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Mutual Annihilation of Two Diffusing Particles in One- and Two-Dimensional Lattices

Claude Aslangul[1]

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The probabilistic dynamics of a pair of particles which can mutually annihilate in the course of their random walk on a lattice is considered and analytically found for $d=1$ and $d=2$. In view of available recent experiments achieved on the femtosecond scale, emphasis is put on the necessity of a full continuous-time, discrete-space solution at all times. Quantities of physical interest are calculated at any time, including the total pair survival probability $N(t)$ and the two-particle correlation function. As a by-product, the lattice version allows for a precise regularization of the continuous-space framework, which is ill-conditionned for $d \geqslant 2$; this being done, formal generalization to any real dimensionality can be straightforwardly performed.

KEY WORDS: Random walks; low-dimensional systems.

I. INTRODUCTION

Recent experiments[1] on polydiacetylene (PDA) chains ($d=1$) immersed in their single crystal monomer matrix have shed light on the dynamics of a pair of triplet excitations in long isolated organic low dimensional polymers. Comparison of experimental data with the results of a theoretical model built for purpose also lead to explicit numerical values for the hopping terms and for the annihilation rate by triplet fusion. Aside from allowing the apparently first determination of these physical quantities of interest, good agreement between experiments and the outcomes of a diffusive theoretical model allows to conclude that, for reasons to be more thoroughly investigated, the actual motion of the triplets is indeed diffusive; let us remind that in a rigid perfect crystal of any dimensionality, quantum

[1] Groupe de Physique des Solides (Laboratoire associé au CNRS, UMR 75-88), Universités Paris 7 et Paris 6, 75251 Paris Cedex 05, France; e-mail: aslangul@gps.jussieu.fr.

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coherence entails that, on the contrary, the motion is purely coherent, characterized by a mean square displacement increasing as t^2. Since the PDA chains are of rather good quality on a structural level, it seems nearly obvious that the rapid relaxation of quantum coherence mainly results from strong exciton-phonon coupling, all the more since many low-frequency degrees of freedom are available.

Obviously enough, the present problem has close connections with the simpler one of a single brownian particle in the presence of an imperfectly absorbing barrier. Indeed, starting from the lattice calculations and taking the limit of continuous space allow to display the relations (see Section IV for details) between the present problem and the diffusion of a (fictitious) particle subjected to an imperfectly absorbing barrier,[2, 3] a problem which arises in various contexts and has been considered many times in the past.[4–9] All these studies use the space-continuum framework; although this is a worthwhile description on a macroscopic level, such as the one which is physically relevant for, e.g., propagation of light in living tissues,[9] it turns out to be inapropriate in view of the above-mentioned experiments on PDA chains: when femtosecond experiments are achieved, results obtained in the continuum simply cannot account for experimental results and the full solution at any time in a continuous time, discrete space, framework is required. The shortcomings of the continuous framework stand in two points: (i) the initial decay is quasi-exponential, for obvious physical reasons, since the two triplets (initially created on the same site by rapid internal conversion) annihilate at a constant rate on a time-scale short as compared to the diffusion time; the continuous description is unable to reproduce such a feature—it yields an infinite initial slope, which useless for experimentalists. (ii) due to the high-time resolution of experiments, the "transient" dynamics covers nearly the entire experimental range, so that the asymptotic regimes, which indeed coincide in both lattice and continuum frameworks, are of very little interest. More crudely stated, it can be said that the continuous description is here simply wrong in view of the experimental data obtained with a high time-resolution, which clearly exhibits linear decay at short times and reveal the whole dynamics from which much can be learned. Only the lattice description given below is able to fit with experimental outcomes and is able to reprodure the observed decay over seven decades (see Fig. 1).

The aim of this paper is thus to present in details the exact solution at all times of the simple lattice model used previously to understand the experiments on PDA chains and to extend it in two dimensions. Up to my knowledge, the lattice results contained in the present paper do not appear in previous works. As done below, the full solution is achieved when the two-particle distribution probability is obtained, in one or another

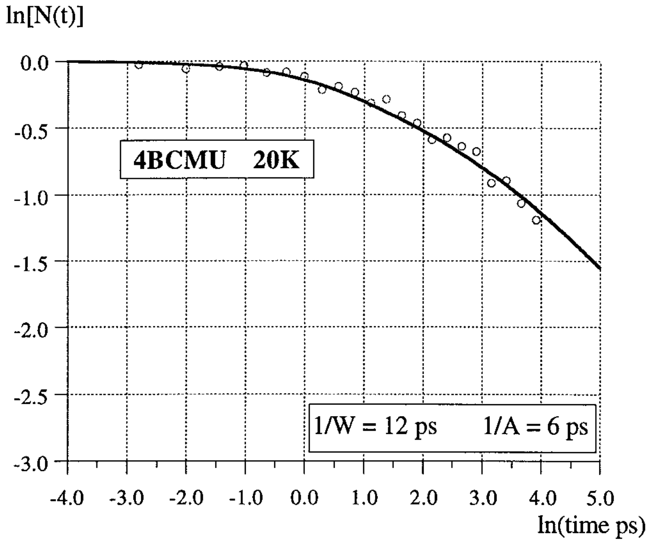

Fig. 1. Comparison between experimental (circles) and theoretical results (solid line), Eq. (2.10), for the polydiacetylene known as BCMU, at 20 K. The fit yields explicit numerical values for the annihilation time A^{-1} and the diffusion time W^{-1}, both being of the order of a few picoseconds.

representation. From this, physically relevant quantities can be calculated such as the total triplet population, $N(t)$, the correlations between the motions of the particles and the marginal (reduced) one-body distributions.

As well-known,[10] problems formulated in discrete space are more difficult to analyze than their space continuous versions, when the latter exist. By nature, lattice problems are less "universal" than continuous ones in the sense that most results obtained in such a framework usually depend on microscopic details such as the lattice structure.[11] On the other hand, working on a lattice is here the most natural approach on physical grounds, and is even a theoretical necessity when no continuous limit exists; an example of such a situation is the pure growth problem, equivalent to a directed walk, for which the continuous limit of the master equation generates a purely mechanical Liouville equation, in which diffusive effects have disappeared.[12] When the continuous limit exists, it can be expected on physical grounds that both versions provide essentially the same results in the long time limit, when most of the microscopic details become irrelevant. On the other hand, the lattice version is required for physical purposes since, due to ultra-violet divergencies, the continuous approximation is ill-conditionned for $d \geqslant 2$.

