

Fluorescence intermittency in blinking quantum dots: Renewal or slow modulation?

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(Received 30 March 2005; accepted 8 September 2005; published online 1 November 2005)

We study the time series produced by blinking quantum dots, by means of an aging experiment, and we examine the results of this experiment in the light of two distinct approaches to complexity, renewal and slow modulation. We find that the renewal approach fits the result of the aging experiment, while the slow modulation perspective does not. We make also an attempt at establishing the existence of an intermediate condition. © 2005 American Institute of Physics. [DOI: 10.1063/1.2102903]

I. INTRODUCTION

In the last few years there has been an increasing interest for the intermittent fluorescence of new nanomaterials,^{1,2} which for this reason have been called³ *blinking quantum dots* (BQD). The theoretical interest for these new materials is due, to a great extent, to the properties of their power spectrum. Pelton *et al.*,⁴ as well as Chung and Bawendi,⁵ have studied macroscopic samples of quantum dots, and have proved that they generate $1/f$ noise. Thus, understanding these new materials is a problem directly connected with the origin of the $1/f$ noise, an issue that according to the proponents of self-organized criticality (SOC) should be settled using their theoretical perspective.⁶ The search for the dynamical origin of complexity, meant to be a statistical condition departing from the Poisson prescription, is a hot topic, and recently another proposal of approach to complexity, called *superstatistics*, was made by Beck and Cohen⁷ (see also Ref. 8). On the other hand, there is an increasing conviction^{9–12} that anomalous diffusion, and especially subdiffusion, might find a satisfactory theoretical framework in the *subordination* perspective. In this paper we shall illustrate the subordination perspective with physical arguments, and shall refer to this theoretical approach simply as subordination. Here we limit ourselves to saying that according to the original work of Montroll and Weiss,¹³ the time distance between two consecutive jump events, generating the walker diffusion, is not fixed but is randomly drawn from a distribution of waiting times. This is a case used to generate a new form of diffusion (anomalous), through subordination to the

ordinary diffusion. The subordination perspective is also applied to generate anomalous fluctuation-dissipation processes. In this case the original events are processes where diffusion is balanced by friction. By assuming that the time distance between two consecutive events of this kind is not fixed, we derive a nonordinary fluctuation-dissipation process subordinated to the ordinary one.¹⁴

Subordination yielding anomalous transport can be imagined as a theoretical perspective where the collisional events generating randomness are rare and separated by large time intervals with a nonexponential distribution. This important property requires, in turn, a physical explanation that hopefully might relate the deviation from exponential distribution to the cooperation among the elementary constituents of the system. The subordination perspective is closely related to renewal, insofar as the jump occurrence is assumed to reset to zero the system's memory.

In the case of BQD fluorescence, many researchers have been studying the microscopic origin of intermittency, and, on top of that, of why the intermittency of these materials is characterized by a non-Poisson distribution of the time of sojourn in the *on* and *off* states.^{15–18} At first sight, all these papers seem to share the same theoretical perspective as superstatistics. According to Cohen,⁸ the process yielding the deviation from the canonical distribution is realized by the system as follows. The particle resides in a cell in local equilibrium for a time extended enough as to reach the corresponding canonical equilibrium, then it moves to another condition of local equilibrium, and so on, in such a way that the resulting distribution will turn out to be distinctly nonexponential, insofar as the superposition of many exponential functions with different probabilistic weights is not an exponential function. The sojourn in a condition of local equilib-

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rium must be extended in time enough for the system to adapt itself to this condition. For this reason superstatistics is equivalent to a form of very slow modulation.

The model discussed in Ref. 15 might be thought of as a form of superstatistics. In fact, these authors propose a two-state model with barrier height or barrier width fluctuation. This automatically yields a waiting time distribution as a sum of infinitely many exponential functions, one exponential for each of the barrier heights or widths. However, as the authors point out, these fluctuations cannot be slow. In fact, the case of slow fluctuations would produce a correlation between two successive on times or two successive off times, while the analysis of Ref. 15 shows that no significant correlation of this kind exists. Similar remarks apply to the model of Refs. 16–18. In all these models there are traps with exponential waiting time distribution densities. However, the system resides in each exponential trap corresponding to a given state, for instance the state off, only once, and it jumps back to the state on before being trapped again in the state off. This property ensures the renewal property. In conclusion, superstatistics is a form of very slow modulation, whereas renewal is compatible with a theory based on non-exponential distribution densities emerging from the superposition of many exponential waiting time distributions, provided that the system does *not* adopt the same exponential well for too many successive trapping events.

As an example of a physical process that might be conveniently described by the slow modulation perspective, we quote the interesting recent papers of Refs. 19 and 20. These authors find¹⁹ that their experimental result cannot be described by the two-state semi-Markov models proposed in Refs. 21 and 22, being therefore incompatible with the renewal perspective. The chronological ordering of the off waiting times suggests the occurrence of a modulation corresponding to molecular conformational changes.

It is therefore convenient to develop a technique of analysis of the experimental data that might help the investigators to establish the real nature of the process under study, namely whether renewal, slow modulation, or an intermediate condition, applies. This is the main purpose of this paper. We shall show that, although renewal and superstatistics can be used to produce the same waiting time distribution density, the former approach to complexity generates renewal aging, while the latter does not. The aging technique has already been adopted by Brokmann *et al.*²³ to prove that the physics of BQD is characterized by renewal. In this paper, in addition to confirming the conclusions of this earlier work, using the same aging technique, we make also an attempt at assessing if a condition intermediate between renewal and very slow modulation (superstatistics) might exist.

The outline of the paper is as follows. In Sec. II we show that renewal rests on resetting the system's memory after any event (collision). In Sec. III we define modulation as a condition of time-dependent rate, with no renewal. We explain the form of modulation adopted in this paper, and we show that in the fast condition it becomes compatible with non-Poisson renewal. We devote Sec. IV to reviewing the phenomenon of renewal aging and we explain why the condition

of very slow modulation should yield no aging. In Sec. V, with the help of artificial sequences, we illustrate the aging experiment that we propose for the analysis of experimental sequences. At the same time we explore the unknown region between renewal and very slow modulation. We examine and discuss real experimental data in Sec. VI. Finally, we devote Sec. VII to concluding remarks.

