"Random-Force-Dominated" Reaction Kinetics: Reactants Moving under Random Forces

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We investigate the reaction kinetics for systems in which the dynamics of the particles is governed by a Langevin equation with negligible damping, and we find the expressions for the survival probability, residual concentrations, and reaction rates. We discover that the integral in time of the reaction front for $d=1$ is $t^{1-\beta}\exp(-|x|/t^{\alpha})$ for both the low and high damping limits, and we estimate the exponents α and β in each case.

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Considerable recent attention has been focused on the study of simple irreversible chemical reactions in which the reactants are transported by diffusion, and react on contact [1,2]. Diffusion is modeled by random walkers —particles whose motion is characterized by random and, in general, uncorrelated velocities. However, there may be situations where it is more realistic to assume that particles move solely under the influence of random forces. These situations might arise in low-viscosity liquids that are being mixed, in systems that display turbulence, or in systems undergoing a fast increase in temperature.

In a general random-force model, the motion of the particle is a second-order process whose dynamical evolution is governed by the Langevin equation

$$\ddot{x}+\gamma\dot{x}=f(t)\,. \tag{1}$$

Here γ represents a damping coefficient, and the force $f(t)$ is a random variable. In the simplest case, we can assume that the force is Gaussian distributed with mean zero [3]. According to the value of γ, two regimes can be identified. In the large γ limit, the behavior of the particle quickly becomes that of a normal random walker; we call this regime "diffusion limited." The second regime corresponds to the limit where γ is negligible, and the dynamics of the particles is dominated by the random-force term of Eq. (1). The kinetics in this regime, which we call the "random-force-dominated" regime, have not been treated previously—in contrast to the much more studied diffusion-limited case [1,2].

In the random-force-dominated regime, the absence of damping results in a superdiffusive motion [4] of the reactants and enhanced reaction rates. In particular, we find that the survival probability of a particle in the presence of a random distribution of traps is much smaller than in the classical diffusion-limited regime [5,6]. We also find that for reactions of the form $A+B\rightarrow C$, with homogeneous initial distribution of the reactants in equal concentrations ($c_A=c_B$), this dynamics leads to residual concentrations that decay as t^{-1} for dimensions above the critical dimension $d_c=\frac{4}{3}$. This is consistent with experimentally measured decays which have been interpreted in terms of mean-field formalisms [7]. For $d=1$ we find that the concentrations decay as $t^{-3/4}$. If the reactants are initially separated, we find that the form of the time-integrated distribution of C particles for $d=1$ is $t^{1-\beta}\exp(-|x|/t^{\alpha})$ for both the simple diffusion case (with $\alpha\simeq 0.3$ and $\beta\simeq 0.8$) and the random-force case (with $\alpha\simeq 1.0$ and $\beta\simeq 0.5$).

The asymptotic behavior of the mean-square displacement for a particle moving solely under the influence of the random force is given by $\langle x^2\rangle\sim t^3$ [8], a relation reminiscent of the classic Richardson expression for turbulent diffusion [9]. This provides the fundamental scaling relation between time and distance to be used throughout this paper. In the general case when $\gamma\neq 0$, we expect $\langle x^2\rangle\sim t^3$ for $t\ll t_x$, and $\langle x^2\rangle\sim t$ for $t\gg t_x$ with $t_x\sim 1/\gamma$.

The conventional approaches to investigate reaction kinetics are through the study of the survival probability of particles in the presence of stationary sinks, and the study of the reaction rate and residual concentrations of each species of particles in the reaction $A+B\rightarrow C$. We begin by calculating the survival probability of a particle placed at random within a system of linear dimension L with absorbing boundary conditions. We find that the survival probability decays exponentially in time:

$$S_L(t)\sim\exp(-c_1 t/L^{2/3})\,. \tag{2}$$

Numerical tests of this relation are shown in Fig. 1. The average time $\langle t\rangle$ for the walker to get trapped scales with the size of the system as

$$\langle t\rangle\sim L^{2/3}\,, \tag{3}$$

which is the same scaling law as for the mean-square displacement of the particle.

From $S_L(t)$, we can estimate the survival probability for independent particles placed in a system of randomly distributed traps with concentration c. The probability to have a trap-free region of volume L^d is $p_c(L)\sim(1-c)^{L^d}=\exp[-L^d|\ln(1-c)|]$. Hence the average survival probability is

