t_{\xi_\parallel} \sim \xi_\parallel$ is the characteristic time for a particle to drift through a region of volume $\xi_\parallel \xi_\perp^{d-1}$. Employing similar reasoning as in the case of unbiased diffusion, we find that the relations between f_A and f_B, and between the constants C_A and C_B, are the same as for unbiased diffusion, but that the exponent equals $(d+1)/4$. This prediction for α should be valid below an upper critical dimension of 3, while above this dimension, the t^{-1} decay predicted by the rate equation should hold. The lowering of the critical dimension compared to the case of isotropic diffusion stems from the fact that a drifting particle can explore a larger volume per unit time than a purely diffusing particle. Therefore fluctuations should play a relatively less important role in the case of a finite drift. A similar situation occurs for a number of percolation models and transport problems in which there is a preferred direction.[11]

To obtain the long-time decay law when the initial particle densities are unequal, we require the dependence of the scaling functions $f_A(x)$ and $f_B(x)$ for $x \gg 1$. We expect the following asymptotic behaviors:

$$f_{A,B}(x) \to \begin{cases} \text{const}, & x \ll 1, \\ \exp(-x^\alpha), & x \gg 1. \end{cases} \tag{13}$$

The limiting behavior for $x \ll 1$ is required to give the known short-time algebraic decay, while the long-time behavior of f is suggested by the following heuristic argument. The rate equation, Eq. (1), can be modified to yield the correct $t^{-\alpha}$ decay law in the case $\rho_A(0) = \rho_B(0)$ by allowing for a time-dependent rate constant. The requisite time dependences are

$$\begin{aligned} k(t) &\sim t^{d/4-1} \quad \text{(unbiased diffusion)}, \\ k(t) &\sim t^{(d+1)/4-1} \quad \text{(biased diffusion)}. \end{aligned} \tag{14}$$

For unequal initial densities, we assume that an effective rate equation with a time-dependent rate coefficient and a density dependence of $\rho_A(t)\rho_B(t)$ will continue to be valid. This, together with the assumption of a scaling form for $\rho_A(t)$, gives

$$\rho_A(t) \sim \exp(-\{[\rho_B(0)]^{1/2} - [\rho_A(0)]^{1/2}\} t^\alpha), \tag{15}$$

