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Formal solution of a class of reaction-diffusion models: Reduction to a single-particle problem

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We consider the trapping reaction $A+B\rightarrow B$ in space dimension $d\leqslant 2$. By formally eliminating the B particles from the problem, we derive an effective dynamics for the A particles from which the survival probability of a given A particle and the statistics of its spatial fluctuations can be calculated in a rather general way. The method can be extended to the study of annihilation and coalescence reactions, $B+B\rightarrow 0$ or B, in $d=2$.

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First-passage problems involving more than a few degrees of freedom are notoriously difficult to solve [1,2]. In this paper, we use a technique that enables one to solve a class of first-passage problems involving an infinite number of degrees of freedom. For definiteness, we develop the method in the context of the "trapping reaction," $A+B\rightarrow B$, but the applications are more general, as emphasized in the latter part of the paper. The main result of our approach is to reduce the problem to one described by a single degree of freedom whose late-time behavior can be extracted analytically.

The asymptotic dynamics of the trapping reaction has been a long-standing problem. The main question is how the density of A particles decreases with time. A related problem, much studied in the context of chemical kinetics [3,4] is the two-species annihilation reaction, $A+B\rightarrow 0$, with initial densities $\rho_A(0)<\rho_B(0)$. This is equivalent to the trapping reaction at late times when $\rho_A(t)\ll\rho_B(t)$ and $\rho_B(t)$ is essentially constant. Again, the standard problem is to compute the asymptotic form of the A-particle density $\rho_A(t)$ or, equivalently, the probability $Q(t)$ that a given A particle survives until time t. Since the particles do not interact with other particles of the same species, to compute $Q(t)$ it suffices to consider a *single* A particle moving in an infinite sea of B particles with density ρ $(=\rho_B)$.

Since the A particle dies on the first contact with a B particle, a natural approach to this type of first-passage problem would be to treat the A particle as an absorbing boundary for the B particles (or vice versa). Unfortunately, for an arbitrary A-particle trajectory, the absorbing-boundary problem cannot be solved. In this paper, we introduce a different approach in which we treat the A and B particles as if they were *noninteracting*. We exploit the initial condition that each B particle is randomly located anywhere in the system to show that certain "events," where a B particle meets the A particle *for the first time* (remember that we are treating them as noninteracting, so they can meet more than once), have a Poisson distribution, i.e., the probability p_n that n such events have occurred up to time t is given by $p_n=(\mu^n/n!)\exp(-\mu)$, where the mean μ of the distribution is a functional $\mu[\vec{z}]$ of the trajectory $\vec{z}(\tau)$, $0\leqslant\tau\leqslant t$ of the A particle. The probability that the trajectory $\vec{z}(\tau)$ has survived, in the original interacting problem, is simply $p_0[\vec{z}]=\exp(-\mu[\vec{z}])$. Finally, $Q(t)$ is obtained by averaging $\exp(-\mu[\vec{z}])$ over all possible A-particle trajectories $\vec{z}(\tau)$ with the appropriate (Wiener) measure, $\exp[-(1/4D')\int_0^t d\tau(d\vec{z}/d\tau)^2]$, where D' is the A particle's diffusion constant. In this way, the B particles have been eliminated from the problem, and one has an effective A-particle dynamics described by the Wiener measure and the functional $\mu[\vec{z}]$. The final step which makes further analytical progress possible, is the observation that the path integral over $\vec{z}(\tau)$ is dominated at late times by a single A-particle trajectory.

The main results of this approach are the following.

(i) The trajectory where the A particle is stationary is proved to be the dominant trajectory and determines the asymptotic form of the A particle's survival probability [4], $Q(t)\sim\exp(-\lambda_d t^{d/2})$ for $d<2$ (with a logarithmic correction in $d=2$), where λ_d is a calculable constant [5] and d is the dimensionality of space.

(ii) Typical *fluctuations* of the surviving A-particle trajectories around this dominant path have variance $\langle z^2(t)\rangle\sim t^{2\phi}$ for $d<2$, where $\phi\geqslant(2-d)/4$.

(iii) Exact results are obtained for $Q(t)$ and the form of the dominant path in a system with a nonuniform initial density of B particles.

(iv) This approach provides a powerful method for calculating the first-passage properties for a deterministically moving boundary $\vec{z}(t)$.