$$S(t)\sim\int_0^{\infty}S_L(t)p_c(L)d^dL\,. \tag{4a}$$

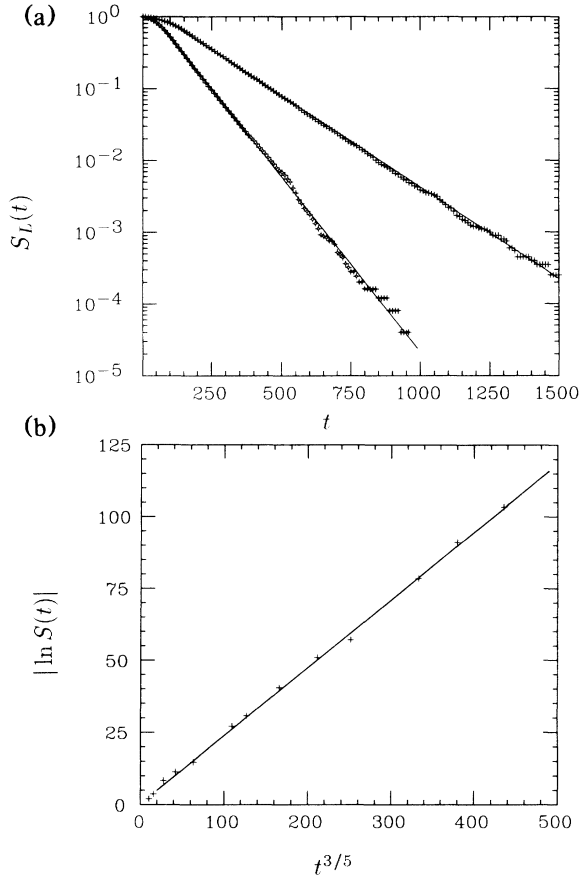

FIG. 1. (a) Semilogarithmic plot of the survival probability for a particle moving under a random force in a $d=1$ system with $L=1000$ (⊕) and $L=2500$ (+) for absorbing boundary conditions. (b) Linear plot of the absolute value of the logarithm of $S(t)$ as a function of $t^{3/5}$ in order to test our result (4b) for $d=1$.

The dominant contribution to the integral comes from values $c_1 t/L^{2/3} \sim \beta L^d$, where β is the constant $|\ln(1-c)|$. Thus the dominant term in $S(t)$ is given by

$$S(t) \sim \exp[-c_2 t^{3d/(3d+2)}], \tag{4b}$$

where c_2 is a constant. The exponent $3d/(3d+2)$ of Eq. (4b) is quite different from that for a random walker in the diffusion-limited regime, which is $d/(d+2)$ [5]; in particular, for $d=1$ the exponent is $\frac{3}{5}$, so the survival probability is much smaller than the diffusion-limited result which has exponent $\frac{1}{3}$.

To test the result of Eq. (4b), we perform simulations for the case $d=1$ [3]. Figure 1(b) shows the logarithm of $S(t)$ as a function of $t^{3/5}$. The straight-line behavior supports the prediction of Eq. (4).

Next we consider the simple irreversible chemical reaction in which the reactants move and react on contact. Previously such systems have been simulated under the assumption that the reactants move only by diffusion. For such systems, the decay of concentration with time is strongly affected by the initial fluctuations in the local concentrations of the reactants. Here we investigate what happens to the reaction kinetics when the dynamics of the reactants is dominated by random forces.

We study the reaction $A+B \rightarrow C$, assuming that when an A and a B particle meet they instantly and irreversibly combine to form an inert species C. We treat two different initial configurations of the reactants: (i) A and B particles are randomly distributed, as may be expected in a homogeneous system; and (ii) the A and B particles are initially separated in space, so they react in a "reaction zone" as would be the case in an inhomogeneous system. In particular, the experiments by Koo, Li, and Kopelman [10] were done with these initial conditions.

Case (i).— Initially each site either is occupied by an A or a B particle (with equal probability) or is empty. Within a region of linear dimension L the average number of particles of either species is proportional to L^d, and the fluctuations in this quantity are proportional to $L^{d/2}$. Therefore, within this region there will be an excess of one of the reactants, say, the A particles, and at large time the concentration of these particles will be given by

$$c_A(t) \sim L^{d/2}/L^d \sim L^{-d/2}. \tag{5}$$

To express this relation as a function of time we use the scaling relation for the length covered by a moving particle $L \sim t^{3/2}$. Substituting in Eq. (5) we get

$$c_A(t) \sim t^{-3d/4}, \tag{6}$$

suggesting that the "critical dimension" may be $\frac{4}{3}$ since $1/t$ is the fastest possible decay under these initial conditions, obtained by ignoring the spatial fluctuations in the system. In the diffusion-limited regime, under the same initial conditions, the concentration decay is $c_A(t) \sim t^{-1/4}$ [1,2].

To test the prediction of (6), we carry out simulations for the case $d=1$. Figure 2 shows the time evolution $c_A(t)$ of the concentration of A particles, for systems of different lengths. Our results fully support the above arguments.

