

Diffusion-limited coalescence, $A + A \rightleftharpoons A$, with a trap

Daniel ben-Avraham*

Physics Department, and Clarkson Institute for Statistical Physics (CISP), Clarkson University, Potsdam, New York 13699-5820

(Received 15 June 1998)

We study diffusion-limited coalescence, $A + A \rightleftharpoons A$, in one dimension, and derive an exact solution for the steady state in the presence of a trap. Without the trap, the system arrives at an *equilibrium* state that satisfies detailed balance, and can therefore be analyzed by classical equilibrium methods. The trap introduces an irreversible element, and the stationary state is no longer an equilibrium state. The exact solution is compared to that of a reaction-diffusion equation—the habitual approximation method of choice. The reaction-diffusion equation can also be obtained exactly in this case, making the present model particularly useful. [S1063-651X(98)12310-3]

PACS number(s): 05.70.Ln, 82.20.Mj, 02.50.-r, 68.10.Jy

I. INTRODUCTION

Nonequilibrium kinetics of diffusion-limited reactions has been the subject of much recent interest [1–6]. In contrast to equilibrium systems—which are best analyzed with standard thermodynamics—or reaction-limited processes—whose kinetics is well described by classical rate equations [7,8]—there is no general approach to nonequilibrium, diffusion-limited reactions.

In this communication we study a diffusion-limited coalescence process in one dimension: $A + A \rightleftharpoons A$, which can be analyzed *exactly* [9–19]. When a trap is introduced, the resulting steady state is a nonequilibrium state. We derive an exact description of this state and compare it to the prediction from a reaction-diffusion equation—the standard approximation method of choice. The pertinent reaction-diffusion equation can too be solved exactly, making the model useful for the study of this popular approximation method.

The rest of this paper is organized as follows. In Sec. II we present a lattice model of diffusion-limited reversible coalescence, along with the exact method of analysis; the method of empty intervals, also known as the method of interparticle distribution functions. The stationary state in the presence of a trap is derived and analyzed in Sec. III. In Sec. IV we compare the exact solution to that of a reaction-diffusion equation, and devise strategies to determine the appropriate rate coefficients. We conclude with a discussion and open questions in Sec. V.

II. REVERSIBLE COALESCENCE

Our model [9,10] is defined on a one-dimensional lattice of lattice spacing a . Each site is in one of two states: occupied by a particle A , or empty. Particles hop randomly into nearest neighbor sites, at rate D/a^2 . A particle may give birth to an additional particle, into a nearest neighbor site, at rate $v/2a$ (on either side of the particle). If hopping or birth occurs into a site that is already occupied, the target site remains occupied. The last rule means that coalescence, A

$+ A \rightarrow A$, takes place *immediately* upon encounter of any two particles. Thus, together with hopping and birth, the system models the diffusion-limited reaction process $A + A \rightleftharpoons A$.

An exact treatment of the problem is possible through the method of interparticle distribution functions (IPDF). The key concept is $E_{n,m}(t)$ —the probability that sites $n, n+1, \dots, m$ are empty at time t . The probability that site n is occupied is

$$\text{Prob}(\text{site } n \text{ is occupied}) = 1 - E_{n,n}. \quad (1)$$

The event that sites n through m are empty (prob $E_{n,m}$) consists of two cases: site $m+1$ is also empty (prob. $E_{n,m+1}$), or it is occupied. Thus the probability that sites n through m are empty, but site $m+1$ is occupied, is $E_{n,m} - E_{n,m+1}$. With this (and with a similar rule for when the particle is to the left of the empty segment) one can write down a rate equation for the evolution of the empty interval probabilities:

$$\begin{aligned} \frac{\partial E_{n,m}}{\partial t} = & \frac{D}{a^2}(E_{n,m-1} - E_{n,m}) - \frac{D}{a^2}(E_{n,m} - E_{n,m+1}) \\ & - \frac{D}{a^2}(E_{n,m} - E_{n-1,m}) + \frac{D}{a^2}(E_{n+1,m} - E_{n,m}) \\ & - \frac{v}{2a}[(E_{n,m} - E_{n,m+1}) + (E_{n,m} - E_{n-1,m})]. \end{aligned} \quad (2)$$

Equation (2) is valid for $m > n$. The special case of $m = n$ yields the boundary condition

$$E_{n,n-1} = 1. \quad (3)$$

The fact that the $\{E_{n,m}\}$ represent *probabilities* implies the additional condition that $E_{n,m} \geq 0$. Finally, if the system is not empty then $E_{n,m} \rightarrow 0$ as $n \rightarrow -\infty$ and $m \rightarrow \infty$.

