Statistical Aging and Nonergodicity in the Fluorescence of Single Nanocrystals

X. Brokmann,[1] J.-P. Hermier,[1,2] G. Messin,[1] P. Desbiolles,[1] J.-P. Bouchaud,[3] and M. Dahan[1]

[1]*Laboratoire Kastler Brossel,* 75231 Paris Cedex 05, France*

[2]*Pôle Matériaux et Phénomènes Quantiques, Université Denis Diderot, 2, place Jussieu, 75251 Paris Cedex 05, France*

[3]*Service de Physique de l'Etat Condensé, Commissariat à l'Énergie Atomique, Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France.*

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The relation between single particle and ensemble measurements is addressed for semiconductor CdSe nanocrystals. We record their fluorescence at the single molecule level and analyze their emission intermittency, which is governed by unusual random processes known as Lévy statistics. We report the observation of statistical aging and ergodicity breaking, both related to the occurrence of Lévy statistics. Our results show that the behavior of ensemble quantities, such as the total fluorescence of an ensemble of nanocrystals, can differ from the time-averaged individual quantities, and must be interpreted with care.

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The relation between single particle and ensemble measurements is at the core of statistical physics. It is usually expressed in terms of the ergodic hypothesis which states that time averaging and ensemble averaging of an observable coincide [1,2]. This question has attracted renewed attention given that experiments are now able to resolve individual nanometer-sized systems. It is addressed here for semiconductor CdSe nanocrystals. The fluorescence properties of these colloidal quantum dots (QDs) have raised great interest due to their size-induced spectral tunability, high quantum yield, and remarkable photostability at room temperature [3], all of which make QDs a promising system for biological labelling [4], single-photon sources [5], and nanolasers [6].

When studied at the single molecule level, CdSe QDs share with a large variety of other fluorescent nanometer-sized systems [7–10] the property of exhibiting fluorescence intermittency [11]. This means that the fluorescence intensity randomly switches from bright ("on") states to dark ("off") states under continuous excitation. Although the very origin of the intermittency for CdSe QDs remains a matter of investigation, its statistical properties have been studied. For a given QD, the durations $\tau_{\rm on}$ and $\tau_{\rm off}$ of the on and off periods follow slowly decaying power-law distributions $P_{\rm on}(\tau_{\rm on} > \tau) = (\tau_0/\tau)^{\mu_{\rm on}}$, $P_{\rm off}(\tau_{\rm off} > \tau) = (\tau_0/\tau)^{\mu_{\rm off}}$, where $\mu_{\rm on}$ and $\mu_{\rm off}$ are close to 0.5 [12,13]. This behavior extends over several orders of magnitude, from the detection integration time τ_0 up to hundreds of seconds, with very small dependence on temperature or excitation intensity.

The crucial point for our analysis is that both $\mu_{\rm on}$ and $\mu_{\rm off}$ are smaller than 1. In this case, the decay is so slow that the mean value of $P_{\rm on}$ and $P_{\rm off}$ is formally infinite, and very long events tend to dominate the fluorescence signal, producing strong intermittency. The duration of the on and off periods are thus governed by "Lévy statistics," which have been encountered in various fields [14–22] such as laser cooling of atoms [15], dynamics of disordered [16] and chaotic [18] systems, glassy dynamics [20], or economics and finance [21].

In this Letter, we show that single QD measurements can be used to explicitly compare ensemble- and time-averaged properties and explore some of the unusual phenomena induced by Lévy statistics, such as statistical aging and ergodicity breaking. Using an epifluorescence microscopy setup and a low-noise CCD camera, we simultaneously recorded at room temperature the fluorescence intensity of 215 individual QDs for the duration of 10 min with a time resolution of 100 ms [23]. The blinking of the fluorescence intensity was observed for each QD detected in the field of the camera (Fig. 1). Because of the binary behavior of the blinking process, each intensity time trace was considered simply as a sequence of n on and off times $\{\tau_{\rm on}^{(1)}, \tau_{\rm off}^{(1)}, \tau_{\rm on}^{(2)}, \tau_{\rm off}^{(2)}, \ldots, \tau_{\rm on}^{(n)}, \tau_{\rm off}^{(n)}\}$ from which the distributions $P_{\rm on}$ and $P_{\rm off}$ were derived. In our measurements, the on and off periods both followed power-law distributions [25]. After adjustment of the cumulative distributions of the on and off periods for each of the 215 QDs, the exponents $\mu_{\rm on}$ and $\mu_{\rm off}$ were