Case (ii).— Next consider a $d=1$ system of size L where initially each reactant (A or B) fills uniformly half of the system. Under these conditions, the reactions take place only in a localized region around the interface of the two species. This region is called the reaction front, and it is "marked" by the presence of the inert and immobile C particles. We define a rate of reaction R as the number of C particles produced per unit time. We find that in the random-force-dominated case $R_{RF} \sim t^{1/2}$, as opposed to the diffusion-limited situation for which $R_{DL} \sim t^{-1/2}$ at long times [10–12]. These results can be understood in a simple way by noticing that the total number of reactions up to time t must be proportional to the mean number N of particles that can reach the interface. Since the particles are initially uniformly distributed, then $N \sim \xi(t)$, where $\xi(t)$ is the characteristic dis-

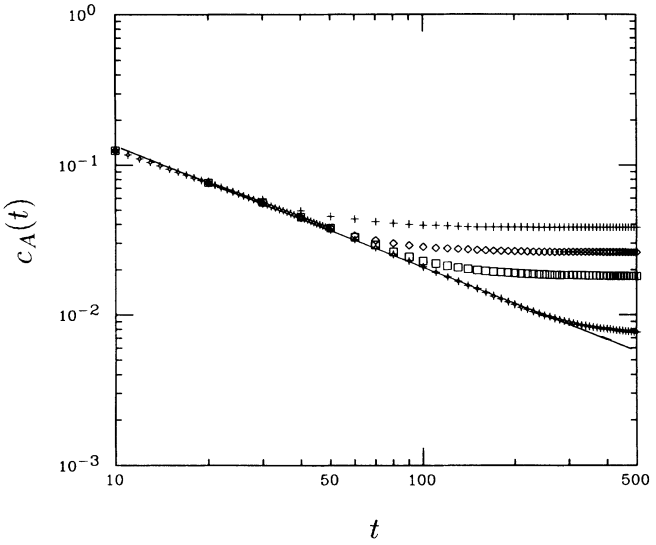

FIG. 2. Log-log plot of the residual concentration of one of the reactants as a function of time for case (i), homogeneous initial conditions, for different system sizes: $L=250$ (+), 500 ($\diamond$), 1000 ($\square$), and 5000 ($\oplus$). The plateau at large t reflects the fluctuations in initial concentrations due to finite-size effects.

tance traveled by a particle up to time t, $\xi \sim t^{3/2}$ in our case, whereas $\xi \sim t^{1/2}$ for the diffusion-limited case. Then using the fact that $R = \partial N/\partial t$ immediately leads to the scaling expressions for R in both cases.

We also study the spatial distribution of C particles as a function of time. Until now studies have been limited to the scaling properties of the width and the height of this distribution in the diffusion-limited case, and there is still debate on the values of the exponents [10–13]; thus in order to compare the effects of the different dynamics we investigate the reaction fronts for both cases.

We find that the integral in time of the reaction front $c(x,t)$ has the form

$$I(x,t) \equiv \int_0^t c(x,t')dt' \sim t^{1-\beta} \exp(-|x|/t^{\alpha}), \qquad (7)$$

where α and β are the exponents related to the width and the height of the distribution, respectively, and x is measured from the position of the original interface. The exponential form of Eq. (7) is inferred from Figs. 3(a) and 3(b) and was used to estimate the exponents for both cases. For the pure diffusion case, we find that $\alpha \simeq 0.30 \pm 0.01$ and $\beta \simeq 0.80 \pm 0.02$; while in the random-force-dominated case we obtain $\alpha \simeq 1.00 \pm 0.01$ and $\beta \simeq 0.50 \pm 0.02$. Our exponents for the diffusion-limited case are in close agreement with the values obtained by Cornell, Droz, and Chopard [13] by direct measurements of the height and the width of the reaction front in cellular automata simulations. These values should be valid for $d=1$ systems and are different from those obtained through the "mean-field" formalism of Galfi and Racz [11], which is expected to be valid in higher dimensions.