In many applications, it is simpler to pass to the continuum limit. We write $x = na$ and $y = ma$, and replace $E_{n,m}(t)$ with $E(x, y; t)$. Letting $a \rightarrow 0$, Eq. (2) becomes

$$\frac{\partial E}{\partial t} = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) E - \frac{v}{2} \left(\frac{\partial E}{\partial x} - \frac{\partial E}{\partial y} \right), \quad (4)$$

*Electronic address: qd00@polaris.clarkson.edu

with the boundary conditions,

$$E(x, x; t) = 1, \tag{5}$$

$$E(x, y; t) \geq 0, \tag{6}$$

$$\lim_{\substack{x \rightarrow -\infty \\ y \rightarrow +\infty}} E(x, y; t) = 0. \tag{7}$$

The concentration of particles is obtained using Eqs. (1) and (3), and passing to the continuum limit:

$$c(x, t) = - \left. \frac{\partial E(x, y; t)}{\partial y} \right|_{y=x}. \tag{8}$$

It can also be shown [9,10] that the conditional joint probability for having particles at x and y but none in between, is

$$P(x, y; t) = - \frac{\partial^2 E(x, y; t)}{\partial x \partial y}. \tag{9}$$

Given a particle at x , the probability that the next nearest particle is at y , i.e., the IPDF, is $p(x, y; t) = (1/c)P$.

III. STEADY STATE WITH A TRAP

The steady state of Eq. (4), with the boundary conditions (5)–(7), when $\partial E/\partial t = 0$, is

$$E_{eq} = e^{-(v/2D)(y-x)}. \tag{10}$$

This corresponds to the equilibrium concentration of particles [using Eq. (8)]

$$c_{eq} = \frac{v}{2D} \equiv \gamma. \tag{11}$$

Another trivial solution is $E(x, y) = 1$; it represents a totally empty system. But the solution (10) is stable, while the vacuum state is not. In fact, when the initial state of the system is a mixture of the two phases, $c(x, t=0) = 0$ for $x < 0$ and $c(x, t=0) = c_{eq}$ for $x > 0$, say, then the stable phase invades the unstable phase. The front between the two phases propagates at a constant speed, similar to the case of Fisher waves [20]. Here we wish to study another inhomogeneous situation, where there is a perfectly absorbing trap at the origin instead of the initial empty half-space. The trap depletes its immediate neighborhood, but a nontrivial steady state is expected as the depletion zone created by the trap is continually replenished by a stream of particles from the stable phase.

To derive the appropriate boundary condition, we turn back to the discrete representation. In the presence of a perfect trap at $n=0$, Eq. (2) is then limited to $0 < n < m$. The special equation for $n=0$ is

$$\begin{aligned} \frac{\partial E_{0,m}}{\partial t} &= \frac{D}{a^2} (E_{0,m-1} + E_{0,m+1} + E_{1,m} - 3E_{0,m}) \\ &\quad - \frac{v}{2a} (E_{0,m} - E_{0,m+1}). \end{aligned} \tag{12}$$