II. RENEWAL

Let us consider a two-state renewal process, and, for simplicity, let us assume that the distribution of sojourn times in the state on is the same as the distribution in the state off. This assumption will prevent us from discussing with our techniques the interesting effect recently discussed by Verberk *et al.*²⁴ These authors discussed the case where both distributions have an inverse power-law form with different indices, μ_{off} and μ_{on} , and found that a Gibbs ensemble of trajectories moving from the beginning of the state on produces a fluorescence intensity decaying in time as a function proportional to $1/t^{\mu_{\text{off}}-\mu_{\text{on}}}$, with $\mu_{\text{off}} > \mu_{\text{on}}$. We leave the discussion of this interesting effect as a subject for future work.

We assign to the survival probability (SP) of this process, $\Psi(t)$, the inverse power-law form,

$$\Psi(t) = \left(\frac{T}{T+t} \right)^{\mu-1}, \quad (1)$$

with $\mu > 1$. This corresponds to the joint action of the time-dependent rate²⁵ $r(t) = r_0/(1+r_1t)$, with $r_0 = (\mu-1)/T$ and $r_1 = 1/T$, and of a resetting prescription. To illustrate this condition, let us imagine the random drawing of a number from the interval $I = [0, 1]$ at discrete times $i = 0, 1, 2, \dots$. The interval I is divided into two parts, I_1 and I_2 , with I_1 ranging from 0 to p_i , and I_2 from p_i to 1. Note that $p_i = 1 - q_i < 1$ and $q_i \ll 1$, and, as a consequence, the number of times we keep drawing numbers from I_1 , without moving to I_2 , is very large.

Let us evaluate the distribution of these persistence times, and let us discuss under which conditions we get the SP of Eq. (1). The SP function is the probability of remaining in I_1 after n drawings, and is consequently given by

$$\Psi(n) = \prod_{i=1}^n p_i. \quad (2)$$

Using the condition $q_i \ll 1$, and evaluating the logarithm of both terms of Eq. (2), we obtain

$$\log(\Psi(n)) = - \sum_{i=1}^n q_i. \quad (3)$$

The condition $q_i \ll 1$ implies that i and n of Eq. (3) are so large as to make q_i virtually identical to a function of the continuous time t , $q_i = r(t) = r_0 \eta(t)$, with $\eta(t) = 1/(1+r_1t)$. Therefore $r(t)$ is a time-dependent rate, with resetting as we hereby shall see. Thus, Eq. (3) yields the SP of Eq. (1), and the corresponding waiting time distribution density, $\psi(\tau)$, reads

$$\psi(\tau) = (\mu - 1) \frac{T^{\mu-1}}{(\tau + T)^\mu}. \quad (4)$$

We denote as *collisions* the rare drawings of a number from I_2 , followed by resetting. Thus the collisions occurring at times $\tau_1, \tau_1 + \tau_2, \dots$, yield $\eta(t) = 1/(1+r_1t)$, $0 < t < \tau_1$, $\eta(t) = 1/(1+r_1(t-\tau_1))$, $\tau_1 < t < \tau_1 + \tau_2$, and so on. Note that $\eta(0) = 1$ means that we *prepare* the system at time $t=0$. We might adopt a coin tossing prescription to decide whether to keep or to change sign, after any collision. However, in this paper, as earlier pointed out, we do not pay attention to the problem of fluorescent intensity changing in time as an effect of ensemble average. Thus, for simplicity, our theoretical remarks refer to a sequence $\{\tau_{ij}\}$, where the times τ_i are randomly drawn so as to yield the analytical form of Eq. (4), without assigning to them either an on or an off symbol.

III. MODULATION

The renewal condition described in Sec. II must not be confused with the case of a time-dependent rate, with no renewal. The time dependence of $r(t)$, with no renewal, might obey a deterministic or a stochastic prescription. An example of the former case is $q(t) = A + B \cos(\omega t)$, with no renewal. We think that the physical process studied by the authors of Refs. 19 and 20 might be adequately described by a prescription of this kind, not necessarily periodic, or quasiperiodic, reflecting, however, the molecular conformational changes in time.

The specific cases discussed in this paper are closer in spirit to the condition of stochastic dependence on time. This means that $r(t)$ is a stochastic function of time, so that we have to study

$$\Psi(t) = \left\langle \exp\left(-\int_0^t dt' r(t')\right) \right\rangle. \quad (5)$$

An interesting example of treatment of this kind is offered by the recent work of Brown.²⁶ It has to be pointed out that the evaluation of the characteristic function of Eq. (5) might be a difficult problem, but in the limiting cases of very fast or very slow modulations. The first condition departs from the non-Markov condition of interest for us in this paper. The latter condition does not, and can be adopted to derive the nonexponential behavior of $\Psi(t)$.

Let us assume that the fluctuation $r(t)$ has an equilibrium distribution, $p_{\text{eq}}(r)$. In the special case where the time scale of the fluctuation $r(t)$ is virtually infinite, the SP $\Psi(t)$ becomes

$$\Psi(t) = \int_0^\infty dr p(r) \exp(-rt). \quad (6)$$

In fact, let us consider a Gibbs ensemble of identical systems, obeying Eq. (5). At the moment when the observation begins, at time $t=0$, each of these systems has a rate r , given by the distribution $p_{\text{eq}}(r)$. If the time scale of the rate fluctuations is virtually infinite, during the observation process each system will keep unchanged its own rate, thereby producing Eq. (6). This makes this picture essentially identical to the approach to complexity recently proposed by Beck.²⁷

According to a mathematical prescription borrowed from Beck,²⁷ we find that the analytical expression of Eq. (1) is recovered by using the following form:

$$p_{\text{eq}}(r) = \frac{T^{\mu-1}}{\Gamma(\mu-1)} r^{\mu-2} \exp(-rT). \quad (7)$$

This proposal was used in a later paper⁷ to develop a new approach to complexity, denoted as superstatistics. This approach is attracting the attention of an increasing number of researchers (see, for instance, Refs. 28–30), and for this reason is worth of consideration.