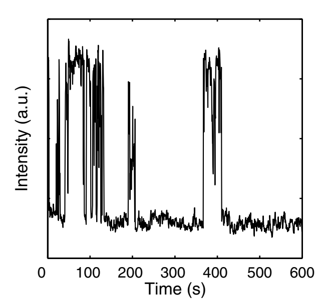

FIG. 1. Fluorescence intermittency of a single CdSe nanocrystal measured over 10 min with 100 ms time bins. Because of the broad distribution of the on and off states, the signal is dominated by a few long events.

estimated to be, respectively, 0.58 (0.17) and 0.48 (0.15), consistent with previous experiments [12,13]. For all pairs of QDs, we also computed the Kolmogorov-Smirnov (KS) likelihood estimator [26] to compare the on (respectively, off) distributions between each pair of QDs. For our set of data, the KS tests yield the same average value of 0.4 (0.3) for both on and off distributions, well above the value 0.05 usually considered as an inferior limit to assume that two data sets have identical distributions. In the following, the 215 QDs are therefore considered as statistically identical, with $\mu_{\rm on} = 0.58$ and $\mu_{\rm off} = 0.48$ [27].

The first observation is that, for purely statistical reasons, the fluorescence of QDs is nonstationary, i.e., time translation invariance is broken in the intermittency process. This is best evidenced by studying the rate at which the QDs jump back from the off to the on state (a "switch on" event). For this purpose, we computed the ensemble average of the probability density $s(\theta)$ to observe a QD switching on between θ and $\theta + d\theta$ after a time θ spent in the off state. For off periods following a "narrow" distribution (with a finite mean value $\langle \tau_{\rm off} \rangle$), $s(\theta)$—also called the renewal density—would be independent of θ and equal to $1/\langle \tau_{\rm off} \rangle$. The situation is drastically changed for CdSe QDs due to the fact that $\mu_{\rm off} < 1$, $\langle \tau_{\rm off} \rangle$ no longer exists and $s(\theta)$ is then expected to decay as $\theta^{-(1-\mu_{\rm off})}$ [15]. This means that as time grows the switch on events occur less and less frequently. Figure 2(a) shows that our data match these theoretical predictions: the measured value of $s(\theta)$ decreases as $\theta^{-\alpha}$, with $\alpha = 0.5$ in agreement with the value $(1 - \mu_{\rm off})$ expected from our measurement of $\mu_{\rm off}$.

This nonstationary behavior can be understood by considering, for each QD, the quantity

$$\theta(N) = \sum_{i=1}^{N} \tau_{\rm off}^{(i)}, \qquad (1)$$

i.e., the total time spent in the off state during the N first off periods [Fig. 2(b)]. Assuming that the $\tau_{\rm off}^{(i)}$ are independent and $\tau_{\rm off}$ having no mean value, the sum of N such independent random variables must be evaluated by means of the generalized central limit theorem (see, e.g., [15]). This theorem states that $\theta(N)$, instead of scaling as N, grows more rapidly, as $N^{1/\mu_{\rm off}}$. As shown in Fig. 2(b), the sum $\theta(N)$ is dominated by few events. This central property, distinctive of Lévy statistics, means that, as time grows, one observes long events that are of the order of $\theta(N)$ itself [28]. Hence, the probability for a QD to switch on decreases with time: the system ages [20] and the signal is nonstationary.