(v) The method also provides a formalism for calculating $Q(t)$ in the highly nontrivial situation where the B particles themselves interact, e.g., $B+B\rightarrow 0$, at least in $d=2$ where the density correlations induced by these reactions are negligible.

We begin by deriving the Poisson property that plays a central role in the analysis. We consider a finite volume V containing $N=\rho V$ B particles (diffusion constant D), randomly distributed within it, and a single A particle (diffusion constant D'), initially located at the origin. Let $\vec{z}(t)$ be the A-particle trajectory, and let $P(\vec{x},t)$ be the probability that a given B particle, starting at $\vec{x}$, has met the A particle before time t. The average of this quantity over the initial position $\vec{x}$ is $(1/V)\int_V dV\, P(\vec{x},t)=R(t)/V$, where $R(t)$ is an implicit functional of $\vec{z}(t)$. The probability that n distinct B particles have met the A particle, averaged over their initial positions, is $p_n(t)=\binom{N}{n}(R/V)^n(1-R/V)^{N-n}$. Taking the limit $N\to\infty$, $V\to\infty$, with $\rho=N/V$ and n held fixed, one recovers the Poisson distribution, $p_n=(\mu^n/n!)\exp(-\mu)$, with $\mu=\rho R$.

One can derive an equation for the functional $\mu[\vec{z}]$ by calculating, in two ways, the probability density to find a B particle at the point $\vec{z}(t)$ at time t. First, since the particles are treated as noninteracting, and the B particles start in a steady-state configuration of uniform density ρ, this probability density is just ρ. Second, from the Poisson property, the probability that a B particle (i.e., any B particle) meets the A particle for the first time in the time interval $(t',t'+dt')$ is $\dot{\mu}(t')dt'$. The probability density for such a particle to subsequently arrive at $\vec{z}(t)$ at time t is given by the diffusion propagator $G(\vec{z}(t),t|\vec{z}(t'),t')=[4\pi D(t-t')]^{-d/2}\exp\{-[\vec{z}(t)-\vec{z}(t')]^2/4D(t-t')\}$. Equating the results from these two methods gives our fundamental equation

$$\rho=\int_0^t dt'\,\dot{\mu}(t')G(\vec{z}(t),t|\vec{z}(t'),t'), \tag{1}$$

which is an implicit equation for the functional $\mu[\vec{z}]$ [noting that $\mu(t=0)=0$, since no B particle can meet the A particle in zero time]. Finally, $Q(t)=\langle\exp(-\mu[\vec{z}])\rangle_z$, where the average is over all paths $\vec{z}(t)$ weighted with the Wiener measure.

As the first application of this equation we prove that the trajectory $\vec{z}=0$ is the dominant path, i.e., that it gives the smallest possible value of $\mu[\vec{z}]$ for all t. This function $\mu_0(t)$ satisfies Eq. (1) with $\vec{z}=0$:

$$\rho=\int_0^t dt'\,\dot{\mu}_0(t')[4\pi D(t-t')]^{-d/2}. \tag{2}$$

By inspection, $\mu_0(t)$ must have the form $\mu_0(t)=\lambda_d t^{d/2}$ (for $d<2$) in order that the right-hand side be independent of t. Substituting this form in Eq. (2), and evaluating the integral, gives

$$\lambda_d=\rho\left(\frac{2}{\pi d}\right)\sin\left(\frac{\pi d}{2}\right)(4\pi D)^{d/2},\quad d<2, \tag{3}$$

while for $d=2$ one finds for $t\to\infty$, $\mu_0(t)\to 4\pi\rho Dt/\ln t$ [6]. The corresponding A-particle survival probability is $Q_0(t)=\exp[-\mu_0(t)]$. This simple case of a static A particle is sometimes called the "target annihilation problem," and our method reproduces the known results for that problem [7] in a very simple way. To prove that $\vec{z}(t)=0$ gives the global minimum of $\mu[\vec{z}]$, we write $\mu=\mu_0+\mu_1$ in Eq. (1). This equation can then be rearranged, with the help of Laplace transform techniques, to give an implicit equation for $\mu_1[\vec{z}]$:

$$\mu_1[\vec{z}]=\frac{\sin(\pi d/2)}{\pi}\int_0^t\frac{dt_1}{(t-t_1)^{(2-d)/2}}\times\int_0^{t_1}\frac{dt_2}{(t_1-t_2)^{d/2}}\dot{\mu}(t_2)K(t_1,t_2), \tag{4}$$

where $K(t_1,t_2)=1-\exp\{-[\vec{z}(t_1)-\vec{z}(t_2)]^2/4D(t_1-t_2)\}$.