Comparison to Eq. (2) yields the discrete boundary condition

$$E_{-1,m} = E_{0,m}, \tag{13}$$

which in the continuum limit becomes

$$\left. \frac{\partial E(x, y; t)}{\partial x} \right|_{x=0} = 0. \tag{14}$$

In addition, the boundary condition (7) is now replaced by

$$\lim_{y \rightarrow \infty} E(0, y; t) = 0. \tag{15}$$

The stationary solution to Eq. (4), confined to the wedge ($0 \leq x \leq y$), which satisfies the boundary conditions (5), (6), (14), and (15), is

$$E_s(x, y) = e^{-\gamma(y-x)} + \gamma(y-x)e^{-\gamma y}. \tag{16}$$

Far away from the trap, as $x, y \rightarrow \infty$, this converges to the equilibrium result of Eq. (10). From Eq. (8), we obtain the stationary concentration profile:

$$c_s(x) = \gamma(1 - e^{-\gamma x}). \tag{17}$$

As expected, there is a depletion zone of size $1/\gamma = 2D/v$ near the trap, and the concentration grows asymptotically to c_{eq} as $x \rightarrow \infty$.

The IPDF between nearest particles is surprising. From Eqs. (9) and (16) we obtain the conditional joint probability

$$P_s(x, y) = \gamma^2 e^{-\gamma y} (e^{\gamma x} - 1). \tag{18}$$

Dividing $P_s(x, y)$ by $c_s(x)$ yields the ‘‘forward’’ IPDF—the probability that given a particle at x the next nearest particle *to its right* is at y :

$$p_s(z) = \gamma e^{-\gamma z}, \quad z \equiv y - x. \tag{19}$$

The notation chosen here emphasizes the unexpected result that p_s is translationally invariant. What is more, this Poissonian IPDF is characteristic of particles at *equilibrium*, when there are no correlations between their various positions. Indeed, exactly the same IPDF is obtained for the equilibrium state of Eq. (10), without the trap.

To obtain the ‘‘backward’’ IPDF—the probability that given a particle at y the next nearest particle *to its left* is at a distance z —we divide $P_s(x, y)$ by $c_s(y)$:

$$q_y(z) = \gamma \frac{e^{-\gamma z} - e^{-\gamma y}}{1 - e^{-\gamma y}}. \tag{20}$$

The fact that $q_y(z)$ is not translationally invariant comes as no surprise, because of the trap at $x=0$. However, $q_y(z)$ does not normalize properly. The reason for that is that there is a finite chance that there are no particles between the particle at y and the trap, i.e., the particle at y is the nearest particle to the trap. The probability that this happens is $p_0(y) = -\partial E/\partial y|_{x=0}$, or

$$p_0(y) = \gamma^2 y e^{-\gamma y} \tag{21}$$

With this understanding, the proper normalization condition is

$$c_s(y) \int_0^y q_y(z) dz + p_0(y) = c_s(y), \quad (22)$$

which is indeed met.

IV. REACTION-DIFFUSION EQUATION

So far, we have presented an exact solution to the problem of diffusion-limited reversible coalescence with a trap. Exactly solvable models of diffusion-limited reactions, however, are rare. We now wish to discuss one of the most widely used approximation methods, in light of the exact results.

The method is that of reaction-diffusion equations. Here one assumes the existence of a *mesoscopic* length scale within which the system is homogeneous and well mixed, and where the reaction rates can be accounted for as in classical rate equations. At longer length scales, variations in the concentration, $c(x,t)$, give rise to diffusion. In our case, the appropriate reaction-diffusion equation is

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + k_1 c - k_2 c^2, \quad (23)$$

where k_1 and k_2 represent the ‘‘effective’’ rates of birth and coalescence, respectively. The trap at the origin imposes the boundary condition

$$c(0,t) = 0. \quad (24)$$

An alternative approach is that of writing down an infinite hierarchy of rate equations for the n -point density correlation functions, and truncating the hierarchy with a Kirkwood ansatz at some convenient stage. In the simplest case, one truncates the hierarchy at the level of single-point density functions. This is achieved by neglecting all correlations, and by expressing multiple-point density functions as products of single-point densities. In view of the peculiar IPDF in our problem [Eq. (19)], this seems a promising approximation.