To test the assumption that the off events are independent and to gain further insight into this aging effect, we computed the persistence probability $\Pi_0(\theta, \theta + \theta')$, defined as the probability that no switch on event occurs between θ and $\theta + \theta'$. In the case of independent off periods with an exponential distribution (with mean value $\langle \tau_{\rm off} \rangle$), $\Pi_0(\theta, \theta + \theta')$ is independent of θ, and given by $e^{-\theta'/\langle \tau_{\rm off} \rangle}$, illustrating that the switching process is stationary. The computation of Π_0 from our data set reveals a completely different pattern: the probability that no switch on event occurs within a given duration θ' decreases with θ [Fig. 2(c)], consistent with the behavior of $s(\theta)$. Furthermore, $\Pi_0(\theta, \theta + \theta')$ is found to depend only on the reduced variable $\theta/(\theta + \theta')$ and to vanish for $\theta/(\theta + \theta')$ close to 0 [Fig. 2(d)]. This result proves that one has to wait a time θ' of the order of θ to have a chance to observe a switch on event, in qualitative agreement with the fact that the largest term of the sum $\theta(N)$ is of the order of $\theta(N)$ itself. Quantitatively, for independent off events distributed according to a Lévy distribution $P_{\rm off}$ with exponent $\mu_{\rm off}$, the persistence probability is expected to read

$$\Pi_0(\theta, \theta + \theta') = \int_0^{\theta/(\theta+\theta')} \beta_{\mu_{\rm off}, 1-\mu_{\rm off}}(u) du, \qquad (2)$$

where β is the beta distribution on $[0, 1]$ [20,29]. Our data follow this prediction with $\mu_{\rm off} = 0.55$, in agreement both with our previous estimations of $\mu_{\rm off}$ [Fig. 2(d)] and with the assumption that the off events

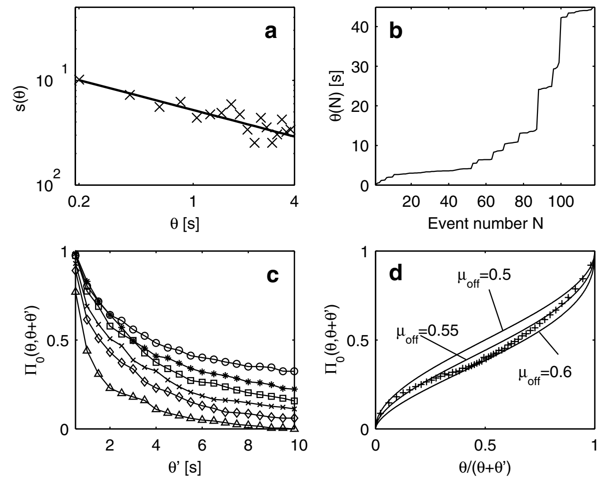

FIG. 2. Statistical aging measured from a sample of 215 QDs. (a) Logarithmic plot of the probability density $s(\theta)$ for a QD to jump in the on state after having spent a total time θ in the off state. The solid line is a power-law adjustment $\theta^{-\alpha}$ with $\alpha = 0.5$. (b) Evolution of the total time spent in the off state $\theta(N)$ with the number N of off periods for a given QD; the sum $\theta(N)$ is dominated by a few events of the order of $\theta(N)$ itself. (c) Persistence probability $\Pi_0(\theta, \theta + \theta')$ measured from the set of 215 QDs for $\theta = 0.1$ s (△), $\theta = 0.5$ s (◇), $\theta = 1$ s (×), $\theta = 2$ s (□), $\theta = 4$ s (*), and $\theta = 8$ s (○). $\Pi_0(\theta, \theta + \theta')$ depends on θ, indicating that the process is aging. (d) Persistence probability $\Pi_0(\theta, \theta + \theta')$ measured for θ and θ' ranging between 0 and 10 s with 0.1 s time bins and expressed as a function of $\theta/(\theta + \theta')$ (+). Each point corresponds to the average over 200 adjacent data points. The solid lines are the theoretical predictions for exponents $\mu_{\rm off} = 0.5$, $\mu_{\rm off} = 0.55$, and $\mu_{\rm off} = 0.6$.

are independent. These results show that the aging effect has a pure statistical origin and is not related to an irreversible process (such as photodestruction). Because of the statistical properties of Lévy distributions, nonstationarity emerges despite the time independence of the laws governing the microscopic fluorescence process.