Note that once the inverse power-law form of Eq. (1) for the SP $\Psi(t)$ is realized, the corresponding waiting time distribution density is given by

$$\psi(t) = \int_0^\infty dr p(r) r \exp(-rt). \quad (8)$$

In principle, the adoption of the time-dependent rate prescription of Sec. II would make it possible to describe modulation processes of any kind. It would be enough to set $r_1 = 0$ and replace r_0 with $q(t)$, and make it either deterministic or stochastic. However, to generate the time series $\{\tau_{ij}\}$ corresponding to the modulation prescription, fast, slow, or of intermediate speed, we adopt a different procedure. We select from the distribution of Eq. (7) the sequence $\{r_j\}$. For any exponential waiting time distribution $\psi_j(t) = r_j \exp(-r_j t)$, we select N_m^j times, $\tau_1^j, \dots, \tau_{N_m^j}^j$. A more realistic picture might allow N_m^j to fluctuate. We expect, however, that for ordinary fluctuations about a common value $\langle N_m^j \rangle = N_m$, the physics of the process does not change. Thus, for simplicity we assign to all the number N_m^j the same value N_m . The time series to compare to the one derived according to the prescription of Sec. II is defined by $\{\tau_{ij}\} = \tau_1^1, \dots, \tau_{N_m}^1, \tau_1^2, \dots, \tau_{N_m}^2, \dots$. The benefit of this criterion is that $N_m = 1$ makes the resulting time series equivalent to that generated by the models of Refs. 15–18 and, consequently, to the renewal prescription of Sec. II.

It is important to stress that the ideal condition of a total renewal process and the ideal condition of infinitely slow modulation are characterized by a marked difference concerning ergodicity. This important issue has been recently discussed by Margolin and Barkai.³¹ In the total renewal case, with $\mu < 2$, the system does not admit any stationary condition³² and the stationary correlation function does not exist. The nonstationary correlation function can be defined making an ensemble average, as illustrated, for instance, by the authors of Ref. 33. The authors of Ref. 31, on the contrary, adopt a single trajectory picture and study the time-averaged intensity correlation function of the BQD signal, supposed to be a total renewal, as well as with identical on and off distributions, as assumed in this paper. The correlation function is a stochastic property characterized by U - and W -shaped distributions.

The case of infinitely slow modulation would suggest the adoption of an ensemble rather than an individual trajectory treatment. However, in this paper we adopt the individual trajectory treatment also for the case of slow, but not infi-

nately slow, modulation. It is expected that in this case ergodicity is not violated, in a striking contrast with the condition of total renewal.³¹

We think that moving from $N_m=1$, where the properties found by Margolin and Barkai³¹ apply, to $N_m=\infty$, where only the ensemble treatment is possible, implies the exploration of an unknown region, of which this paper affords a preliminary treatment. For the reader to appreciate this aspect, we would like to introduce the concept of a pseudoevent. This concept is similar to that proposed in an earlier publication.³⁴ The authors of this paper³⁴ found that in some problems of medical interest the connection between scaling and waiting time distribution does not correspond to the prescription of the renewal theory. This is so as a consequence of the fact that the times of the series under study turned out to be correlated.³⁴

In the case of modulation, we define as pseudoevents all the drawings of waiting times from the same Poisson distribution, after the first drawing. In the case $N_m=1$ there are no pseudoevents. In the case $N_m=2$ there is one pseudoevent, and so on. The quantity N_m-1 defines the number of pseudoevents per critical event. By critical event, we denote the drawing of a given Poisson parameter r . In practice, the occurrence of a critical event corresponds to the first drawing of a waiting time from a Poisson distribution with rate r_j , namely the time r_j^i .

The drawing of the next waiting times from the same distribution, implies a subtle deviation from renewal. This form of correlation is not easy to detect. In fact, although consecutive sojourn times are drawn from the same Poisson distribution, they are by definition independent one from another. If the time correlation function is $\langle \tilde{\tau}_i \tilde{\tau}_j \rangle$, with $\tilde{\tau} \equiv \tau - \langle \tau \rangle$ for a finite portion of the sequence, we expect it to yield $(\langle \tau^2 \rangle - \langle \tau \rangle^2) \delta_{i,j}$, with $\delta_{i,j}$ as the delta of Kronecker.

It is a striking and surprising fact that the correlation produced by modulation is invisible to the ordinary correlation test. This is so because the sojourn times, although derived for an extended period of time from the same Poisson distribution, are randomly drawn. The aging experiment reveals this subtle form of correlation. We refer to the times that are correlated to one another as pseudoevents, regardless of the origin of this correlation, which might occur in the form discussed in the earlier publication³⁴ or in the even more subtle form of this paper. We think that the aging reduction depends on the ratio of pseudoevents to critical events, regardless of the origin of correlation. In this paper we find that the aging reduction depends indeed on the ratio of pseudoevents to critical events, of the type here introduced. On the basis of this result, with the help of artificial sequences we make also an attempt at evaluating the amount of pseudoevents that might be present in the real BQD time series.

IV. AGING AND MODULATION

For an intuitive description of the concept of aging we shortly review the treatment of the earlier work of Ref. 35.

The renewal condition of Sec. II can also be realized with the following dynamical model. A particle moves in the interval $I \equiv [0, 1]$ driven by the equation of motion,

$$\frac{dy}{dt} = \alpha y^z, \quad (9)$$

with $0 < \alpha \ll 1$ and $z > 1$. When it reaches the point $y=1$ it is injected back in a random position between 0 and 1 with uniform probability, thereby producing another extended time of sojourn within the interval I . The connection between the waiting time distribution density and the uniform initial distribution is given by

$$\psi(t)dt = p(y_0)dy_0. \quad (10)$$

It is easy to prove that the resulting time distribution density is given again by Eq. (4) with

$$\mu \equiv \frac{z}{z-1} \quad (11)$$

and

$$T \equiv \frac{\mu-1}{\alpha}. \quad (12)$$

The uniform back injection is equivalent to the resetting prescription of Sec. II, and, in fact, this model is a renewal, and it is equivalent to the model of Sec. II, but its adoption in this section serves better the purpose of explaining renewal aging and the lack of aging in the case of very slow modulation.