Let the probability of having a particle at site n be $\rho_n(t)$, then the joint probability of having particles at both n and m at time t may be approximated as $\rho_{n,m}^{(2)}(t) \approx \rho_n(t)\rho_m(t)$. In this fashion, our model is described by the equation

$$\begin{aligned} \frac{\partial \rho_n}{\partial t} = & \frac{D}{a^2} [-2\rho_n + (1-\rho_n)(\rho_{n-1} + \rho_{n+1})] + \frac{v}{2a}(1-\rho_n) \\ & \times (\rho_{n-1} + \rho_{n+1}), \end{aligned} \quad (25)$$

and the boundary condition $\rho_0(t) = 0$. Notice that in the stationary limit, and without the trap, Eq. (25) is *exact*, since in the equilibrium state of the infinite system the particles really are uncorrelated. Indeed, solving Eq. (25) when $\partial \rho_n / \partial t = 0$ yields $c = \rho/a = v/(2D + av)$, which agrees with c_{eq} of Eq. (11) when $a \rightarrow 0$.

It is tempting to try and connect Eq. (25) to the reaction-diffusion approach, by passing to the continuum limit. This,

however, does not work: writing $c(x,t) = \rho_n(t)/a$, and letting $a \rightarrow 0$ while keeping only up to first-order terms in a , yields

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \frac{v}{a} c - \left(\frac{2D}{a} + v \right) c^2. \quad (26)$$

Thus, it is impossible to identify k_1 and k_2 in this manner, and one is forced to work with the discrete equation (25). [An approximate solution could be found by proceeding with Eq. (26) anyway, ignoring the fact that a is supposed to be infinitesimally small.]

We now use the exact solution of Sec. III to attempt and determine k_1 and k_2 . We note that without the birth and coalescence reactions the particles would simply diffuse with a diffusion constant D —the same D as in the hopping rate D/a^2 of the microscopic rules.

First consider the stationary solution of Eq. (23), for an infinite system without the trap: $c_{\text{eq}} = k_1/k_2$. To conform with the exact solution of Eq. (11), we must have

$$\frac{k_1}{k_2} = \frac{v}{2D}. \quad (27)$$

The stationary solution to Eq. (23) with the trap—the boundary condition (24)—is

$$\frac{c_s(x)}{c_\infty} = \frac{3}{2} \tanh^2 \left(\sqrt{\frac{k_1}{3D}} x + \tanh^{-1} \sqrt{\frac{1}{3}} \right) - \frac{1}{2}, \quad (28)$$

where $c_\infty = c_{\text{eq}}$ is the concentration of particles infinitely far away from the trap.

The concentration profile described by Eq. (28) looks similar to the exact result of Eq. (17). One could now use different criteria to further constrain k_1 and k_2 . Demanding the same asymptotic behavior far away from the trap; $\lim_{x \rightarrow \infty} \ln[1 - c_s(x)/c_{\text{eq}}]/x = -v/2D$, we get

$$k_1 = \frac{3}{8} \frac{v^2}{2D}. \quad (29)$$

On the other hand, if we require the same behavior close to the trap; $(\partial c_s / \partial x)_{x=0} = (v/2D)^2$, we get

$$k_1 = \frac{9}{8} \frac{v^2}{2D}. \quad (30)$$

Clearly, it is impossible to fix the short range behavior and the long range behavior simultaneously. Instead, one may write

$$k_1 = \alpha \frac{v^2}{2D}, \quad \text{and} \quad k_2 = \alpha v, \quad (31)$$

where α is a single fitting parameter of order unity. A least square fit in the range $0 \leq c_{\text{eq}} x \leq 5$ is achieved with $\alpha = 1.27$.

V. DISCUSSION

We have solved the problem of diffusion-limited reversible coalescence with a trap, in one dimension, exactly. The

result is tantalizingly simple: the stationary concentration profile is exponential. Moreover, the distribution of distances between nearest particles (the IPDF) is also exponential, similar to that of particles in an *equilibrium* process—the same process in the absence of the trap. This does not mean, however, that the distribution of particles in the two cases is identical: it is just a peculiarity of the IPDF in this particular model. To be sure, the distribution of particles in the equilibrium situation is fully random and uncorrelated, whereas in the presence of the trap it is not!

We have also contrasted the exact solution with the alternative, traditional approach of reaction-diffusion equations, highlighting the fact that the latter is merely an approximation method. Our model provides a clear example where the effective rates of the reaction-diffusion equation can be related to the microscopic rates of the underlying process, without appealing to renormalization.