From a more general standpoint, this nonstationary behavior also has profound consequences on basic data interpretation, such as the ensemble-averaged total fluorescence emitted by a population of QDs. We illustrated this by studying $\Phi_{\text{on}}(t)$, the fraction of QDs in the on state at a given time t [Fig. 3(a)]. In the context of Lévy statistics, the time evolution of $\Phi_{\text{on}}(t)$ is intimately linked to the relative amount of time spent in the on and off states for each QD. Qualitatively, the off events tend to be dominant whenever $\mu_{\text{off}} < \mu_{\text{off}}$ since $\theta(N) = \sum_{i=1}^{N} \tau_{\text{off}}^{(i)}$ grows faster than its counterpart $\hat{\theta}(N) = \sum_{i=1}^{N} \tau_{\text{on}}^{(i)}$. When analyzed in a more quantitative way, the fraction $\Phi_{\text{on}}(t)$ can be shown to decrease asymptotically as $t^{\mu_{\text{off}}-\mu_{\text{on}}}$ [15]. Experimental results confirm this analysis: $\Phi_{\text{on}}(t)$ decays as $t^{-\beta}$, with an exponent $\beta = 0.13$ indeed consistent with the previous determination of μ_{on} and μ_{off} [Fig. 3(a)]. We also observed that the average signal over the whole CCD detector, i.e., the sum of the fluorescence of all the QDs, decays as $t^{-0.18}$, in agreement (within experimental uncertainty) with the fact that time increasing, less and less QDs are in the on state, causing the total fluorescence to decrease as $\Phi_{\text{on}}(t)$ [Fig. 3(b)]. Importantly, we also observed that this fluorescence decay is laser induced and reversible: after a continuous laser illumination of 10 min, leaving the sample in the dark for about 10–15 min systematically lead to a complete recovery of its initial fluorescence. This confirms that this decay is again purely statistical, and not related to an irreversible bleaching of the QDs.

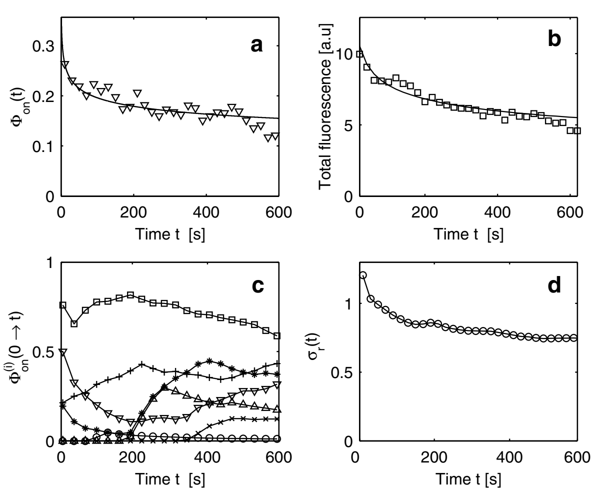

FIG. 3. Nonstationarity and nonergodicity in a sample of QDs. (a) Time evolution of the fraction $\Phi_{\text{on}}(t)$ of QDs in the on state at time t (∇). $\Phi_{\text{on}}(t)$ decays as $t^{-0.13} = t^{\mu_{\text{off}}-\mu_{\text{on}}}$ (solid line). (b) Time evolution of the total fluorescence signal emitted by the sample ($\square$): the darkening effect follows a $t^{-0.18}$ power-law decay (solid line). (c) Typical time evolution of $\Phi_{\text{on}}^{(i)}(0 \mapsto t)$—the fraction of time spent in the on state between 0 and t - for seven QDs. The time averages are widely fluctuating, even in the long integration time limit. (d) Evolution of the relative dispersion $\sigma_r(t)$ of $\Phi_{\text{on}}^{(i)}(0 \mapsto t)$ at time t over the ensemble of QDs ($\bigcirc$). As time grows, $\sigma_r(t)$ tends to a constant value, illustrating that the time averages trajectories do not converge to any asymptotic value.