The waiting time distribution density given by Eq. (10) corresponds to beginning the observation at the moment when the system is prepared in the uniform distribution $p(y_0)=1$. As a result of the injection back process this distribution changes upon time change. If the observation of the first times of sojourn is made at a later time $t_a > 0$, the corresponding waiting time distribution density is given by

$$\psi_{t_a}(t)dt = p(y_0, t_a)dy_0. \quad (13)$$

The dependence of $\psi_{t_a}(t)$ on t_a is the renewal aging that we want to assess in this paper by means of a numerical experiment. An exact expression for $\psi_{t_a}(t)$ is available,^{35,36} but, since it is not expressed as a simple analytical formula, it is not suitable for the practical purposes of this paper. For this reason, we prefer to adopt the expression

$$\psi_{t_a}(t) = \frac{\int_0^{t_0} dy \psi(t+y)}{K_{t_a}}, \quad (14)$$

where K_{t_a} is a suitable normalization constant. The meaning of this approximated expression is evident. We assume that the first sojourn times observed might have begun prior to $t=t_a$, anywhere between $t=0$ and $t=t_a$, with the restrictive condition that the earlier laminar region, only one, began at $t=0$. Actually, the last laminar region might be at the end of a sequence of an arbitrarily large number of jumps, thereby generating corrections to Eq. (14). In Ref. 37 the accuracy of this approximation, in the case of inverse power-law waiting time distributions, was examined, and was found to be very

good. In this paper we shall make a discussion of the key results on the aging experiment on BQD systems, taking into account the error associated to this approximated formula.

It is possible to predict that the case of very slow modulation does not yield aging. In the case of a modulated Poisson process, we replace the model of Eq. (9) with

$$\frac{dy}{dt} = r(t)y. \quad (15)$$

This means that we set $z=1$ and we replace the parameter α with the time-dependent rate $r(t)$. The equation of motion for $p(y,t)$ is given by

$$\frac{\partial}{\partial t} p(y,t) = r(t) \left[-\frac{\partial}{\partial y} y p(y,t) + p(1,t) \right]. \quad (16)$$

Note that the second term on the right-hand side of this equation corresponds to the back injection of the particle, when it reaches the border $y=1$, and thus to the resetting process of the renewal model of Eq. (9). When $r(t)$ does not depend on time, Eq. (16) represents a Poisson process. Let us focus our attention on the case where $r(t)$ is a stochastic function of time. If it is very fast, $r(t)$ must be replaced by $\langle r(t) \rangle$, the process becomes Poisson again, and it departs from the modulation model adopted in this paper (see Sec. III). Anyway, in accordance to a well-known notion, this Poisson process does not yield aging. The model of Eq. (16) becomes equivalent to the modulation model of this paper when the fluctuation of $r(t)$ is very slow. We see that the equilibrium distribution coincides with the initial flat distribution. Thus, we cannot adopt the departure from the initial distribution as a way to define the system's age. In the case of a virtually infinitely slow modulation, the system leaves for a virtually infinite time in a Poisson condition, with no aging whatsoever.

V. AGING EXPERIMENT ON ARTIFICIAL DATA

This section is devoted to illustrating, with the help of artificial data, a technique of analysis aiming at a quantitative evaluation of the degree of renewal properties of a given time series. We refer to this kind of analysis as *aging experiment*.

It is important to notice that the analysis of real data implies the observation of only one single sequence. In this case we must turn a single sequence into a very large number of sequences of the same age. The first sequence is the sequence, artificial or experimental, to analyze, beginning at time $t=0$ with the system being located at the beginning of a state, either on or off. The second sequence is obtained from the first, canceling the first state, namely, shifting the first sequence towards the time origin by the quantity equal to the time duration of the first state, so that the second sequence begins at time $t=0$, when the system begins sojourning in the second state of the first, or original, sequence. On the same token, the third sequence begins at time $t=0$, when the system begins sojourning in the third state, and so on. Thus the waiting time distribution $\psi(t), t_a=0$, is the distribution of the time durations of the first states. To do the aging experiment we set $t_a > 0$ and we record the time lengths of the first states

observed in that time position. With this prescription we define $\psi_{t_a}(t)$. A quantitative definition of amount of aging is more properly done using the SP, defined by

$$\Psi_{t_a}(t) \equiv \int_t^\infty \psi_{t_a}(t') dt', \quad (17)$$

rather than $\psi_{t_a}(t)$.

From now on we denote by $\psi^{\text{exp}}(t)$ and $\Psi^{\text{exp}}(t)$ the waiting time distribution densities and the SPs, respectively, derived from the experimental data. Of course, in the case of artificial data, where the sequence is realized for the specific purpose of producing the function $\Psi(t)$ of Eq. (1) and $\psi(t)$ of Eq. (4), the experimental functions coincide with the corresponding theoretical prescriptions. Then, we define the corresponding aged distributions using Eq. (14). This expression is not exact. However, it is convenient for the purposes of this paper, where the experimental error is expected to be larger than the discrepancy between Eq. (14) and the exact prescription. Then, we denote with $\Psi_{t_a}^{\text{ren}}(t)$ the SP derived from the experimental observation, namely, from $\Psi_0^{\text{exp}}(t) \equiv \Psi_{t_a=0}^{\text{exp}}(t)$, by means of Eq. (14).

The prescription adopted in Sec. III to produce the time series $\{\tau_{ij}\}$ with a changing N_m for $N_m \rightarrow \infty$ becomes coincident with the slow modulation of Eq. (16). Thus, we expect no aging in this limiting case. In the opposite limit with $N_m=1$, the sequence is renewal. Thus, we expect the maximum amount of aging. In other words, the renewal condition should yield

$$\Psi_{t_a}^{\text{exp}}(t) = \Psi_{t_a}^{\text{ren}}(t), \quad (18)$$

whereas the condition of very slow modulation should produce no aging, a property described by

$$\Psi_{t_a}^{\text{exp}}(t) = \Psi_0^{\text{ren}}(t) \equiv \Psi_0^{\text{exp}}. \quad (19)$$

Equations (18) and (19) refer to two limiting conditions: the condition of Eq. (18) corresponds to total aging, with no pseudoevents, while the condition of Eq. (19) stems from a process dominated by Poisson pseudoevents, with a total lack of aging. It is important to point out that the results presented in Sec. VI, do not involve any assumption on the form of the waiting time distribution.