Clearly, the dimensionality d plays a major role in the present situation, as it does in the famous Polyà problem.[13–15] Once created on the same site due to rapid internal conversion following high excitation, the two triplets undergo a random walk and can annihilate each other when, in the course of time, their trajectories meet again. This fact implies close connection with the Polyà's results: for $d=1$ and $d=2$, a single random walker goes back to its starting point with probability one. As contrasted, for $d=3$, the return probability is less than one, its precise value depending on microscopic details such as the lattice structure.[11]

It is thus expected that for one- and two-dimensional organic polymers of the type considered, the triplet pair population $N(t)$ will eventually decay to zero at infinite times, faster and faster as the dimensionality is lowered. Indeed, asymptotical analysis of the exact expression of $N(t)$ found below at any time yields the characteristic decays $t^{-1/2}$ for $d=1$ and $(\ln t)^{-1}$ for $d=2$. The exact expressions clearly show that, $\forall d$, the asymptotic regime is realized only at very large times. Obviously, the vanishing exponent for $d=2$ is specific of a marginal case.

Eventually, the space continuous limit will be analyzed for completeness. Not surprinsingly, this limit is much simpler and, in addition, allows formally to investigate any *real* dimensionality $d \geqslant 0$, provided proper regularizations are done for $d \geqslant 2$. In such a simplified framework, the problem can be solved in two steps by analyzing first a single-particle problem (in the center-of-mass frame), using standard methods for the brownian motion of a fictitious particle in the presence of an imperfect absorbing barrier. This does not mean that the present problem reduces to a single-particle one; indeed, the center-of-mass itself has a diffusive motion, which contributes to the spreading of the density of probability. Such a feature is illustrated by the fact that the two-body probability is not the product of two one-particle densities, a trivial consequence of the fact that the annihilation process, as a true interaction, definitely induces correlations between the motions of the two particles. Thus, it will be recovered that, for any real $d>2$, $N(t)$ converges toward a finite value N_∞ at infinite times, N_∞ being closer and closer to one as the dimensionality is increased. The trivial zero-dimensional case will even be recovered by extrapolating the general results to $d=0$, producing a plain exponential decay as it must.

II. THE ONE-DIMENSIONAL CASE

The basic assumptions of the lattice model are as follows:

(i) at some time ($t=0$), a pair of (triplet) excitations is created on a given lattice site (labelled $n=0$ for $d=1$). Physically, this results from rapid internal conversion following the creation of a high-energy singlet excitation (singlet fission).

(ii) each member of the pair has a diffusive motion, independently of the other; for simplicity, it is assumed that hopping can occur between one site and its nearest-neighbours. The hopping probability per unit time is denoted as W and allows to define a diffusion constant $D = a^2 W$, where a is the lattice spacing.

(iii) when the two triplets are located on the same site, they can mutually annihilate to give a high energy singlet (triplet fusion). This annihilation process is characterized by a constant probability per unit time denoted as A.

With these assumptions, it is easy to write down a master equation for $p_{n_1 n_2}$, the probability to find the two particles (triplets) located on sites n_1 and n_2 at time t. Standard arguments yield the following (δ_{nm} is the Kronecker symbol):

$$\frac{d}{dt} p_{n_1 n_2} = -4W p_{n_1 n_2} + W[p_{n_1 - 1 n_2} + p_{n_1 + 1 n_2} + p_{n_1 n_2 - 1} + p_{n_1 n_2 + 1}] - A\delta_{n_1 n_2} p_{n_1 n_2} \tag{2.1}$$

$p_{n_1 n_2}$ allows to find all the two-particle weighted sums describing the positions of the particles, such as:

$$\langle x_1 \rangle = \sum_{n_1 = -\infty}^{+\infty} \sum_{n_2 = -\infty}^{+\infty} n_2 p_{n_1 n_2} \tag{2.2}$$

$$\langle x_1 x_2 \rangle = \sum_{n_1 = -\infty}^{+\infty} \sum_{n_2 = -\infty}^{+\infty} n_1 n_2 p_{n_1 n_2} \tag{2.3}$$

Note that, at this point, one could be tempted to introduce the coordinate of the center-of-mass, $M = (n_1 + n_2)/2$, and the distance $r = n_1 - n_2$ between the two particles. Although in the continuous approximation (see below) this can be useful—but still remains a mere affair of taste—this change of variables achieved in the lattice version does not help so much; it would even somewhat obscure the analysis and furthermore would require an additional inverse transformation to get the desired probabilities.

Our aim is to obtain the solution of (2.1) at all times and to deduce from it all quantities of physical interest. As always in pure (non disordered) translationnally-invariant lattices, the easiest way to the full solution is to find the characteristic (generating) function, which first contains all the information on the stochastic process at hand and, second, is certainly the most convenient technique on a purely algebraic level. Indeed, (2.1) can be easily solved by introducing the function $f(\phi, \psi, t)$ defined as:

$$f(\phi, \psi, t) = \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} e^{in_1\phi} e^{in_2\psi} p_{n_1 n_2}(t) \tag{2.4}$$

allowing to find each $p_{n_1 n_2}$ by the inverse relation:

$$p_{n_1 n_2}(t) = \int_0^{2\pi} \frac{d\phi}{2\pi} \int_0^{2\pi} \frac{d\psi}{2\pi} e^{-in_1\phi} e^{-in_2\psi} f(\phi, \psi, t) \tag{2.5}$$

or to find directly all the moments by successive derivations at ϕ and/or $\psi = 0$. Obviously, if one is interested only in a few quantities, for instance only in the total population $N(t)$, a shorter route exists; indeed by summing (2.1) side by side, one finds:

$$\frac{dN}{dt} = -A \sum_{n=-\infty}^{+\infty} p_{nn}(t) \tag{2.6}$$

This means that the total population can be obtained once all the diagonal terms are known and also shows that the initial slope is finite and equal to $-A$. Our goal here is to solve completely the present problem, not to focus on some given quantities. Introducing the Laplace transform $f_L(\phi, \psi, z)$ of $f(\phi, \psi, t)$, it is readily seen that the former satisfies the following homogeneous integral equation:

$$\begin{aligned} &z f_L(\phi, \psi, z) - f(\phi, \psi, 0) \\ &\quad = -2W(2 - \cos\phi - \cos\psi) f_L(\phi, \psi, z) - A \int_0^{2\pi} \frac{d\phi'}{2\pi} f_L(\phi', \phi + \psi - \phi', z) \end{aligned} \tag{2.7}$$