An interesting open question is at what dimension reaction-diffusion equations accurately describe the kinetics of the system. Previously, we had conducted numerical studies of Fisher waves in the coalescence process, suggesting

that the critical dimension is $d_c=3$ [20]. The present model could present an advantage in future numerical studies, because of its nontrivial *stationary* state.

Future work will also include the investigation of two-point density correlation functions, as well as the influence of a drift away from the trap. Both problems can be formulated rigorously within the framework of the IPDF method [10]. Multiple-point density correlation functions would shed further light on the breakdown of reaction-diffusion equations in low dimensions. Drift away from the trap could potentially give rise to an interesting phase transition: from a system with a nontrivial steady state (such as in our case, when the drift is zero), to a system with only a trivial steady state (the vacuum), as the drift increases beyond a critical point.

ACKNOWLEDGMENTS

I thank L. Glasser, P. Krapivsky, S. Redner, and L. Schulman for valuable discussions.

-
- [1] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
- [2] H. Haken, *Synergetics* (Springer-Verlag, Berlin, 1978).
- [3] G. Nicolis and I. Prigogine, *Self-Organization in Non-Equilibrium Systems* (Wiley, New York, 1980).
- [4] T. M. Liggett, *Interacting Particle Systems* (Springer-Verlag, New York, 1985).
- [5] K. Kang and S. Redner, *Phys. Rev. A* **32**, 435 (1985); V. Kuzovkov, and E. Kotomin, *Rep. Prog. Phys.* **51**, 1479 (1988).
- [6] Proceedings of the conference on Models of Non-Classical Reaction Rates, NIH, 1991 [*J. Stat. Phys.* **65**, (5/6) (1991)].
- [7] K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1965).
- [8] S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960).
- [9] D. ben-Avraham, M. A. Burschka, and C. R. Doering, *J. Stat. Phys.* **60**, 695 (1990).
- [10] C. R. Doering, *Physica A* **188**, 386 (1992).
- [11] H. Hinrichsen, K. Krebs, and M. P. Pfannmüller, *J. Stat. Phys.* **78**, 1429 (1995); B. Wehefritz, K. Krebs, and M. P. Pfannmüller, *J. Stat. Phys.* **78**, 1471 (1995); H. Hinrichsen, K. Krebs, and I. Peschel, *Z. Phys. B* **100**, 105 (1996).
- [12] M. Henkel, E. Orlandini, and G. M. Schütz, *J. Phys. A* **28**, 6335 (1995); M. Henkel, E. Orlandini, and J. Santos, *Ann. Phys. (N.Y.)* **259**, 163 (1997).
- [13] H. Simon, *J. Phys. A* **28**, 6335 (1995).
- [14] D. Balboni, P.-A. Rey, and M. Droz, *Phys. Rev. E* **52**, 6220 (1995); P.-A. Rey and M. Droz, *J. Phys. A* **30**, 1101 (1997).
- [15] M. Bramson and D. Griffeath, *Ann. Prob.* **8**, 183 (1980); *Z. Wahrscheinlichkeitstheor. Verwandte Geb.* **53**, 183 (1980).
- [16] D. C. Torney and H. M. McConnell, *Proc. R. Soc. London, Ser. A* **387**, 147 (1983).
- [17] J. L. Spouge, *Phys. Rev. Lett.* **60**, 871 (1988).
- [18] H. Takayasu, I. Nishikawa, and H. Tasaki, *Phys. Rev. A* **37**, 3110 (1988).
- [19] V. Privman, *Phys. Rev. E* **50**, 50 (1994); *Mod. Phys. Lett. B* **8**, 143 (1994); V. Privman, A. M. R. Cadilhe, and M. L. Lawrence, *J. Stat. Phys.* **81**, 881 (1995); *Phys. Rev. E* **53**, 739 (1996).
- [20] J. Riordan, C. R. Doering, and D. ben-Avraham, *Phys. Rev. Lett.* **75**, 565 (1995).