Statistical Aging and Nonergodicity in the Fluorescence of Single Nanocrystals

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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 labeling [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 \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) of the on and off periods follow slowly decaying power-law distributions \( P_{\text{on}}(\tau_{\text{on}} > \tau) = (\tau_{0}/\tau)^{\mu_{\text{on}}}, \) \( P_{\text{off}}(\tau_{\text{off}} > \tau) = (\tau_{0}/\tau)^{\mu_{\text{off}}}, \) where \( \mu_{\text{on}} \) and \( \mu_{\text{off}} \) are close to 0.5 [12,13]. This behavior extends over several orders of magnitude, from the detection integration time \( \tau_{0} \) up to hundreds of seconds, with very small dependence on temperature or excitation intensity.

The crucial point for our analysis is that both \( \mu_{\text{on}} \) and \( \mu_{\text{off}} \) are smaller than 1. In this case, the decay is so slow that the mean value of \( P_{\text{on}} \) and \( P_{\text{off}} \) is formally infinite, and very long events tend to dominate the fluorescence signal, producing strong intermittency. The duration of the on and off periods is 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 trace was considered simply as a sequence of on and off states, \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \), from which the distributions \( P_{\text{on}} \) and \( P_{\text{off}} \) 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 \( \mu_{\text{on}} \) and \( \mu_{\text{off}} \) 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.](image-url)
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 $\mu_{\text{on}} = 0.58$ and $\mu_{\text{off}} = 0.48$ [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 $\theta$ and $\theta + d\theta$ after a time $\theta$ spent in the off state. For off periods following a “narrow” distribution with $\tau_{\text{off}} < 1$ and equal to $1/0.0018$, the off periods [Fig. 2(b)]. Assuming that the off events have no mean value, the sum of such independent random variables must be evaluated by

\begin{equation}
\tau_{\text{off}} = 0.6
\end{equation}

and to vanish for $\theta < 0$ [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 $\theta'$ of the order of $\theta$ 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 $P_{\text{off}}$ with exponent $\mu_{\text{off}}$, the persistence probability is expected to read

\begin{equation}
\Pi_0(\theta, \theta + \theta') = \int_0^{\theta/(\theta + \theta')} \beta_{\mu_{\text{off}}, 1 - \mu_{\text{off}}}(u)du,
\end{equation}

where $\beta$ is the beta distribution on $[0, 1]$ [20,29]. Our data follow this prediction with $\mu_{\text{off}} = 0.55$, in agreement both with our previous estimations of $\mu_{\text{off}}$ [Fig. 2(d)] and with the assumption that the off events periods with an exponential distribution (with mean value $\tau_{\text{off}}$), $\Pi_0(\theta, \theta + \theta')$ is independent of $\theta$, and given by $e^{-\theta/(\tau_{\text{off}})}$, illustrating that the switching process is stationary. The computation of $\Pi_0$ from our data set reveals a completely different pattern: the probability that no switch on event occurs within a given duration $\theta'$ decreases with $\theta$ [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 $\theta'$ of the order of $\theta$ 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 $P_{\text{off}}$ with exponent $\mu_{\text{off}}$, the persistence probability is expected to read

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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 $\mu_{\text{off}} < \mu_{\text{on}}$ since $\theta(N) = \sum_{i=1}^{N} \tau_{\text{off}}^{(i)}$ grows faster than its counterpart $\bar{\theta}(N) = \sum_{i=1}^{N} \tau_{\text{on}}^{(i)}$. 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 $\mu_{\text{off}}$ and $\mu_{\text{on}}$ [Fig. 3(a)]. We also observed that the average signal over the whole CCD detector, i.e., the sum of the fluorescence emitted by a population of QDs, grows faster than its counterpart $\Phi_{\text{on}}(t)$ [Fig. 3(b)]. We also observed that the average signal over the whole CCD detector, i.e., the sum of the fluorescence emitted by a population of QDs, $\Phi_{\text{on}}(t)$ decays deterministically as $t^{-0.13}$ [Fig. 3(a)], each time average widely fluctuates over time and for a given $i$, 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 $\Phi_{\text{on}}^{(i)}(0 \rightarrow t)$ 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 times, $\Phi_{\text{on}}^{(i)}(0 \rightarrow t)$ does not converge and no information on the ensemble value $\Phi_{\text{on}}$ can be obtained by time averaging an individual trajectory.

While we found that accurate estimates of $\mu_{\text{on}}$ and $\mu_{\text{off}}$ 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 $\mu_{\text{off}}$ 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 $\mu_{\text{off}}$ [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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[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/cm². 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.
[25] In agreement with previous measurements [13], we also observed that the on periods display a truncation time τ_{trunc} after which P_{on} would fall more rapidly. However, for our experimental conditions, τ_{trunc} is greater than tens of seconds, fluctuating from QD to QD. On the time scale of our analysis, the occurrence of this truncation does not affect our results.
[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_{on} and 0.63 (0.30) for P_{off}, confirming the statistical homogeneity of the sample.
[28] This result is in striking contrast with the case of narrow distributions. For an exponential distribution $ae^{-at}$, the largest event is only of the order of $log(N)/a$.
[33] F. Amblard (private communication).