Equation (2.7) yields a homogeneous Fredholm integral equation with a degenerate kernel;[16] as such, its solution can be readily obtained in a closed form. By labelling $n = 0$ the site where the pair of triplets arises at $t = 0$, one has $f(\phi, \psi, t = 0) = 1$ and, with such an initial condition, the solution of (2.7) writes:

$$f_L(\phi, \psi, z) = \frac{1}{1 + [\mu/(R[(\phi + \psi)/2, Z)])]} \frac{1}{z + 2W(2 - \cos\phi - \cos\psi)} \tag{2.8}$$

with

$$R(x, Z) = (Z^2 + 2Z + \sin^2 x)^{1/2}, \qquad \mu = \frac{A}{4W} \qquad Z = \frac{z}{4W} \tag{2.9}$$

Note that the expression (2.8) is of the typical form found in a large variety of (linear) problems incorporating a contact interaction or a local defect (often called Koster–Slater formula in condensed matter literature); it also resembles, for obvious reasons, to the Laplace transform of the characteristic function for a single particle on a lattice with a partially absorbing barrier located at the origin. In the following, all multiform functions are continuously defined by analytical continuation, starting from the branch which assumes real values on the real positive semi-axis.

Equations (2.8) and (2.9) fully solve the present 1-d problem in the Laplace representation. This being achieved, it is easy to go back to physical expectation values. The simplest one, and also of great physical interest, is the total triplet pair population, $N(t)$, given by

$$N(t) = \sum_{n_1, n_2 = -\infty}^{+\infty} p_{n_1 n_2} \equiv f(\phi = \psi = 0, t) \tag{2.10}$$

and is now known by its Laplace transform $f_L(\phi = \psi = 0, z)$:

$$N(t) = \int_C \frac{dz}{2i\pi} N_L(z)\, e^{zt} \qquad N_L(z) = \left[z \left(1 + \frac{A}{\sqrt{z^2 + 8zW}} \right) \right]^{-1} \tag{2.11}$$

An explicit expression for $N(t)$ can be found as usual by deforming the contour C and by first calculating the residue at the simple pole $z_- = -4W - \sqrt{16W^2 + A^2}$. Obvious manipulations on the remaining contour integral allow to eventually write the exact expression of $N(t)$ as the following ($T = 4Wt$):

$$N(t) = \frac{\mu^2\, e^{-(1+\sqrt{\mu^2+1})\,T}}{\mu^2 + 1 + \sqrt{\mu^2+1}} + \frac{2\mu}{\pi} \int_0^{\pi} \frac{\cos^2(x/2)}{\mu^2 + \sin^2 x}\, e^{-2T \sin^2(x/2)}\, dx \tag{2.12}$$

$$\equiv \frac{\mu^2\, e^{-(1+\sqrt{\mu^2+1})\,T}}{\mu^2 + 1 + \sqrt{\mu^2+1}} + \mu\, e^{-T} \frac{1 + (d/dT)}{\mu^2 + 1 - (d^2/dT^2)} I_0(T) \tag{2.13}$$

where I_0 is the ordinary modified Bessel function. This exact result first shows that, for $d = 1$, and $\forall \mu > 0$, $N(t)$ goes to zero at infinite times, a limit which is reached in fact for any dimensionality $d \leqslant 2$ (see below). This is closely related to the Polyà problem: in one spatial dimension, a single random walker goes back to its starting point with probability one, although the return time, being distributed according a Smirnov law,[11] is infinite on the average.

In expressions (2.12), (2.13), the first term in the RHS is the residue originating from the pole z_- and is a short exponential transient expressing the fact that on a time scale short as compared to the diffusion time, the two triplets simply annihilate each other locally at a constant rate A. It results a *finite* initial slope (see Eq. (2.6)), a fact which played a crucial role for determining explicitly the first good estimates of W and A for PDA chains.[1] When $A \ll W$ (small annihilation rate and fast diffusion), this first term is negligible at any time and the second one can be given a quite good approximate expression in terms of the error function Φ, namely:

$$N(t) \simeq [1 - \Phi(\sqrt{A^2 t/(8W)})]\, e^{A^2 t/(8W)} \qquad (0 < \mu \ll 1) \tag{2.14}$$

As a consequence, $N(t)$ decays as $t^{-1/2}$ at large times. On the contrary, for $A \gg W$, one has approximately:

$$N(t) \simeq \frac{\mu\, e^{-At}}{\mu + 1} + \frac{1}{\mu}\, e^{-4Wt} \left[1 + \frac{1}{4W} \frac{d}{dt} \right] I_0(4Wt) \qquad (\mu \gg 1) \tag{2.15}$$

This again yields a $t^{-1/2}$ decay at (very) large times, once the transient exponential regime $\propto e^{-At}$ has disappeared. Note however that this power-law, characteristic of 1d-diffusion in presence of annihilation or with an absorbing barrier in the space continuous framework,[9] is relevant only once $N(t)$ achieves very small values; obviously, when $A \gg W$, the probability is quite small that each triplet can in fact undergo a diffusive walk. Indeed, for any positive value of μ, a cross-over occurs, separating an initial exponential decay from an asymptotical power-law behaviour (see Fig. 2); at intermediate times, and on almost the whole experiment time interval, the decay is neither exponential nor governed by a single exponent. The precise asymptotic $t^{-1/2}$ law can be found by an asymptotic analysis of the integral in (2.12), which leads to the following expansion:

$$N(t) \sim \sqrt{\frac{8W}{\pi A^2}}\, t^{-1/2} \left[1 - \sqrt{\frac{8\pi W}{A^2}}\, t^{-1/2} + \cdots \right] \qquad \left(t \gg \frac{W}{A^2} \right) \tag{2.16}$$

This entails that the pure $t^{-1/2}$ decay at large times is realized for t much larger than W/A^2, all the more since the correction has itself a quite slow decay. The above expansion allows to identify the relevant time scale τ in one dimension:

$$\tau = \frac{8W}{A^2} = \frac{8D}{(aA)^2} \tag{2.17}$$

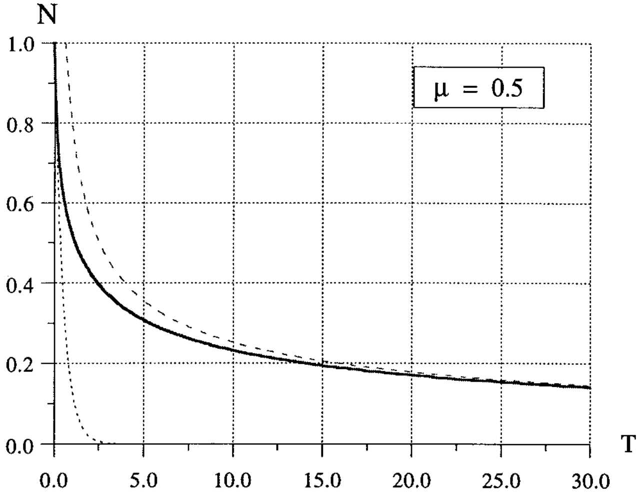

Fig. 2. Theoretical decay (solid line) of the triplet pair population in the one-dimensional case (Eq. 2.10), as a function of $T = 4Wt$ for $A/4W = 0.5$; the dotted line is the pure exponential decay arising from the pole z_-, whereas the dashed line is the dominant term in Eq. (2.14).