Let us introduce here another important ingredient of our analysis, the aging intensity function,

$$I_a(\tau) = \frac{\Psi_{t_a}^{\text{exp}}(\tau) - \Psi_0^{\text{exp}}(\tau)}{\Psi_{t_a}^{\text{ren}}(\tau) - \Psi_0^{\text{exp}}(\tau)}. \quad (20)$$

Equations (18) and (19) yield $I_a(\tau)=1$ and $I_a(\tau)=0$, respectively, thereby indicating that Eq. (20) is a proper aging intensity indicator, with 1 and 0 representing total aging and lack of aging, respectively. In principle, this function should decrease from 1 to 0 upon increase of the number of pseudoevents.

The numerical results of Figs. 1(a)–1(c) confirm the expectation that the larger the number of pseudoevents, the smaller the aging intensity. In fact, in accordance with the earlier theoretical remarks, we see that in the case of no pseudoevent, $N_m=1$, reported in Fig. 1(a), modulation and

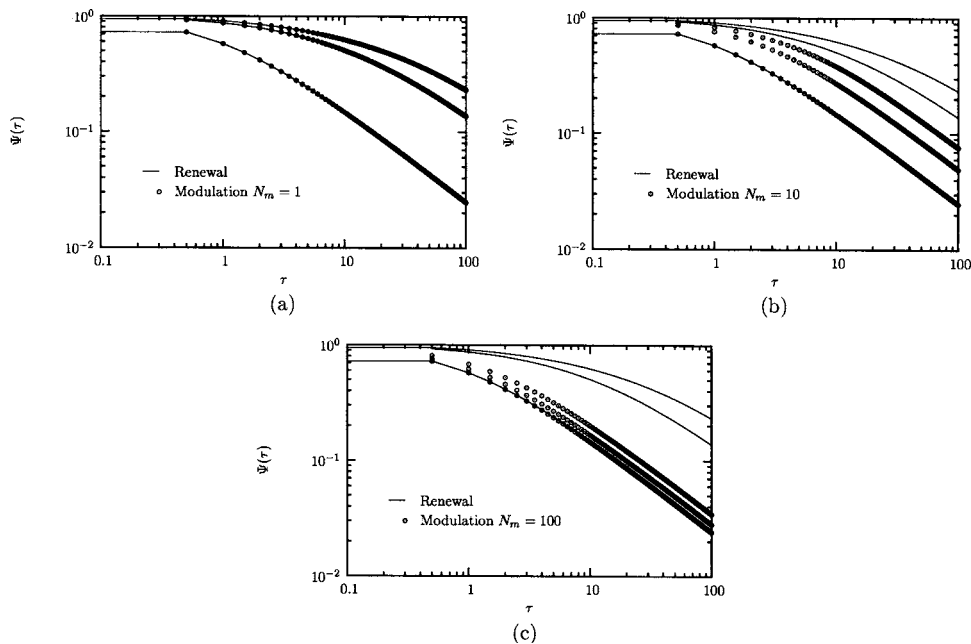


FIG. 1. The SP $\Psi_{t_a}^{\text{exp}}(t)$ as a function of time. The three figures, Figs. 1(a)–1(c), refer to $N_m=1$, $N_m=10$, and $N_m=100$, namely to 0, 9, and 99 pseudoevents per critical event, respectively. The curves of each figure are obtained from artificial sequences yielding for the waiting time distribution density the same inverse power-law form of Eq. (1), with $\mu=1.8$. For each figure the three distinct ages $t_a=0, 20$, and 60 (from the bottom to the top) are considered. The renewal predictions and the modulation results are denoted by full lines and circles, respectively.

renewal yield the same amount of aging. The occurrence of nine pseudoevents, namely, the case $N_m=10$ illustrated in Fig. 1(b), is already enough to significantly reduce modulation aging. Figure 1(c) shows that $N_m=100$ yields an even larger aging intensity reduction. In conclusion, these numerical results confirm the theoretical expectation that the infinitely slow modulation, $N_m=\infty$, should produce no aging.

The adoption of the aging intensity function of Eq. (20) allows us to express the aging reduction illustrated by the earlier figures in a quantitative way. The analysis of the numerical simulations of both renewal and modulation models shows that the aging intensity function $I_a(\tau)$ for $\tau \rightarrow \infty$ tends to an asymptotic value, $I_a(\infty)$. This property is shared by the real data analyzed in Sec. VI. We estimate this value and we use it, in both the case of artificial sequences of this section and in the case of real data of Sec. VI to define the time asymptotic intensity of the aging indicator.

Figure 2 illustrates the application of this procedure to the case of artificial sequences. We see that the aging intensity decreases with the increase of the number of pseudoevents per critical event. We fit $I_a(\infty)$, as a function of N_m , with the inverse power law $(N_m)^{-\alpha}$, with $\alpha=0.70 \pm 0.02$. The aging

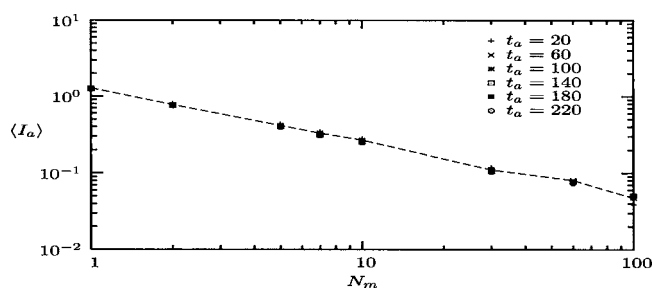


FIG. 2. The aging intensity indicator $I_a(\infty)$ as a function N_m , that is N_m-1 pseudoevents per critical event, at different ages, namely different values of t_a . The aging intensity is defined by Eq. (20). These results refer to artificial sequences with $\mu=1.8$. Physical conditions with different ages and the same number of pseudoevents collapse into the same $I_a(\infty)$, thereby becoming indistinguishable in the scale of this figure.

intensity indicator, $I_a(\infty)$, which should hold the value of 1 when there are no pseudoevents, actually slightly exceeds this value with no pseudoevent and decreases by a factor of 10, with increasing the number of pseudoevents per critical event from 0 to 99. In Sec. VI, we shall refer to Fig. 2 to estimate the amount of pseudoevents per critical event present in the real BQD data.