with $\alpha = d/4$ and $\alpha = (d+1)/4$ for unbiased and

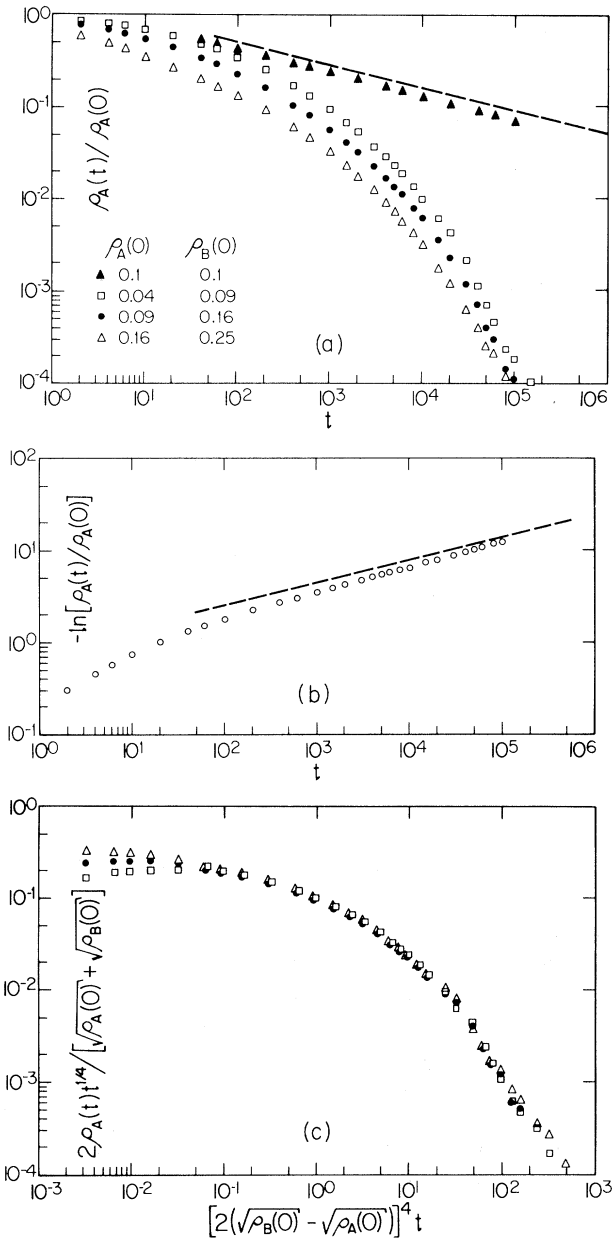

FIG. 1. Sample computer simulations for isotropic diffusion in one dimension. In (a), we show the dependence of $\rho_A(t)/\rho_A(0)$ vs t for a number of initial conditions, while in (b), we show $-\ln[\rho_A(t)/\rho_A(0)]$ vs t for the case $\rho_A(0) = 0.1$, $\rho_B(0) = 0.2$. The dashed lines have slopes of $-\frac{1}{4}$ and $+\frac{1}{4}$, respectively. These data represent one run on a chain of 10^6 sites in (a), and ten runs on a chain of 2.5×10^6 sites in (b). Because of the large system size, statistical uncertainties are negligible until the final stages of the decay. In (b), these errors are of the order of the size of the data points or less. In (c), the use of scaled variables leads to a collapsing of the data of (a) onto a single universal curve. The scatter of the data at long times provides an estimate of the statistical error.

biased diffusion, respectively.

To test these ideas, as well as the scaling results, we have performed numerical simulations in one and two dimensions. For simplicity, we consider the situation where the A particles are moving and the B particles are stationary. In one unit of time, each A particle randomly hops to one of its nearest-neighbor sites. If an A particle happens to land on a site occupied by a B particle, both particles are immediately removed from the system. Typical results are shown in Fig. 1. For $\rho_A(0) < \rho_B(0)$, the decay follows the power law of the $\rho_A(0) = \rho_B(0)$ case for short times, and at longer times there is a crossover to a faster decay. In one dimension this can be well fitted by the form $\exp(-At^{\alpha})$ with $\alpha = \frac{1}{4}$ [Fig. 1(b)]. In Fig 1(c), the data of Fig. 1(a) are displayed in terms of scaled variables, and the collapsing of the data supports the general validity of the scaling approach.

Our scaling analysis can also be extended to study a much wider range of decay processes. One example is the decay $A + A \rightarrow$ inert. This decay is in a different universality class than the reaction $A + B \rightarrow$ inert because there is no conservation of the particle density difference. From scaling, we find that the decay of $A + A \rightarrow$ inert, under conditions of isotropic diffusion, should be $t^{-d/2}$, below an upper critical dimension of 2, in agreement with the observation of Toussaint and Wilszek.[5] In addition to regular lattices, both reactions may also be studied on self-similar structures, such as a percolation cluster at the threshold; some of these situations have been considered independently by Meakin and Stanley.[12] In this case, the characteristic length scale introduced in Eq. (5) will involve the power $2/d_f$, where d_f is the fractal dimension of the structure, while the relation between time and length scale can be expressed as $t \sim \xi^{d_w}$, with $d_w \geq 2$.[13] These considerations lead to a decay of $t^{-\tilde{d}/4}$ for the reaction $A + B \rightarrow$ inert, and $t^{-\tilde{d}/2}$ for $A + A \rightarrow$ inert, when the initial densities are equal and when the diffusion is isotropic. Here $\tilde{d}$ is the *fracton* dimension[14] of the structure on which the decay is taking place. For percolation clusters at threshold, we therefore expect superuniversal decays *independent* of the spatial dimension, if the Alexander-Orbach conjecture that $\tilde{d} = \frac{4}{3}$ is correct. These decay laws have been recently confirmed through computer simulations.[12] A final interesting situation is N-body reaction processes such as $NA \rightarrow$ inert (no conservation law), or $A_1 + A_2 + \ldots + A_N \rightarrow$ inert (conservation law $\sum_{l=1}^{N} \rho_{A_l} \times e^{2\pi i l/N} = 0$). We find evidence of new universality classes for these systems.

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