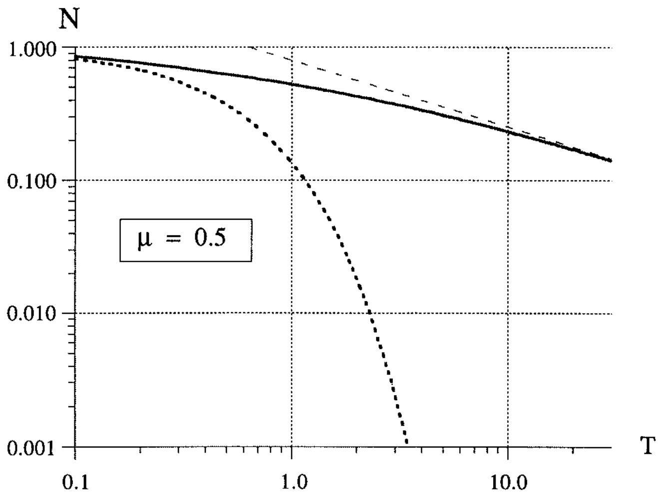

Fig. 3. Same as Fig. 2 but with a double logarithmic scale.

The characteristic function (2.8) is indeed the full solution of the present problem since all the probabilities $p_{n_1 n_2}(t)$ can be theoretically extracted from it by Laplace inversion and use of the Fourier relation (2.5). As an example, straightforward manipulations yield the following for the two-particle survival probability at the origin:

$$p_{00}(t) = \mathrm{e}^{-4Wt} \int_{\mathrm{C}} \frac{dZ}{2\mathrm{i}\pi} \, \mathrm{e}^{4WtZ} \int_0^{\pi} \frac{dx}{\pi} \frac{1}{\mu + \sqrt{Z^2 - \cos^2 x}} \tag{2.18}$$

Explicit Laplace inversion yields ($T = 4Wt$):

$$p_{00}(t) = \mathrm{e}^{-T} \sum_{k=0}^{+\infty} \sum_{r=0}^{+\infty} \frac{(-\mu)^r}{(k!)^2} \left(\frac{T}{2}\right)^{r+2k} \frac{\Gamma(k+\frac{1}{2})}{\Gamma((r+1)/2)\, \Gamma((r/2)+k+1)} \tag{2.19}$$

where Γ is the Euler function. The first term $r = 0$ clearly produces[17, 18, 20] $\mathrm{e}^{-T} I_0^2(T)$, as it must. The asymptotic behaviour of $p_{00}(t)$ follows:

$$p_{00}(t) \sim \frac{1}{\pi A^2 t^2} \tag{2.20}$$

as contrasted to $\sim t^{-1}$ in the absence of annihilation.

Obviously, the contact interaction between the particles induces correlations between the motion of the latter, which are most simply measured by the normalized correlator:

$$C(t) = \frac{\langle x_1 x_2 \rangle}{\langle x_2^2 \rangle} \tag{2.21}$$

where $\langle x_1 x_2 \rangle$ and $\langle x_1^2 \rangle$ are defined in Eqs. (2.2) and (2.3). The numerator is readily obtained from the full characteristic function (2.8): its Laplace transform is the opposite of the coefficient of the product $\phi\psi$ in the expansion of $f_L(\phi, \psi, z)$ near $\phi = \psi = 0$, whereas the denominator is related to the coefficient of ϕ^2 in the same expansion. Asymptotic analysis shows that $C(t)$ tends toward a finite constant:

$$C(t) \sim -\tfrac{1}{3} \qquad (t \gg W^{-1}, A^{-1}) \tag{2.22}$$

which means that strong correlations persist for ever, by a combined effect of interaction and low dimensionality.

The characteristic function (2.8) also allows to find the characteristic function $f(\phi, t)$ of the marginal one-particle probabilities $p_n(t)$ defined as:

$$p_n(t) = \sum_{n_2=-\infty}^{+\infty} p_{nn_2}(t) \tag{2.23}$$

$f(\phi, t)$ is equal to $f(\phi, \psi = 0, t)$. Laplace inversion yields:

$$f(\phi, t) = \mathrm{e}^{-T\sin^2(\phi/2)}[1 - \mu H(T)] \tag{2.24}$$

where $H(T)$ denotes the function:

$$H(T) = \sqrt{\pi} \sum_{r=0}^{+\infty} \frac{(-\mu)^r}{\Gamma((r+1)/2)[2\cos(\phi/2)]^{r/2}} \times \int_0^T dT'\, \mathrm{e}^{-T'\cos^2(\phi/2)}\, T'^{r/2}\, I_{r/2}[T'\cos(\phi/2)] \tag{2.25}$$

By successive derivations at $\phi = 0$, Eq. (2.24) provides, via their Laplace transforms, all the moments of the marginal distribution. For instance, the Laplace transform of the marginal mean square dispersion is given by $(Z = z/4W)$:

$$m_{2L}(z) = \frac{1}{16W} \frac{\mu(3+2Z) + 2Z^{1/2}(Z+2)^{3/2}}{Z^{3/2}(Z+2)^{1/2}\,[\mu + Z^{1/2}(Z+2)^{1/2}]^2} \tag{2.26}$$

leading to the asymptotic behaviour:

$$m_2(t) \sim 6\sqrt{\frac{2}{\pi}}\,\frac{W^{3/2}}{A}\, t^{1/2} \tag{2.27}$$

The conditional ratio m_2/N is the mean square displacement, given the pair is still alive at time t; taking Eqs. (2.27) and (2.16) into account, one recovers the ordinary linear variation at large times. In addition, Eq. (2.27) shows that the typical distance d_{typ} travelled by one particle asymptotically grows as $t^{1/4}$:

$$d_{\mathrm{typ}}(t) \sim \left(\frac{72W^3}{\pi A^2}\right)^{1/4} t^{1/4} \tag{2.28}$$

This slower increase in time, as compared to $t^{1/2}$ in the absence of annihilation, merely expresses the fact that a mortal walker travels a smaller distance than a walker having an infinite lifetime.