The aging intensity overestimation, with no pseudoevents, is a consequence of the fact that Eq. (14) is not exact. Let us study the effects of this inaccuracy by means of artificial sequences. We use artificial sequences derived from the renewal prescription, namely, by random drawings of numbers from the inverse power-law distribution of Eq. (4), yielding a SP of the form of the Eq. (1). We use the values $\mu=1.65$ and $\mu=1.8$, which are typical values of the off sequences studied in Sec. VI. We make a Monte Carlo simulation and we produce curves of the kind illustrated in Fig. 3, showing the time dependence of the aging intensity function. We see that $I_a(\tau)$ becomes virtually time independent after a short transient. Let us notice that the levels of these plateaus exceed the maximum value of 1. However, we see that this

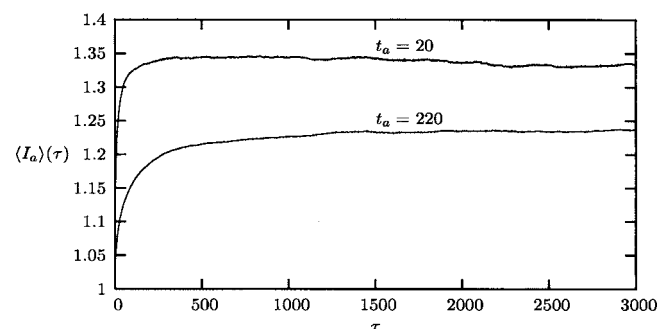


FIG. 3. The aging intensity $I_a(\tau)$ of Eq. (20) as a function of τ . We study the case of renewal artificial sequences with an inverse power-law form, with $\mu=1.8$. We study the time evolution of this indicator at two different ages, $t_a=20$ and $t_a=220$. The attenuation of the overestimation effect with the increasing t_a is evident.

TABLE I. This table summarizes the results of Monte Carlo simulations done to evaluate the aging intensity $I_a(\infty)$. These results refer to the case of renewal artificial sequences, with an inverse power-law form. The values of μ adopted, $\mu=1.65$ and $\mu=1.8$, are the typical values of the real BQD sequences of off states. σ_{ren} is the standard deviation.

t_a	$\mu=1.65$		$\mu=1.8$	
	$I_a(\infty)$	$\sigma_{\text{ren}}(I_a)$	$I_a(\infty)$	$\sigma_{\text{ren}}(I_a)$
20	1.3734	0.0011	1.3378	0.0047
60	1.318 28	0.000 70	1.2765	0.0026
100	1.3007	0.0012	1.2608	0.0017
140	1.293 25	0.000 40	1.2502	0.0014
180	1.287 64	0.000 36	1.2420	0.0014
220	1.282 43	0.000 37	1.2344	0.0012

level becomes closer to 1 with the age increasing from $t_a = 20$ to $t_a = 220$. Of course, the property of a fast attainment of a plateau is shared also by the cases, not shown here, of a nonvanishing number of pseudoevents, with the plateau height significantly smaller than 1 for N_m of the order of 10: the results of Fig. 2 have been obtained by evaluating the level of this plateau. Applying the same criterion to the case of no pseudoevents, we get the asymptotic values $I_a(\infty)$, illustrated by Table I.

In conclusion, the aging indicator $I_a(\infty)$ should be independent of the system age and equal to 1: in fact, we are analyzing artificial sequences corresponding to the renewal model. We see, on the contrary, that the aging intensity indicator exceeds the maximum value of 1. This is due to the inaccuracy of the formula of Eq. (20), which is known³⁵ to become accurate for $t_a \rightarrow \infty$. In accordance with this fact, we see from Table I that the aging intensity overestimation tends to vanish with increasing values of t_a .

VI. AGING EXPERIMENT ON REAL DATA

We are now in a position to analyze the experimental results on real BQD data sequences. The experimental data discussed in this section have been obtained by Professor M. Kuno and V. Protasenko, Department of Chemistry and Biochemistry, University of Notre Dame. Our data set consists of 32 sequences of BQD fluorescence intensities. Each sequence contains 1 h of records, sampled every millisecond, for a total amount of 360 000 data per sequence. A sample of the data studied in this section is shown in Fig. 4.

In order to separate the on from the off states it is necessary to define a threshold intensity, above which the signal corresponds to an on state and below which it signals the off state. We establish this separation along the lines adopted in an earlier work (see Ref. 15), namely, with an iterative procedure for the search of a repartition that makes it possible

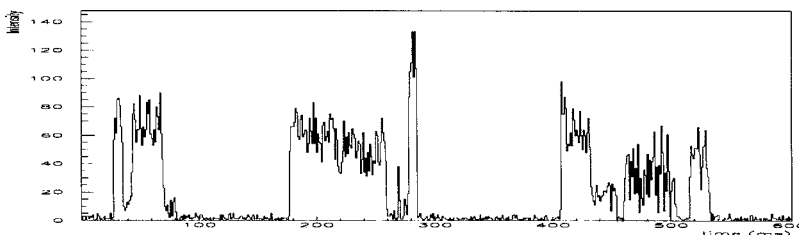


FIG. 4. A sample of the BQD data examined in this section.