Equation (4) is "implicit" because the full μ appears on the right-hand side. Now note that $K(t_1,t_2)\geqslant 0$ and $\dot{\mu}\geqslant 0$ [because $\mu(t)$ is the mean number of different B particles that have met the A particle up to time t – clearly a nondecreasing function]. Therefore, $\mu_1[\vec{z}]\geqslant 0$ for all paths $\vec{z}(t)$, with equality when $\vec{z}(t)=0$ for all t. It follows that $Q(t)\equiv\langle\exp(-\mu_0-\mu_1)\rangle_{\vec{z}}\leqslant\exp[-\mu_0(t)]$. This rigorous upper bound for $Q(t)$, combined with the identical rigorous lower bound derived in [5], proves that the asymptotic form of $Q(t)$ is the same as for the target problem, where the A particle is stationary, for all $d\leqslant 2$. The interpretation of this result is that, since μ is large for $t\to\infty$ ($\mu\sim t^{d/2}$), the path integral for $Q(t)$ is dominated by the path that minimizes μ, i.e., we are essentially evaluating the path integral by the method of steepest descents. Small fluctuations around the dominant path will determine the corrections to the asymptotic form.

We next discuss the probability distribution $P(z,t)$ of the position z of the A particle at time t, given that it survives. Numerical studies [8] suggest that in $d=1$, $\langle z^2(t)\rangle^{1/2}\sim t^{\phi}$, with $\phi=0.25$–0.3, while similar studies in $d=2$ are inconclusive. Our methods suggest that $\phi=(2-d)/4$ for all $d<2$. The technique is to expand $\mu_1[\vec{z}]$, given by Eq. (4), to order $\vec{z}^2$ to compute the variance of the Gaussian fluctuations around the dominant trajectory $\vec{z}(t)=0$. To this order, one can replace $\mu(t_2)$ on the right-hand side by $\mu_0(t_2)=\lambda_d t_2^{d/2}$, and expand the function $K(t_1,t_2)$ to order $\vec{z}^2$. Specializing to $d=1$, the result is, at time t,

$$\mu_1[z]=\frac{\lambda_1}{8\pi D}\int_0^t\frac{dt_1}{\sqrt{t-t_1}}\int_0^{t_1}dt_2\frac{[z(t_1)-z(t_2)]^2}{\sqrt{t_2}(t_1-t_2)^{3/2}}. \tag{5}$$

The probability distribution for z at time t is given, up to an overall normalization, by the path integral

$$P(z,t)=\int\mathcal{D}z(t)\exp\left(-\frac{1}{4D'}\int_0^t d\tau\,\dot{z}^2(\tau)-\mu_1[z]\right), \tag{6}$$

where the integral is over all paths satisfying the boundary conditions $z(0)=0$, $z(t)=z$.

The path integral has the form $\int\mathcal{D}z(t)\exp(-S[z])$, where the action $S[z]=S_T[x]+S_V[z]$ is a quadratic functional of $z(\tau)$, where $S_T[z]=(1/4D')\int_0^t d\tau\,\dot{z}^2(\tau)$ and $S_V[z]=\mu_1[z]$. Since the integrand is Gaussian, the z dependence of the path integral is exactly captured by the path of minimum action connecting $z(0)=0$ and $z(t)=z$. Although we have been unable to find this path analytically, we can obtain a lower bound on $\langle z^2(t)\rangle$ by noting that $S[z]$ for any trial function $z(t)$ provides an upper bound on the minimum action. The linear path $z(\tau)=(\tau/t)z$ gives $S_V=c_V\lambda_1 z^2/D\sqrt{t}$ and $S_T=c_T z^2/D' t$, where c_V and c_T are unimportant constants. For this path, therefore, S_V dominates at large t. The probability weight for the fluctuations $z(t)$ of surviving trajectories is Gaussian, with variance $\langle z^2(t)\rangle \geqslant (D/2c_V\lambda_1)\sqrt{t}$ for large t, i.e., $\langle z^2(t)\rangle \sim t^{2\phi}$, with $\phi \geqslant 1/4$, consistent with the numerical estimate $\phi=0.25-0.3$. A more detailed study [9] strongly suggests that the lower bound $\phi \geqslant 1/4$ is saturated, i.e., $\phi=1/4$. Similar arguments [9] give the generalization $\phi \geqslant (2-d)/4$ for $d<2$.