III. THE TWO-DIMENSIONAL CASE

For $d=2$, let us denote by $p_{n_1m_1n_2m_2}$ the probability to find a pair at sites with coordinates (n_1, m_1) and (n_2, m_2) on a square lattice of lattice spacing a. The master equation now reads:

$$\begin{aligned}\frac{d}{dt} p_{n_1m_1n_2m_2} = & -8Wp_{n_1m_1n_2m_2} + W[p_{n_1-1m_1n_2m_2} + p_{n_1+1m_1n_2m_2} \\ & + p_{n_1m_1-1n_2m_2} + p_{n_1m_1+1n_2m_2} + p_{n_1m_1n_2-1m_2} \\ & + p_{n_1m_1n_2+1m_2} + p_{n_1m_1n_2m_2-1} + p_{n_1m_1n_2m_2+1}] \\ & - Ap_{n_1m_1n_2m_2}\delta_{n_1n_2}\delta_{m_1m_2}\, p_{n_1m_1n_2m_2} \end{aligned} \tag{3.1}$$

together with the initial condition $p_{n_1m_1n_2m_2} = \delta_{n_10}\delta_{m_10}\delta_{n_20}\delta_{m_20}$. The generating function $f(\phi_1, \psi_1, \phi_2, \psi_2, t)$ is now:

$$f(\phi_1, \psi_1, \phi_2, \psi_2, t) = \sum_{n_1m_1}\sum_{n_2m_2} e^{i(n_1\phi_1+m_1\psi_1)}\, e^{i(n_2\phi_2+m_2\psi_2)}\, p_{n_1m_1n_2m_2}(t) \tag{3.2}$$

A straightforward calculation yields the Laplace transform of f, $f_L(\phi_1, \psi_1, \phi_2, \psi_2, z)$, found under the following form generalizing Eq. (2.8) for $d=2$:

$$\begin{aligned} f_L(\phi_1, \psi_1, \phi_2, \psi_2, z) = G(\phi_1, \psi_1, \phi_2, \psi_2, z)\left\{1 + \frac{A}{4\pi W[\xi(\phi, \psi, Z)]^{1/2}}\right. \\ \left.\times \mathbf{K}\left[\frac{\cos(\phi/2)\cos(\psi/2)}{\xi(\phi, \psi, Z)}\right]\right\}^{-1} \end{aligned} \tag{3.3}$$

where $\mathbf{K}$ is the elliptic function of the first kind[17] and with:

$$G(\phi_1, \psi_1, \phi_2, \psi_2, z) = \frac{1}{z + 2W(4 - \cos\phi_1 - \cos\psi_1 - \cos\phi_2 - \cos\psi_2)} \tag{3.4}$$

$$\xi(\phi, \psi, Z) = (Z+1)^2 - \frac{1}{4}[\cos(\phi/2) - \cos(\psi/2)]^2 \qquad \phi = \phi_1 + \phi_2$$

$$\psi = \psi_1 + \psi_2 \qquad Z = \frac{z}{8W} \tag{3.5}$$

Note that all the quantities arising in the two-dimensional lattice version are well-defined, as opposed to their analogous in the continuum limit (see Section IV). The knowledge of the characteristic function of the two-particle probability distribution, Eq. (3.3), fully solves the present problem in the Laplace representation. The total pair population $N(t)$ can be quickly found from this result; its Laplace transform follows from Eqs. (3.3)–(3.5):

$$N_L(z) = \frac{1}{z}\left\{1 + \frac{A}{4\pi W(1+Z)}\mathbf{K}\left[\frac{1}{(1+Z)^2}\right]\right\}^{-1} \tag{3.6}$$

After performing Laplace inversion, the following behaviours are obtained. At the very beginning, the total population decreases as e^{-At}. After this first transient exponential regime, approximate expression of $\mathbf{K}(x)$ for $|x| \simeq 1$ produces the following expression of $N(t)$ in terms of the Ramanujan integral:

$$N(t) \simeq \frac{8\pi W}{A}\int_0^{+\infty} dx\, \frac{e^{-64Wtx}}{x[(\ln x)^2 + \pi^2]} \qquad (t \gg A^{-1}) \tag{3.7}$$

This expression describes the long-lasting cross-over between the initial exponential regime and the final asymptotic regime:

$$N(t) \sim \frac{8\pi W}{A\ln(64Wt)} \qquad (t \gg A^{-1},\, W^{-1}) \tag{3.8}$$

Again, $N(t)$ eventually goes to zero at infinite times, but infinitely slowly. This ultra-slow convergence toward the vanishing value indicates that $d = 2$ is the marginal dimensionality above which $N(t)$ decays to a finite value at infinite times.

Equations (3.3)–(3.5) allow to find all the moments of the two-particle distribution, as well as, for instance, the characteristic function of the one-particle distribution defined as:

$$p_{nm}(t) = \sum_{n_2 m_2} p_{nmn_2m_2}(t) \tag{3.9}$$

The Laplace transform of the latter is given by:

$$f_L(\phi, \psi, z) = \frac{1/[z + 2W(2 - \cos\phi - \cos\psi)]}{1 + \frac{A}{4\pi W[\xi(\phi, \psi, z)]^{1/2}}\mathbf{K}\left[\frac{\cos(\phi/2)\cos(\psi/2)}{\xi(\phi, \psi, z)}\right]} \tag{3.10}$$

This readily yields the Laplace transform of the second marginal moment $m_{2L}(z)$ along anyone of the two principal directions of the lattice:

$$m_{2L}(z) = \frac{1/z}{1 + \frac{A}{4\pi W(Z+1)} \mathbf{K}\left[\frac{1}{(Z+1)^2}\right]} \times \left[\frac{W}{z} - \frac{A}{32\pi W} \frac{\mathbf{K}'\left[\frac{1}{(Z+1)^2}\right]}{Z+1+\frac{A}{4\pi W}\mathbf{K}\left[\frac{1}{(Z+1)^2}\right]}\right] \tag{3.11}$$

Asymptotic analysis of this linear mean square dispersion gives:

$$m_2(t) \sim \frac{8\pi W^2}{A} \frac{t}{\ln(64Wt)} \tag{3.12}$$

This is a marginal subdiffusif behaviour (comp. Eq. (2.27)), resulting from the fact that, here again, the particles eventually disappear, although infinitely slowly. Thus, for $d = 2$, the typical distance travelled by anyone of the particles asymptotically grows as:

$$d_{\text{typ}}(t) \sim \sqrt{\frac{8\pi W}{A}} \left[\frac{Wt}{\ln(64Wt)}\right]^{1/2} \tag{3.13}$$

The correlations between particles (along e.g., the x-axis) can be measured as usual by the weighted crossed-products deduced from the expansion of $f_L(\phi_1, \psi_1 = 0, \phi_2, \psi_2 = 0, z)$ near $\phi_1 = \psi_1 = 0$. The simplest one, $\langle x_1 x_2 \rangle$, here indeed vanishes, since the preceding f_L contains only the combination $(\phi_1 + \phi_2)^4$. This expresses the physical fact that, due to increased dimensionality, spatial correlations are certainly less strong than for $d = 1$.