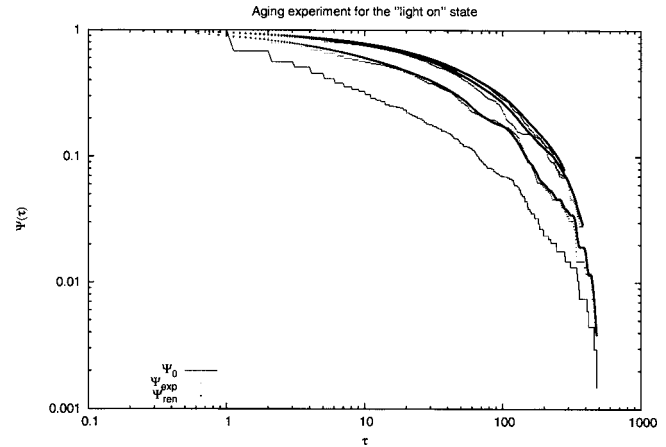


FIG. 5. The SP $\Psi(t)$ as a function of time. The experiment is carried using only the on waiting time distribution. The thin continuous line indicates $\Psi_0^{\text{exp}}(t)$, the dotted line refers to $\Psi^{\text{exp}}(t)$, and the thick continuous line is Ψ^{ren} . From the bottom to the top the curves refer to t_a with the values 20, 120, and 220.

for the fluctuations of the two states not to intersect with the separation line. At the end of this iteration process the variances of the two states get a well-defined value, with σ denoting the variance of the off state: the threshold turns out to be located at the value 2σ over the off state.

After defining an alternate sequence of on and off states, we make the aging experiment with the criterion described in Sec. IV. Actually, we make three different kinds of aging experiment. The first and second, considering the waiting times only of the on and off states, respectively. This means that we sew the beginning of the on (off) state to the end of the immediately preceding “light” on (light off) state. The third experiment is done on the whole sequence of waiting times, with the jump from one state to the other signaling the presence of an event, whose statistical properties are studied regardless of whether it corresponds to jumping from the light on to the light off state, or vice versa.

A. Aging of the light on state

Here we discuss the results of the first kind of aging experiments, on the light on state. Figure 5 shows an example of these aging experiments. This figure refers to a case where the aging experiment on the BQD sequence is done for several values of t_a , ranging from 20 to 220 in steps of 40. The thin continuous line represents Ψ_0^{exp} , the dotted line refers to $\Psi_{t_a}^{\text{exp}}$, while the thick continuous line represents $\Psi_{t_a}^{\text{ren}}$. We see that in this case the condition of Eq. (18) is fulfilled with a very good accuracy. The system ages and it does according to the non-Poisson renewal theory. In fact, aging implies that the system obeys a non-Poisson statistics,

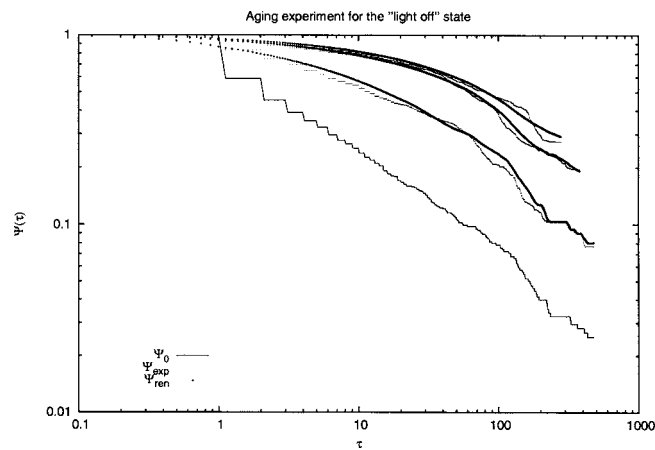


FIG. 6. The SP $\Psi(t)$ as a function of time. The experiment is carried using only the off waiting time distribution. The thin continuous line indicates $\Psi_0^{\text{exp}}(t)$, the dotted line refers to $\Psi^{\text{exp}}(t)$, and the thick continuous line is Ψ_{ren} . From the bottom to the top the curves refer to t_a with the values 20, 120, and 220.

and the fulfillment of Eq. (18) means that this non-Poisson statistics is renewal. It is also worth pointing out again that this observation does not involve that the deviation from Poisson statistics is realized through inverse power laws, as assumed for simplicity in Sec. II. In fact, the experimental waiting time distribution and SP are not inverse power law, or at least do not correspond to an inverse power law with a well-defined index. However, they depart from the exponential condition enough as to generate the aging effects illustrated by Fig. 5.

B. Aging of the off state

Let us discuss aging for the sequence of waiting times in off state. A sample of these results is shown by Fig. 6. Also in this case, the system is aging and its behavior is very well described by the renewal theory.

By visual inspection, we can stress some differences between the result of the latter and the former experiments. The main difference seems to be that the distribution of the time

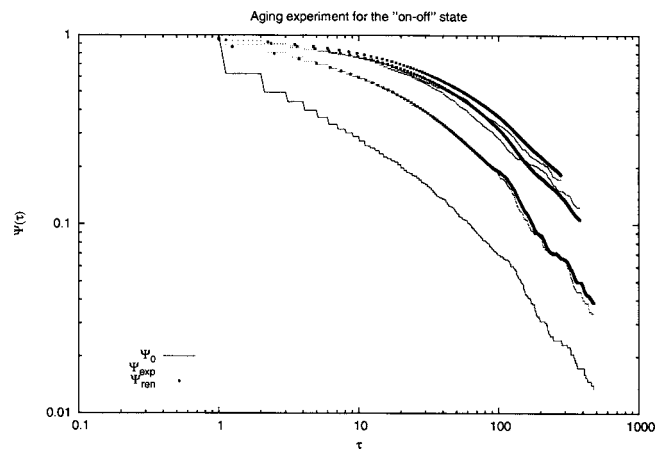


FIG. 7. The SP $\Psi(t)$ as a function of time. The experiment is carried using both the on and off waiting time distributions. The thin continuous line indicates $\Psi_0^{\text{exp}}(t)$, the dotted line refers to $\Psi^{\text{exp}}(t)$, and the thick continuous line is Ψ_{ren} . From the bottom to the top the curves refer to t_a with the values 20, 120, and 220.