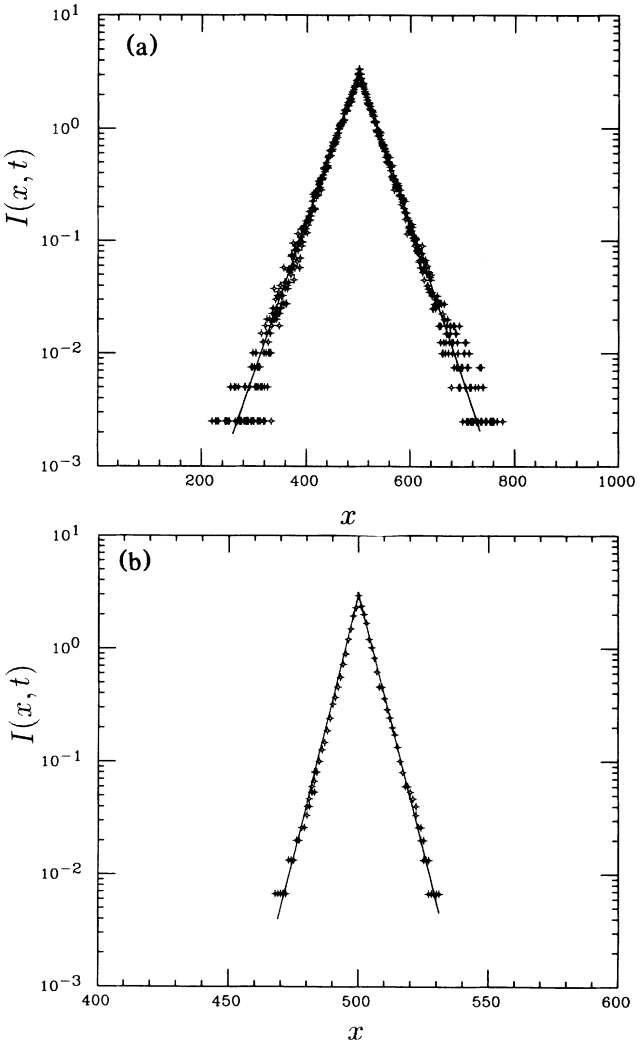

FIG. 3. Semilogarithmic plot of $I(x,t)$ defined in Eq. (7) for a $d=1$ system in (a) the random-force-dominated regime, with $L=1000$ and $t=100$, and (b) the diffusion-limited regime, with $L=1000$ and $t=1000$.

We note that for both the random-force-dominated and the diffusion-limited regimes, the values of the exponents are consistent with the expected scaling relation obtained from $R \sim$ (width) $\times$ (height) [11–13].

In conclusion, we find that the reaction kinetics change drastically from the high damping unit (diffusion-limited regime) to the low damping limit (random-force-dominated regime), and we find expressions for the survival probability, residual concentrations, and reaction rates in the low damping limit. We also find that the functional forms of the reaction front for both the diffusion-limited and the random-force-dominated cases are exponential in the distance, and from these forms we are able to estimate the exponents of the width and height for both cases.

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[1] M. Bramson and J. Lebowitz, Phys. Rev. Lett. **61**, 2397 (1988); I. Sokolov, H. Schnorer, and A. Blumen, Phys. Rev. A **44**, 2388 (1991).

[2] S. F. Burlatsky, Teor. Eksp. Khim. **14**, 483 (1978); P. Meakin and H. E. Stanley, J. Phys. A **17**, L173 (1984); K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984).

[3] Our numerical results are obtained as follows: (a) For the *random-force-dominated regime*, we use Monte Carlo simulations of $d=1$ discrete systems, where the position of each particle is updated according to a discretized version of Eq. (1), and the force term $f(t)$ takes on the values $\pm f_0$ with equal probability at each unit time; the asymptotic transport properties under these conditions are equivalent to the case in which $f(t)$ is Gaussian distributed with mean zero. (b) For the *diffusion-limited regime*, the particles are moved as conventional nearest-neighbor symmetric random walkers.

[4] See, e.g., the recent review by M. F. Shlesinger, Annu. Rev. Phys. Chem. **39**, 269 (1988). For applications to turbulence and chaos, see M. F. Shlesinger, B. J. West, and J. Klafter, Phys. Rev. Lett. **58**, 1100 (1987).

[5] N. D. Donsker and S. R. Varadhan, Commun. Pure Appl. Math. **32**, 721 (1979).

[6] J. W. Haus and K. W. Kehr, Phys. Rep. **150**, 263 (1987); D. Ben-Avraham and S. Havlin, Adv. Phys. **36**, 695 (1987); J. P. Bouchaud and A. Georges, Phys. Rep. **195**, 127 (1990).

[7] P. Erdi and J. Toth, *Mathematical Models of Chemical Reactions* (Princeton Univ. Press, Princeton, NJ, 1988); *The Theory of Kinetics*, edited by C. H. Banford and C. F. Tipper (Elsevier, New York, 1969).

[8] J. Masoliver, Phys. Rev. A **45**, 706 (1992).

[9] G. K. Batchelor and A. A. Townsend, in *Surveys in Mechanics*, edited by G. K. Batchelor and R. M. Davies (Cambridge Univ. Press, London, 1986), p. 352.

[10] Y. E. Koo, L. Li, and R. Kopelman, Mol. Cryst. Liq. Cryst. **183**, 187 (1990); J. Stat. Phys. **65**, 893 (1991).

[11] L. Galfi and Z. Racz, Phys. Rev. A **38**, 3151 (1988).

[12] H. Taitelbaum, S. Havlin, J. E. Kiefer, B. L. Trus, and G. H. Weiss, J. Stat. Phys. **65**, 873 (1991).

[13] S. Cornell, M. Droz, and B. Chopard, Phys. Rev. A **44**, 4826 (1991).