IV. THE SPACE CONTINUOUS LIMIT

For completeness, the space continuous limit will now be discussed. If a is the order of magnitude of the lattice spacing and if τ_{diff} denotes the diffusion time, wave vectors k and time-conjugate Laplace variables z are physically sensible with respect to the underlying discrete space only if they satisfy $k \ll a^{-1}$ and $|z| \ll \tau_{\text{diff}}^{-1}$.

The continuous limit can be taken from the above lattice results; as usual, setting:

$$A = \frac{\tilde{A}}{a^d} \qquad W = \frac{D}{a^2} \tag{4.1}$$

and by formally taking the limit $a \to 0$. For $d = 1$, starting from Eqs. (2.8), (2.9), one obtains the Laplace transform of the characteristic function of the two-particle density, $\tilde{f}_L(k_1, k_2, z)$:

$$\tilde{f}_L(k_1, k_2, z) = \frac{1}{1 + \dfrac{\tilde{A}}{\sqrt{8D}} \dfrac{1}{[z + (D/2)\, K^2]^{1/2}}} \frac{1}{z + D(k_1^2 + k_2^2)} \tag{4.2}$$

where $K = k_1 + k_2$. All physical quantities in the continuous version can be derived from Eq. (4.2). First, Laplace inversion with the help of the the Efrös theorem[19] yields:

$$N(t) = \mathrm{e}^{t/\tau}[1 - \Phi(\sqrt{t/\tau})] \qquad \tau = \frac{8D}{\tilde{A}^2} = \frac{8W}{A^2} \tag{4.3}$$

By comparing with Eq. (2.14), one sees that the exact result of the present continuous version coincides with the (approximate) discrete result only in the limit $\mu \ll 1$. This is easily understood: when the annihilation time is much longer than the diffusion time, each particle can move on a rather long distance and the effect of the underlying lattice is in some way washed out. The initial slope of $N(t)$, as given by Eq. (4.3), is infinite; this fact, characteristic of the continuous limit, is an example of the unability of the latter to reproduce relevant microscopic features properly revealed by high-resolution experiments. On the other hand, Eq. (4.3) yields exactly the same long-time behaviour as Eq. (2.16). From Eq. (4.2), one also readily obtains the the one-particle characteristic function, from which all moments can be deduced; as an example, the second one is:

$$m_2(t) = D(t + \tau)\, \mathrm{e}^{t/\tau}[1 - \Phi(\sqrt{t/\tau})] - D\tau + 2D\sqrt{\frac{\tau t}{\pi}} \tag{4.4}$$

At very large times, this yields exactly the same asymptotic behaviour as in the lattice version, Eq. (2.27).

Of course, results in the continuous framework can be directly found by solving the diffusion equation, either by separation of variables and forming the proper combination of eigenmodes, or by going to the center-of-mass frame; in this last formulation, one recovers the classical problem of a fictitious particle with a imperfectly absorbing barrier,[4–9] the diffusion constant D playing the role of an inverse mass. In one way or another, for $d=1$, the two-particle density is obtained as:

$$P(x_1, x_2, t) = \frac{1}{\sqrt{2\pi Dt}}\, \mathrm{e}^{-(x_1+x_2)^2/(8Dt)} \int_{-\infty}^{+\infty} \frac{dk}{2\pi} \frac{k}{k - \mathrm{i}\tilde{A}/(4D)}\, \mathrm{e}^{ik\,|x_1-x_2|}\, \mathrm{e}^{-2Dk^2 t} \tag{4.5}$$

where the prefactor represents the free diffusion of the center of mass. Note that due to the singularity $|x_1 - x_2|$—which reflects the zero-range contact interaction in one dimension—the Fourier transform of P cannot be simply be read from the above expression.

Obviously, due to the interaction via the annihilation process, $P(x_1, x_2, t)$ is not the product of two functions, one for each coordinate. Equation (4.5) indeed displays the fact that P is a linear combination of such products, weighted by $k/[k - \mathrm{i}\tilde{A}/(4D)]$ (where the sign of $\tilde{A}$ is essential). In this sense, it would be incorrect to consider the problem as a single particle one: the separation of the center-of-mass motion is trivial in the sense that it happens as the consequence of space homogeneity, but this center-of-mass, itself having a diffusive motion (not a purely kinematical one), does participate to the spreading in such a way that correlations are always present.

Analogous calculations can be done for $d=2$, but a regularization has to be achieved due to ultraviolet divergencies. For instance, one now has ($\vec{K} = \vec{k}_1 + \vec{k}_2$):

$$\tilde{f}_L(\vec{k}_1, \vec{k}_2, z) = \frac{G(\vec{k}_1, \vec{k}_2, z)}{1 + \tilde{A} \int_{R^2} \frac{d^2k'}{(2\pi)^2} G(\vec{k}', \vec{K} - \vec{k}', z)} \tag{4.6}$$

$$G(\vec{k}_1, \vec{k}_2, z) = \frac{1}{z + D(\vec{k}_1^2 + \vec{k}_2^2)}$$

Since the integral is logarithmically divergent, a cut-off $k_c \sim a^{-1}$ has to be introduced; its precise value can be obtained from the lattice results by taking the limit $a \to 0$ in Eq. (3.3) and by using:[17]

$$\mathbf{K}\left(\frac{1}{[1 + a^2 z/(8D)]^2}\right) \simeq \ln\left(\frac{8\sqrt{D}}{a\sqrt{z}}\right) \tag{4.7}$$

Comparing now Eqs. (3.3) and (4.6), one precisely finds:

$$k_c = \frac{4\sqrt{2}}{a} \tag{4.8}$$

This choice insures that the continuous approximation possesses the same asymptotical behaviour as the lattice version. With this regularization, one has ($\lambda = \tilde{A}/(8\pi D)$, $\vec{K} = \vec{k}_1 + \vec{k}_2$):

$$\tilde{f}_L(\vec{k}_1, \vec{k}_2, z) = \frac{G(\vec{k}_1, \vec{k}_2, z)}{1 + \lambda \ln[1 + 2Dk_c^2/(z + D\vec{K}^2/2)]} \tag{4.9}$$

Laplace inversion then gives the following exact expression for the pair population in the continuum limit, valid at any times, ($T = 2Dk_c^2 t$) for the two-dimensional case:

$$N(t) = \frac{1}{\lambda(\mathrm{e}^{1/\lambda} - 1)} \exp\left(-\frac{T}{1 - \mathrm{e}^{-1/\lambda}}\right) + \lambda \int_0^1 \frac{d\rho}{\rho} \frac{\mathrm{e}^{-\rho T}}{[1 + \lambda \ln((1/\rho) - 1)]^2 + \lambda^2 \pi^2} \tag{4.10}$$

Asymptotic analysis with the cut-off given by Eq. (4.8) exactly reproduces the Ramanujan integral as in Eq. (3.8).