We turn now to a related problem with a nontrivial dominant path that can be exactly determined. Consider, in $d=1$, a system where the density of B particles at $t=0$ has different values, ρ_L and ρ_R, to the left and right of the A particle. The derivation of an equation for $\mu[z]$ proceeds exactly as before, except that the probability density to find a B particle at the point z at time t in the noninteracting system, which appears on the left-hand side of Eq. (1), has to be recalculated. In terms of the diffusion propagator G introduced earlier, this probability is (quite generally) $P_B(z,t)=\int_{-\infty}^{\infty}dx\,\rho(x)\,G(z,t|x,0)$ where $\rho(x)$ is the initial B-particle density at position x. When $\rho(x)=\rho$, a constant, one finds $P_B(z,t)=\rho$, as before. When $\rho(x)=\rho_L$ for $x<0$ and ρ_R for $x>0$, the generalized version of Eq. (1) becomes

$$\rho\left[1-\Delta\,\mathrm{erf}\left(\frac{z(t)}{\sqrt{4Dt}}\right)\right]=\int_0^t dt'\,\dot{\mu}(t')\,G(z(t),t|z(t'),t'), \tag{7}$$

where $\rho=(\rho_L+\rho_R)/2$ is now the mean density, $\Delta=(\rho_L-\rho_R)/(\rho_L+\rho_R)$ is a measure of the left-right asymmetry, and $\mathrm{erf}(x)$ is the error function.

Physical intuition suggests that, because of the asymmetry, surviving A-particle trajectories will tend to be those that drift into the region (the right, say) where the B-particle density is initially smaller. Upper and lower bounds have been derived earlier [10] for the asymptotics of the A-particle survival probability $Q(t)$, which show that it has the asymptotic form $Q(t)\sim \exp[-g(\Delta)\lambda_1\sqrt{t}]$, where $g(0)=1$ for consistency with the symmetric case $\rho_L=\rho_R$. This form for $Q(t)$ shows that $\mu[z]$ for the optimal path has the time-dependence $\mu \propto \sqrt{t}$. Both sides of Eq. (7) can then be rendered time independent by the choice $z(\tau)=\alpha\sqrt{4D\tau}$ for all $\tau \leqslant t$, where α is a constant to be determined. A more detailed analysis [9] shows that the dominant path is indeed of this form.

Putting $\mu(t)=g(\Delta)\lambda_1\sqrt{t}$ and $z(\tau)=\alpha\sqrt{4D\tau}$, in Eq. (7), and evaluating the integral on the right-hand side gives

$$g(\Delta)=\frac{\exp(-\alpha^2)}{1-\mathrm{erf}^2(\alpha)}[1-\Delta\,\mathrm{erf}(\alpha)]. \tag{8}$$

The final step is to minimize the right-hand side with respect to α to obtain the optimal path. This can be done numerically. The resulting $g(\Delta)$ is shown for $\Delta \geqslant 0$ as the inset in Fig. 1 [note that, by symmetry, $g(\Delta)$ is symmetric around $\Delta=0$]. It clearly satisfies the bounds $1-|\Delta| \leqslant g(\Delta) \leqslant 1$ derived in [10].