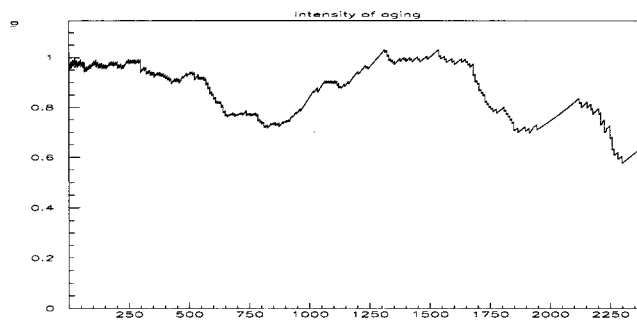


FIG. 8. Example of the aging intensity function $I_a(\tau)$ for the on state.

of sojourn in the on state is truncated after about two decades, while the inverse power-law distribution of the off states holds longer. This result confirms the earlier observations of Chung and Bawendi.⁵ For this reason, it turns out to be difficult for us to estimate the index of the waiting time distribution of the on states. In the case of the off states, instead, we can do that, since the power-law behavior is more distinct than that in the earlier case. Our estimations of the power-law exponent, in this case, ranges from 1.65 ± 0.02 to 1.80 ± 0.05 . We note that the artificial sequences of Table I refer to these values.

C. Aging of the on-off state

Let us discuss now the result of the third aging experiment, done on the whole sequence, with the transitions from the on to the off states as the markers of the significant events to analyze with the aging experiment. Figure 7 shows a sample of this third kind of aging experiment. Also in this case it is evident how the theoretical predictions of the renewal theory fit very well the experimental results.

In order to support quantitatively the conjecture made on the basis of visual inspection of the results, in the next subsection we shall adopt the aging intensity indicator introduced in Sec. V.

D. Aging intensity

We recall that the adoption of Eq. (14) yields for the aging indicator $I_a(\infty)$ values larger than 1, namely, we find that Eq. (14) overestimates the aging intensity (see Table I). With Fig. 2 we also found that a number of pseudoevents of the order of 10 significantly reduces the aging intensity.

We can now use these indications for a rough estimation of the number of possible pseudoevents present in the sequences of sojourn times in the on state. To make the evalu-

TABLE II. This table shows the intensity of aging Eq. (20) for the on state, for different values of t_a , averaged over the ensemble.

t_a	$\langle I_a \rangle$	$\sigma(I_a)$
20	0.676	0.026
60	0.690	0.023
100	0.810	0.021
140	0.795	0.020
180	0.740	0.022
220	0.868	0.019

TABLE III. This table shows the mean aging intensity of Eq. (20) for the off state, at different values of t_a . The average is carried out on the whole experimental sequences.

t_a	$\langle I_a \rangle$	$\sigma(I_a)$
20	1.040	0.020
60	0.992	0.012
100	1.030	0.014
140	1.010	0.014
180	0.947	0.013
220	0.962	0.015

ation of the aging intensity value as statistically accurate as possible, we adopt a Gibbs ensemble average. In other words, we make an average over all the sequences at our disposal, after assigning to them the same age t_a . This is done by preparing all the sequences in such a way that at $t=0$ each of them begin at the beginning of the time of sojourn in the on state, the off state, or the on or off state, according to the kind of experiment under study, of the first, second, and third types, respectively. Then we set for all sequences the beginning of the observation process at the same time t_a . We obtain the mean aging indicator, indicated by $\langle I_a \rangle$. We do the same experiment for different values of t_a . Figure 8 shows the time evolution of $I_a(\tau)$ for a given sequence of on states corresponding to that used to derive the results of Fig. 5. The aging indicator $I_a(\infty)$ for any sequence of this kind is obtained by making an average on τ , and the fluctuations around this mean value are used to define the measurement error.

The average on all the sequences of the Gibbs ensemble are used to obtain the values of $\langle I_a \rangle$ reported in the tables. Tables II–IV report the value of $\langle I_a \rangle$ for the on, off, and on-off waiting time distributions, respectively. In these tables, σ represents the maximum likelihood estimation of the standard deviation of $\langle I_a \rangle$.

These results show that the aging of both the off and on-off waiting time distributions are very well described by the means of the renewal theory. The accuracy of the renewal prediction becomes worse for the on state, especially for low values of the parameter t_a , and it improves with the increase of t_a . By comparing these values to the curve of Fig. 2, and taking into account that with $N_m=1$ the aging intensity indicator overestimates the aging intensity of the artificial sequences, we cannot rule out the possibility that the on state might involve the presence from five to six pseudoevents.

TABLE IV. This table shows the mean aging intensity Eq. (20) for the on-off state, at several values of t_a . The average is carried out on all the experimental sequences.

t_a	$\langle I_a \rangle$	$\sigma(I_a)$
20	0.949	0.013
60	0.894	0.011
100	0.914	0.011
140	0.865	0.011
180	0.823	0.012
220	0.810	0.011

VII. CONCLUDING REMARKS

The main result of this paper is the proof that BQD data obey non-Poisson renewal with a good accuracy. This complexity condition does not stem from modulation (superstatistics). The statistics of the “on” states is not identical to the statistics of “off” states. The latter case is closer than the former to the inverse power-law picture of Sec. II. However, both waiting time distributions depart significantly from the exponential form and produce significant aging effects.

We confirm the general opinion that the BQD phenomenon obeys a renewal prescription, leaving open, however, the possibility that a finite amount of pseudoevents might be involved, especially for the on state. This suggestion emerges from the results of Tables II and III compared to those of Fig. 2.

We have to point out that the field of single-system spectroscopy is wide and there are examples of a process where slow modulation conditions seem to apply.^{19,20,38} This paper affords prescriptions of statistical analysis that might turn out to be useful to study the unknown territory between total renewal and infinitely slow modulation.

ACKNOWLEDGMENTS

We thankfully acknowledge Professor M. Kuno and V. Protasenko for kindly making their experimental data available to us. Two of the authors (S.B. and P.G.) thankfully acknowledge financial support from Welch through Grant No. 70525. One of the authors (P.P.) thankfully acknowledges financial support from MIUR through Grant No. “bando 1105/2002,” Project No. 245, and CNR 2005 short-term mobility program.

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