The continuous limit also allows to formally generalize the above results for any real $d \geqslant 0$. For instance, $N_L(z)$ is given by:

$$N_L(z) = \frac{1}{z} \frac{1}{1 + \tilde{A} \int_{R^d} \frac{d^d k'}{(2\pi)^d} \frac{1}{z + 2D\vec{k}'^2}} \tag{4.11}$$

where the integral has to be regularized with a cut-off k_c when $d \geqslant 2$. In this case, one finds:

$$N_L(z) = \frac{1}{z} \left\{ 1 + \frac{\tilde{A} k_c^{d-2}/D}{2^{d+1} \pi^{d/2} \Gamma(d/2)} \left[\frac{2}{d-2} F(1, 1; 1 - d/2; 2 - d/2, -Z) + \frac{\pi}{\sin \pi d} Z^{d/2} \right] \right\}^{-1} \tag{4.12}$$

where F is the hypergeometric function[17] and $Z = z/(2Dk_c^2)$. For $Z \ll 1$, one has:

$$N_L(z) \simeq \frac{1}{z} \frac{1}{1 + \frac{\nu}{2^d \pi^{d/2} (d-2)\, \Gamma(d/2)} \left[1 + \frac{\pi(d-2)}{2 \sin \pi d} Z^{d/2} \right]} \qquad \left(\nu = \frac{\tilde{A} k_c^{d-2}}{D} \right) \tag{4.13}$$

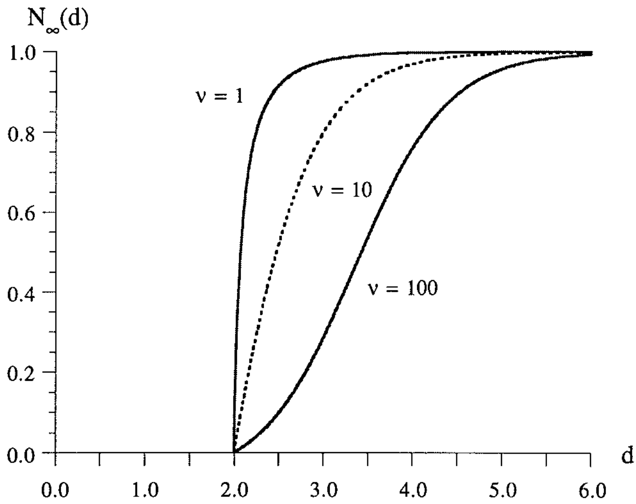

Fig. 4. Variation of the final value $N_{\infty}(d)$ of the pair population as a function of the dimensionality d (Eq. (4.14)). $N_{\infty}(d)$ identically vanishes for $d \leqslant 2$. Each curve is labelled by the dimensionless parameter n (Eq. (4.13)).

From this, one obtains the result:

$$N_{\infty}(d) \equiv \lim_{t \to \infty} N(t) = \frac{1}{1+\alpha} \qquad \alpha = \frac{v}{2^d \pi^{d/2} (d-2)\, \Gamma(d/2)} \tag{4.14}$$

Thus, for any dimensionality $d > 2$, the total pair population does not decay toward zero at infinite times. $N_{\infty}(d)$ is plotted in Fig. 4 for various values of the dimensionless parameter v.

Note that α diverges when $d \to 2$; using the jargon of phase transitions, $N_{\infty}(d)$ can be viewed as the order-parameter of a second-order transition, d^{-1} playing the role of the temperature. Just above $d = 2$, one has:

$$N_{\infty}(d) \sim \frac{4\pi W}{A}(d-2) = \frac{4\pi D a^{d-2}}{\tilde{A}}(d-2) \tag{4.15}$$

implying a "critical exponent" equal to 1.

The approach to this final value is obtained by asymptotic analysis of $N(t)$ based on Eq. (4.12). The relevant time scale can be found by dimensional analysis, leading to the generalization of the time τ previously introduced, Eq. (2.17), expressed with either parameters (lattice or continuum versions):

$$\tau_d = \frac{\tilde{A}^{2/(d-2)}}{(8D)^{d/(d-2)}} = \frac{A^{2/(d-2)}}{(8W)^{d/(d-2)}} \tag{4.16}$$

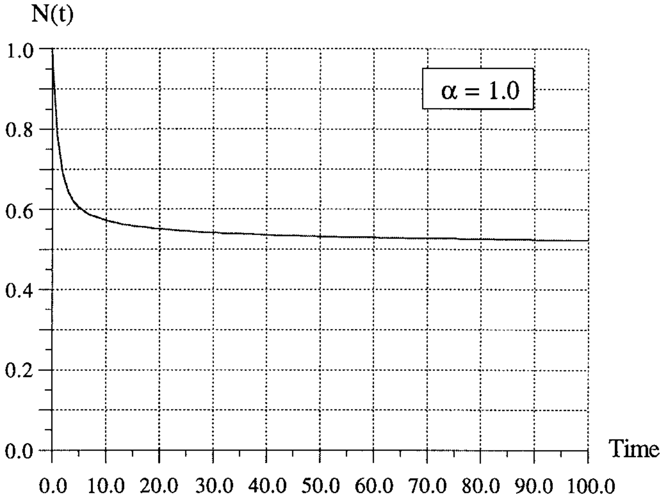

Fig. 5. Variation as a function of time of the pair population in the three-dimensional case, with $\alpha = 1$; the final value N_∞ (see Eq. (4.14)) is here equal to 0.5.