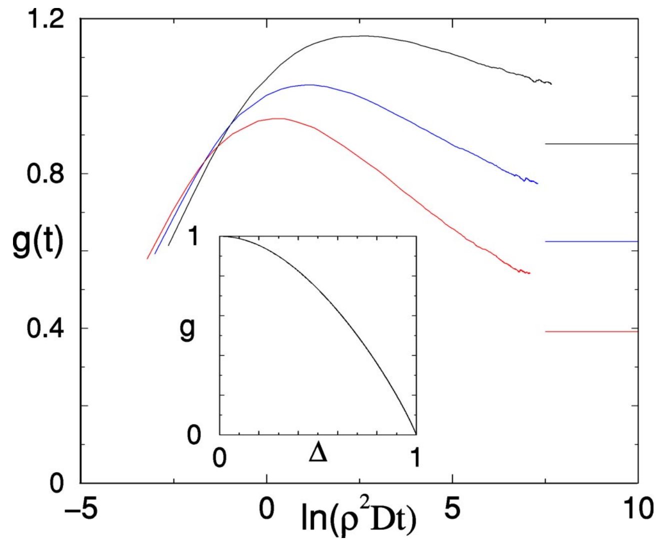

FIG. 1. Time-dependence of $g(t)\equiv -\ln Q(t)/\lambda_1\sqrt{t}$ for density asymmetries $\Delta=1/3$, 3/5, and 7/9 (top to bottom). The horizontal lines show the asymptotic value of g in each case, while the inset shows this value as a function of Δ.

In the main part of Fig. 1, numerical results for $g(t)=-\ln Q(t)/\lambda_1\sqrt{t}$, obtained using the algorithm of Ref. [8], are displayed, with $D=1/2$ and $\rho_L=0.5$ in all cases, while $\rho_R=0.25$, 0.125, and 0.0625 (top to bottom on the right), corresponding to $\Delta=1/3$, 3/5, and 7/9 respectively. The horizontal lines on the right show the asymptotic values obtained from the inset for the corresponding values of Δ. The slow approach to asymptopia is similar to that observed [8,10] in the symmetric case ($\Delta=0$).

As a bonus, the same calculation solves the first-passage problem of B particles with density ρ_L for $x<0$ and ρ_R for $x>0$ moving in the presence of a deterministically moving absorbing boundary located at $x(t)=\alpha\sqrt{4Dt}$. The probability that no particle has reached the boundary up to time t has the simple form $Q(t)=\exp[-g(\Delta)\lambda_1\sqrt{t}]$, with $g(\Delta)$ given by Eq. (8). We are not aware of any other way of obtaining this result. Extensions to deterministically moving absorbing boundaries in dimension $d>1$ are also possible [9].

In the final part of this paper, we apply this approach to a nontrivial problem with $d=2$. Consider the annihilation or coalescence reaction $B+B\to 0$ with probability $1/(q-1)$ and $B+B\to B$ with probability $(q-2)/(q-1)$. The density of B particles is known to decay as $\rho(t)=a_d[(q-1)/q]\times(Dt)^{-d/2}$ for $d<2$, where a_d is a universal constant [11,12] equal to $1/2\pi\epsilon$ for $d\to 2$, with $\epsilon=2-d$. For $d=2$, a logarithmic correction is obtained, $\rho(t)\sim \ln t/t$. Now assume that one of the B particles is tagged and relabeled as an A particle, with diffusion constant D'. We consider the probability (the "walker persistence" probability [13]) $Q(t)$ that the A particle has not met any B particle up to time t. The limit $d\to 2$ provides a simplification because it is the borderline dimension above which the rate equation approach, $d\rho/dt \propto -\rho^2$, which gives $\rho(t)\propto 1/t$, is qualitatively correct because density fluctuations can be ignored [11,12]. Equation (1) is readily adapted to this case. As before, we treat the A particle as if it does not interact with the B particles, while the interactions of the B particles with each other give rise to their decreasing density $\rho(t)$. The Poisson distribution for the number of first crossings of the A particle by B particles still holds for this system. The left-hand side of Eq. (1), i.e., the probability density to find a B particle at the point $\vec{z}(t)$ at time t, becomes $\rho(t)$, while on the right-hand side the propagator $G(\vec{z}(t),t|\vec{z}(t'),t')$ has to be multiplied by a factor $\rho(t)/\rho(t')$, being the probability of a given B particle surviving till time t, given that it survives till time t'. The required generalization of Eq. (1) then reads

$$1=\int_0^t \frac{dt'}{\rho(t')}\dot{\mu}(t')G(\vec{z}(t),t|\vec{z}(t'),t'). \tag{9}$$