Our final observation focuses on nonergodic aspects of random processes driven by Lévy statistics. Single particle measurements allow one to compare directly $\Phi_{\text{on}}(t)$ and the fraction of time $\Phi_{\text{on}}^{(i)}(0 \mapsto t)$ spent in the on state between 0 and t for the ith QD. This provides a direct test of the ergodicity of the QD fluorescence. While the ensemble average $\Phi_{\text{on}}(t)$ decays deterministically as $t^{-0.13}$ [Fig. 3(a)], each time average widely fluctuates over time and for a given t, the values of $\Phi_{\text{on}}^{(i)}$ are broadly distributed between 0 and 1, even after a long time of integration [Fig. 3(c)]. To study the behavior of time averages, we calculated the relative dispersion $\sigma_r(t)$ of the time averages at time t, where $\sigma_r(t)$ corresponds to the standard deviation of the distribution of $\Phi_{\text{on}}^{(i)}(0 \mapsto t)$ over the set of QDs, divided by its mean value. Figure 3(d) shows that $\sigma_r(t)$ does not decay to zero, and is still of the order of 1 on the experimental time scale. Therefore, even for long acquisition times, the fluctuations of the time averages from QD to QD remain of the order of the time averages themselves and do not vanish as expected for ergodic systems. These data indicate ergodicity breaking: due to rare events with a duration comparable to the total acquisition time, there is no characteristic time scale over which physical observables can be time averaged. Even for long acquisition time, $\Phi_{\text{on}}^{(i)}(0 \mapsto t)$ does not converge and no information on the ensemble value Φ_{on} can be obtained by time averaging an individual trajectory.

While we found that accurate estimates of μ_{on} and μ_{off} are essential to analyze and predict the statistical properties of the fluorescence, the microscopic origin of these broad distributions is not yet established. Possible explanations are related to the general question of relaxation in disordered systems [14,20,30]. Distributions of off times are sometimes attributed to distributions of static traps from which the charge of an ionized QD escapes by tunneling effect [12,31]. In these models, the value of μ_{off} strongly depends on microscopic characteristics of the QDs, and it is not clear how this is compatible with the statistical homogeneity of the different QDs suggested by the KS test. The dynamic changes of the particle environment are also often invoked to account for the fluctuating emission of the QD [13,32]. Some authors have thus suggested models in which the trap for the charge of the ionized QD follows a random walk in a 1D parameter space, yielding a universal value $1/2$ for μ_{off} [13]. However, both of these models (static and dynamic) have yet to be more thoroughly tested.

Since intermittency is an ubiquitous process at the nanometer scale, some of the arguments discussed here for QDs might also apply to other systems. In particular, our analysis shows that nonstationary behavior of the fluorescence—sometimes attributed to photochemical processes—can also have purely statistical origins (such as statistical aging). Recent evidence has shown that this may be the case in a system as microscopically different from QDs as green fluorescent proteins [33]. In this respect, aging and nonergodicity might be an important pattern when studying single nanometer-sized objects in complex environments.

In conclusion, our experimental results show that ensemble-averaged fluorescence properties of individual CdSe QDs are deeply affected by the nonstandard statistical properties of the Lévy statistics governing the blinking process. We found that a population of QDs exhibit statistical aging. Hence, despite the fact that blinking statistics are time independent, the fluorescence emitted by an ensemble of QDs under continuous laser excitation is nonstationary. Our data also evidence that, due to the scaling properties of Lévy statistics, CdSe QDs are nonergodic systems: time- and ensemble-averaged properties do not coincide anymore, in full contrast with usual assumptions when studying nanoscale emitters.

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*Unité de recherche de l'Ecole normale supérieure et de l'Université Pierre et Marie Curie, associée au CNRS.

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[23] We spin coated a nanomolar solution of CdSe/ZnS QDs (1.8 nm core radius, 570 nm peak emission) on a glass coverslip, covered by a thin film of PMMA. The nanoparticles were excited using the 488 nm line of an Ar^+ laser at an intensity of 0.1 kW/cm^2. Their fluorescence was recorded using a CCD camera (CoolSnap, Roper Scientific). Using antibunching measurements [5,24] we had previously checked that, for these conditions of sample preparation, the surface concentration of the nanoparticles was low enough so that they could be detected individually.
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[26] See, e.g., *Numerical Recipes* (Cambridge University Press, Cambridge, England, 1993), 2nd ed.
[27] All the results shown in this Letter are found unchanged when working with a subset of QDs for which the average values of the KS test are as high as 0.62 (0.3) for $P_{\rm on}$ and 0.63 (0.30) for $P_{\rm off}$, confirming the statistical homogeneity of the sample.
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