A straightforward calculation leads to:

$$N(t) \sim \frac{1}{1+\alpha}\left[1 + \frac{2\pi^{-d/2}}{(1+\alpha)(d-2)}\left(\frac{\tau_d}{t}\right)^{(d/2)-1}\right] \qquad (t \gg \tau_d) \qquad (4.17)$$

displaying the fact that the exponent characterizing the final regime continuously depends on the dimensionality.

As an illustrative example, $N(t)$ is plotted in Fig. 5 in the three-dimensional case, displaying the finite limiting value given by Eq. (4.14).

For d a positive real number smaller than 2, no cut-off is necessary and $N_L(z)$ is given by:

$$N_L(z) = \frac{1}{z}\frac{1}{1 + C_d(\tau_d z)^{(d/2)-1}} \qquad C_d = \pi^{-(d/2)}\Gamma(1-d/2) \qquad (4.18)$$

By incorporating the time τ_d (Eq. (4.16)), one obtains the exact following expression:

$$N(t) = \frac{1}{\pi}\sin\left(\frac{\pi d}{2}\right)\int_0^{+\infty} d\rho\, \frac{C_d \rho^{-d/2}\, e^{-\rho t/\tau_d}}{\rho^{2-d} - 2C_d\cos((\pi d)/2)\,\rho^{1-d/2} + C_d^2} \qquad (4.19)$$

which has the asymptotic behaviour:

$$N(t) \sim \sin\left(\frac{\pi d}{2}\right)\left(\frac{\tau_d}{\pi t}\right)^{1-d/2} \equiv \pi^{(d/2)-1} \sin\left(\frac{\pi d}{2}\right)\frac{(8Wt)^{d/2}}{At} \tag{4.20}$$

The last form displays the two relevant physical quantities: $(Wt)^{d/2}$, which is the typical d-dimensional volume (in lattice units) swept by the diffusing particles at time t and the product $At = t/A^{-1}$, which is the order of magnitude of the number of possible annihilations up to time t.

Thus, for any positive real $d \neq 2$, the population decays according to a power-law at large times:

$$N(t) \sim N_{\infty} + \gamma_d \left(\frac{\tau_d}{t}\right)^{\beta(d)} \tag{4.21}$$

where γ_d is a d-dependent constant; N_{∞} is given by Eq. (4.14) for $d > 2$ and vanishes for $d \leqslant 2$. The exponent $\beta = |1 - d/2|$ varies continuously with the dimensionality and vanishes for $d = 2$, in which case, according to Eq. (3.8), $N(t)$ has a logarithmic decay toward zero.

It is interesting to note that the above results can even be extrapolated to zero-dimensional space. In such a case, Eqs. (4.16) and (4.18) yield an exponential decay at all times:

$$N(t) = \mathrm{e}^{-\tilde{A}t} \tag{4.22}$$

This was an expected result: in zero space dimension, the two triplets cannot diffuse (and indeed the diffusion time linked to D goes out of the problem, see Eq. (4.16)); they can only annihilate in situ, leading to a plain exponential decay. Note however that the transition to $d = 0$ is quite singular: for any $d \neq 0$ (but $d < 2$), the Laplace inversion of $N_L(z)$ only involves the integral in the RHS of Eq. (4.19), arising from the cut of the integrand—no pole does exist. At precisely $d = 0$, the cut disappears, whereas a pole spontaneously arises at $z = -\tilde{A}$, which the common limit of poles located in other Riemann sheets.

V. SUMMARY AND CONCLUSIONS

A lattice model, successful for describing motion and annihilation of triplet excitations in linear organic polymers,[1] was analyzed in details and generalized in dimension $d = 2$, examplifying the importance of the latter, as it is in random walk problems such as Polyà's one. The problem was fully solved in each case by finding the characteristic functions of the two- and one-particle probability distributions and by calculating explicitely some quantities of physical interest such as the total population and the typical distance travelled by one particle; the latter was shown to behave as $t^{1/4}$ for $d=1$ and as $t/\ln t$ in the marginal $d=2$ case. In addition, it was shown that strong statistical correlations persist for ever in the one-dimensional case, due to a combined effect of interaction and low-dimensionality.

The relations between the above treatment and the simplified continuum approximation used in previous works[4–7, 9] were analyzed, having in mind the availability of experimental data obtained with high-time resolution; such a discussion provides an illustration of the obvious fact that continuum limit is unable to handle physically relevant features of the significant "transient" dynamics, especially when the annihilation and the diffusion times are of the same order of magnitude, which is the case for the organic polymers studied. First, the initial linear decay turns out to play a crucial role for determining the absolute magnitude of the annihilation rate, one of the two basic timescales of the problem. Second, the cross-over between quasi exponential decay and the final power law is so much long-lived that the latter, easily obtained by hand-waving scaling arguments, is of very little physical interest in view of the achieved experiments. All this motivates and justifies a full complete analytical treatment at all times in the lattice framework. In addition, the lattice version also appears as worthy when, as it is the case for $d \geqslant 2$, the continuum version is ill-conditionned, pleagued as it is by ultra-violet divergencies, and requires regularization.

As by-products of the solution at all times, asymptotic results previously obtained in other contexts were recovered. Indeed, the limiting value N_∞ of the survival population is strongly dependent on the dimensionality of space: for any real $d \leqslant 2$, the two excitations mutually annihilate sooner or later and the population goes to zero at infinite times. $d=2$ turns out to be the marginal dimensionality: as soon as $d>2$, N_∞ is *finite* and is an increasing function of d (see Fig. 4). As a whole, N_∞ looks like the order parameter of a second-order transition, d playing the role of an inverse temperature. The precise asymptotic regime was obtained in all cases; for $0<d \leqslant 2$, the vanishing limit is reached according to a power-law in time, with an exponent varying continuously with d ($\sim t^{-(1-d/2)}$). The d-dependence of the exponent arises from the fact that the volume visited by a diffusing particle in d spatial dimension is proportional to $td/2$ (see Eq. (4.20) and the subsequent comment). For $d>2$, the approach to the finite final value again obeys a law of the same type ($\sim t^{(1-d/2)}$). As a whole, at large times (as precisely stated in the text), the total population $N(t)$ is such that:

$$N(t) \sim N_\infty(d) + \gamma_d \left(\frac{\tau_d}{t}\right)^{\beta(d)} \tag{5.1}$$

where N_∞ is plotted in Fig. 4, τ_d is the relevant d-dimensional time scale (see Eq. (4.16)) and where the exponent $\beta = |1 - d/2|$; γ_d is a d-dependent constant. Not surprisingly, the decay toward zero is of the form $(\ln t)^{-1}$ in the marginal case $d = 2$. Finally, the results can be extrapolated to $d = 0$ and yield a pure exponential decay for all times, as it must.

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