It is convenient to approach the limit $d\to 2$ from below. Consider first the case $D'=0$, for which $Q(t)$ becomes the "site-persistence" probability, i.e., the probability that a given point in space (the location of the A particle) has not been visited by any B particle. The static A particle corresponds to $\vec{z}(\tau)=0$ for all τ, and with $\rho(t')=a_d[(q-1)/q]\times(Dt')^{-d/2}$ for large t, Eq. (9) becomes

$$(4\pi)^{d/2}a_d(q-1)/q=\int_0^t dt'\,\dot{\mu}(t')t'^{d/2}(t-t')^{-d/2} \tag{10}$$

for large t. In order that the right-hand side be time independent for large t, $\mu(t)$ must have the asymptotic form $\mu(t)\sim\theta\ln t$. Inserting this form into Eq. (10), and evaluating the integral gives $\theta=2^d\pi^{d/2-1}\sin(\pi\epsilon/2)a_d(q-1)/q$. Taking the limit $\epsilon\to 0$, using $a_d=1/2\pi\epsilon$ in this limit, gives $\theta=(q-1)/q$ for $d=2$. Finally, $Q(t)=\exp[-\mu(t)]\sim t^{-\theta}$ for $t\to\infty$. The result $\theta=(q-1)/q$ in $d=2$ agrees with that obtained by Cardy [12] using field-theoretic methods.

If one now considers the case $D'>0$, i.e., a diffusing A particle, one sees immediately that for $D'=D$ and $q=2$ (so that $B+B\to 0$ always), the A particle is equivalent to another B particle, and $Q(t)=\rho(t)$, the density, since every surviving particle has not met any other particle. Hence, $Q(t)=\rho(t)\sim\ln t/t$ for $D'=D$ and $q=2$. This suggests that, for general D', $Q(t)$ will decay as $t^{-\theta}$, where θ is a nontrivial function of D'/D.

The calculation of θ can readily be extended to $D'>0$ within the present formalism, using a power-series expansion in D'/D. The method is to use a cumulant expansion to write $Q(t)=\langle\exp(-\mu)\rangle_z=\exp(-\langle\mu\rangle_z+\{\langle\mu^2\rangle_z-\langle\mu\rangle_z^2\}/2!+\cdots)$. To first order in D', one needs only the first cumulant. The result is $\theta=(1+D'/D)(q-1)/q$. This class of problems, where $Q(t)$ decays as a power law instead of a stretched exponential, marks the borderline where the path integral for $Q(t)$ is no longer dominated by a single path (and small fluctuations about it), giving a leading large-t form independent of D', but has to be evaluated exactly, with results that depend on D' even for $t\to\infty$. Full details of this calculation, together with results to higher order in D'/D, will be presented elsewhere.

In conclusion, we have applied an analytic approach to a class of reaction-diffusion models, which reduces them to one-particle systems. We hope to use this method in future to address, *inter alia*, the problem of the very slow approach to asymptopia in the trapping reaction.

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[1] S. Redner, *A Guide to First-passage Processes* (Cambridge University Press, Cambridge, 2001).
[2] S.N. Majumdar, Curr. Sci. **77**, 370 (1999).
[3] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).
[4] M. Bramson and J.L. Lebowitz, Phys. Rev. Lett. **61**, 2397 (1988).
[5] A.J. Bray and R.A. Blythe, Phys. Rev. Lett. **89**, 150601 (2002).
[6] To obtain sensible results for $d\geqslant 2$, the A particle has to be given a nonzero radius r_0, which, for $d=2$, only enters the final result as a time scale, $t_0=r_0^2/4D$, in the logarithm: $\mu_0(t)=4\pi\rho Dt/\ln(t/t_0)$. For $d>2$, the present method cannot be used as it stands.
[7] A. Blumen, G. Zumofen, and J. Klafter, Phys. Rev. B **30**, 5379 (1984).
[8] V. Mehra and P. Grassberger, Phys. Rev. E **65**, 050101 (2002).
[9] The details will be presented elsewhere.
[10] R. A. Blythe and A. J. Bray, Phys. Rev. E **67**, 041101 (2003).
[11] B.P. Lee, J. Phys. A **27**, 2633 (1994).
[12] J. Cardy, J. Phys. A **28**, L19 (1995).
[13] C. Monthus, Phys. Rev. E **54**, 4844 (1996); S.N. Majumdar and S.J. Cornell, *ibid.* **57**, 3757 (1998); S.J. O'Donoghue and A.J. Bray, *ibid.* **65**, 051114 (2002).